ANALYTICAL CHEMISTRY

Walter J. Murphy, Editor

The Training of Ph.D.'s for Industry

I. M. KOLTHOFF, in his Fisher Award address before the Division of Analytical Chemistry, expressed the opinion that industry labors under the misconception that a Ph.D. with a major in analytical chemistry should be a specialist in some particular field of analytical chemistry. In support of his opinion Dr. Kolthoff pointed out that he receives many requests from industry for Ph.D.'s who are specialists in spectroscopy, spectrophotometry, x-ray analysis, polarography, etc.

We doubt that industry has done much thinking about the type of training given to Ph.D.'s majoring in analytical chemistry. We do not condone this lack of interest, but merely wish to point out that industry's thinking usually does not extend beyond the immediate problem of filling a specific job with someone highly qualified in a given field of specialization.

If industrial leaders did some serious thinking about the problem—and they should—we believe most of them would agree in principle at least with Dr. Kolthoff's insistence that the academic training of Ph.D.'s should be in the basic aspects of chemistry with special emphasis on the scientific fundamentals of analytical chemistry. This is the only sound approach, whether the postdoctoral career is in teaching or in industry.

The field of analytical chemistry is passing through a period of pronounced evolution and neither our colleges and universities nor industry can be said to have recognized all the ramifications of the changes that have occurred over the past decade or two.

Much of the existing uncertainty may be due to the fact that our academic leaders in analytical chemistry have not had the direct contact with industrial leaders that, for example, the teachers of chemical engineering have experienced. As a result, there has not been a wide exchange of viewpoints so necessary to bring about mutual understanding of what industry expects in the way of training in analytical chemistry and what the colleges and universities can or cannot do in meeting these needs.

Industry has accepted the growth of instrumental analysis with great enthusiasm. The reasons, of course, are perfectly plain. Large-scale manufacturing operations and, particularly, continuous processes have been made possible through the phenomenal expansion in instrumentation, costs for analysis have been reduced, and technicians rather than graduate chemists can be employed for strictly routine and repetitive operations. What industry has not always recognized is that the analytical chemist who directs or supervises analytical work today must be thoroughly grounded in the basic concepts of many branches of both chemistry and physics and that such training is of much more importance than detailed skill in one or two highly specialized fields.

The colleges and universities will cooperate with industry, but they must know the needs of industry. Dr. Kolthoff's proposal that the Division of Analytical Chemistry circulate questionnaires to leaders of industrial laboratories and government and private institutions, and to Ph.D.'s with a major in analytical chemistry employed by industry, is an excellent method of fact finding, or the division might sponsor a symposium where industry, the teaching profession, and the younger Ph.D.'s in industry might present their viewpoints.

Dr. Kolthoff's warning to industry should be brought home to industrial leaders.

> I recognize that few industries provide an opportunity for unlimited fundamental research. However, I am confident that everyone will agree that the number of outstanding analytical chemists in and the output of fundamental analytical research by industry are deplorably small as compared to the size and manpower of our industrial laboratories. If we wish to continue to encourage graduate students to major in analytical chemistry, they should have some assurance that after many years of study and research industrial positions are available which are attractive, not only from a financial view, but especially from the view of scientific satisfaction they can expect to derive from their work. The major question to be settled is whether the emphasis in the education of Ph.D.'s with a major in analytical chemistry should be on the scientific or on the applied side. From the academic view the answer is simple; it should be scientific, the same as it is for physical chemists and as it is or should be for organic or inorganic chemists. In my opinion the death blow would be given to the science of analytical chemistry if it ever were decided to make the education on the Ph.D. level of an applied nature. . . .

It is well to remember that applied research in all fields, including analytical chemistry, prospers and expands as knowledge of a fundamental nature is made available. In analytical chemistry, particularly, we are drying up the fountain of basic knowledge. We must replenish it or the field of practical applications will suffer. Industry cannot afford to permit this condition to arise. The time for seriously reviewing the problem is now. Inaction based on indifference is no longer excusable.

Derivatives of Fatty Acids

Identification by X-Ray Diffraction Powder Patterns

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Three types of derivatives of fatty acids—silver salts, amides, and anilides—have been compared as a means of identification of the acid by use of x-ray diffraction powder patterns. Each type was found suitable. For ease of preparation and pattern differentiation the silver salt series is preferred. Technical details of powder diffraction technique for identification are discussed. Tables of diffraction data (Tables I to III) are given for silver salts of C_2 to C_{22}, amides of C_2 to C_{18}, and anilides of C_{13}, C_{15}, and C_{17}.

IN A previous paper (*10*) the use of anilides as derivatives for the identification of fatty acids by means of x-ray diffraction powder patterns was discussed. As an extension of this work, the amides and silver salts of the saturated straight-chain fatty acids have been examined in the hope that a more suitable derivative for identification of the members of a homologous series of organic compounds might be found.

On the subject of identification of organic compounds by x-ray diffraction powder analysis, a paper by de Lange and Houtman (*5*) describes work with a number of organic derivatives and gives examples of the usefulness of the method where melting point data alone gave inconclusive results. Soldate and Noyes (*13*) give x-ray diffraction data on a number of crystalline components of explosives.

X-RAY APPARATUS AND TECHNIQUE

The x-ray equipment employed was that described in the previous paper (*10*). The high absorption of longer wave-length chromium target radiation increased the exposure time required for silver salts to about 7 hours. With copper radiation very satisfactory patterns were obtained in 2 hours, although the pattern dispersion and the "cutoff" at high d spacings were not as favorable as in the case of the longer wave-length radiation. As a diluent to reduce x-ray absorption and a support material to promote random orientation, 200-mesh beryllium metal was added during grinding in some cases. (Premium grade beryllium powder, 200 mesh, The Brush Beryllium Company, 3714 Chester Ave., Cleveland 14, Ohio. Because of its known toxicity, care should be exercised in handling beryllium and its compounds.)

Table I. X-Ray Diffraction Data on Amides

C_2, Acetamide

d	I/I_1
6.25	0.02
5.7	0.90
4.02	0.20
3.92	0.10
3.63	0.02
3.55	1.00
3.61	0.40
3.21	0.40
2.87	0.50
2.80	0.05
2.71	0.05
2.56	0.20
2.52	0.20
2.34	0.20
2.26	0.05
2.19	0.10
2.17	0.10
2.00	0.10
1.97	0.05
1.96	0.05
1.79	0.05
1.76	0.05
1.74	0.02
1.725	0.20
1.72	0.05

C_3, Propionamide

8.2	0.90
4.8	1.00
4.7	0.80
4.42	0.50
4.13	0.01
4.07	0.01
3.88	0.30
3.87	0.30
3.65	0.01
3.54	0.02
3.50	0.02
3.34	0.50
3.30	0.50
3.21	0.01
2.90	0.02
2.85	0.01
2.80	0.02
2.69	0.10
2.63	0.01
2.46	0.10
2.40	0.10
2.30	0.02
2.21	0.10
2.07	0.02

C_4, n-Butyramide

9.8	1.00
4.9	0.20
4.8	0.10
4.6	0.90
4.23	0.20
4.00	0.20
3.77	1.00
3.69	0.05
3.62	0.02
3.18	0.02
2.86	0.05
2.61	0.02
2.47	0.02

C_4, Isobutyramide

9.7	0.30
5.1	1.00
4.9	0.05
4.8	0.05
4.7	0.30
4.55	0.50
4.16	0.10
3.99	0.10
3.82	0.05
3.78	0.05
3.69	0.20
3.60	0.02
3.22	0.02
2.96	0.10
2.85	0.05
2.82	0.02
2.78	0.02
2.70	0.10
2.55	0.20
2.36	0.02
2.08	0.02

C_5, n-Valeramide

11.1	0.60
5.2	0.15
5.1	0.15
4.8	1.00
4.7	0.20
4.06	0.50
4.02	0.50
3.94	0.50
3.77	0.20
3.58	0.20
3.33	0.20

C_5, n-Valeramide

3.11	0.10
2.91	0.15
2.83	0.15
2.71	0.05
2.50	0.05
2.41	0.05
2.27	0.05
2.23	0.05

C_5, Isovaleramide

11.4	1.00
5.8	0.02
5.5	0.30
5.2	0.30
4.7	0.90
4.56	0.30
4.22	0.40
4.09	0.40
3.42	0.02
3.24	0.10
2.87	0.10
2.61	0.01
2.30	0.01

C_5, α-Methylbutyramide

11.5	0.02
10.5	0.50
6.1	0.03
5.55	1.00
5.2	0.30
4.7	0.10
4.55	0.20
4.12	0.10
4.03	0.05
3.94	0.10
3.81	0.10
3.75	0.02
3.59	0.05
3.53	0.05

C_5, Trimethylacetamide

10.9	0.02
10.2	0.90
5.6	0.02
5.1	1.00
5.0	0.60
4.8	0.03
4.6	0.02

C_5, Trimethylacetamide

4.35	0.40
4.14	0.05
4.03	0.02
3.83	0.80
3.41	0.10
3.34	0.05
2.94	0.60
2.83	0.20
2.68	0.20
2.56	0.20
2.48	0.02
2.40	0.03
2.35	0.03
2.29	0.02
2.18	0.10
2.15	0.10
2.04	0.02
1.93	0.20

C_6, n-Caproamide

13.9	1.00
4.8	0.80
4.44	0.50
4.29	0.30
3.81	0.20
3.59	0.20
3.55	0.20
3.10	0.05
3.04	0.10
2.75	0.10

C_6, Isocaproamide

13.7	1.00
6.9	0.05
5.4	0.05
5.0	0.40
4.9	0.70
4.5	0.50
4.38	0.40
4.12	0.35
3.77	0.02
3.43	0.10
3.07	0.02
2.85	0.02
2.75	0.02
2.08	0.02
2.05	0.40
2.01	0.30
1.89	0.05

C_7, Enanthamide

14.9	0.90
4.9	1.00
4.8	0.40
4.45	0.20
4.23	0.50
3.82	0.10
3.71	0.60
3.67	0.50
3.54	0.20
3.23	0.10
3.13	0.02
3.02	0.02
2.88	0.05
2.80	0.20
2.65	0.02
2.61	0.02
2.30	0.02
2.24	0.02

C_8, Caprylamide

17.2	1.00
5.8	0.02
4.9	0.80
4.7	0.20
4.3	0.50
4.06	0.90
3.61	0.10
3.46	0.05
3.17	0.02
3.13	0.02

C_9, Pelargonamide

19.3	1.00
6.3	0.10
5.6	0.10
4.9	0.50
4.7	0.20
4.39	0.50
3.87	0.80
3.54	0.20
3.39	0.20
3.35	0.50
3.15	0.10
3.02	0.20
2.78	0.20
2.68	0.05
2.57	0.10
2.49	0.05
2.36	0.10
2.30	0.05

C_9, Pelargonamide

2.09	0.05
1.96	0.02
1.93	0.05
1.88	0.02
1.76	0.05
1.72	0.05
1.60	0.05

C_{10}, Capramide

20.8	1.00
6.8	0.02
5.3	0.02
4.9	0.80
4.8	0.50
4.5	0.10
4.40	0.80
4.14	0.10
3.76	0.90
3.45	0.20
3.31	0.30
3.27	0.10
2.74	0.10

C_{11}, Undecylamide

22.0	1.00
12.9	0.02
11.6	0.02
9.9	0.02
7.3	0.10
5.4	0.03
4.9	0.50
4.7	0.05
4.6	0.05
4.40	0.40
4.09	0.04
3.91	0.60
3.67	0.20
3.57	0.05
3.54	0.05
3.44	0.10
3.29	0.03
3.20	0.04
3.11	0.05
3.05	0.04
2.99	0.04
2.87	0.05
2.77	0.07
2.72	0.03
2.64	0.03
2.60	0.03

Table I. X-Ray Diffraction Data on Amides (*Continued*)

C_{11}, Undecylamide

d	I/I_1
2.49	0.02
2.45	0.04
2.42	0.02
2.38	0.02
2.35	0.04
2.29	0.02
2.25	0.02
2.23	0.02
2.20	0.02
2.18	0.02
2.15	0.03
2.06	0.04

C_{12}, Lauramide

d	I/I_1
25.2	1.00
8.2	0.10
5.4	0.02
5.0	0.02
4.9	0.60
4.7	0.10
4.6	0.10
4.47	0.45
4.35	0.05
4.10	0.20

C_{12}, Lauramide

d	I/I_1
3.89	0.02
3.64	0.50
3.57	0.05
3.39	0.02
3.20	0.02
2.99	0.02
2.90	0.05
2.73	0.05
2.57	0.02

C_{13}, Tridecylamide

d	I/I_1
8.6	0.05
4.9	0.70
4.8	0.35
4.45	0.80
4.26	0.40
3.92	0.05
3.75	1.00
3.57	0.30
3.43	0.40
3.26	0.05
3.07	0.05
2.93	0.05
2.72	0.10
2.34	0.02
2.23	0.02

C_{14}, Myristamide

d	I/I_1
13.9	0.02
10.3	0.05
9.4	0.40
7.0	0.02
5.6	0.05
5.3	0.05
5.1	0.05
4.9	0.50
4.7	0.25
4.46	0.60
4.33	0.10
4.24	0.05
3.93	1.00
3.76	0.25
3.61	0.30
3.54	0.10
3.28	0.10
3.18	0.10
3.00	0.10
2.96	0.10
2.79	0.20
2.31	0.10
2.21	0.10
2.06	0.30
2.02	0.20
1.90	0.05
1.87	0.05

C_{15}, Pentadecylamide

d	I/I_1
10.1	0.20
5.1	0.05
4.9	0.50
4.8	0.50
4.5	0.80
4.42	0.02
4.28	0.20
4.13	0.20
3.84	1.00
3.54	0.30
3.46	0.30
3.39	0.25
3.14	0.10
2.95	0.10
2.77	0.20

C_{16}, Palmitamide

d	I/I_1
10.9	0.50
10.6	0.30
9.7	0.10
8.3	0.05

C_{16}, Palmitamide

d	I/I_1
6.5	0.05
5.3	0.05
5.1	0.02
4.9	0.20
4.7	0.10
4.47	0.50
4.39	0.50
4.07	0.10
3.70	1.00
3.45	0.20
3.24	0.20
2.70	0.02
2.57	0.02
2.34	0.10
2.22	0.02
2.17	0.05
2.06	0.02
1.86	0.02

C_{17}, Margaramide

d	I/I_1
11.5	0.02
10.3	0.10
6.3	0.02

C_{17}, Margaramide

d	I/I_1
5.3	0.05
5.2	0.05
4.9	0.20
4.7	0.05
4.33	0.50
4.25	0.05
3.88	1.00
3.55	0.10
3.49	0.10
3.27	0.05
2.68	0.05
2.20	0.05

C_{18}, Stearamide

d	I/I_1
11.9	0.10
4.9	0.10
4.46	1.00
4.37	1.00
4.09	0.30
3.70	0.90
3.23	0.10
2.55	0.02
2.30	0.01
2.16	0.02

Table II. X-Ray Diffraction Data on Silver Salts

C_2, Silver Acetate

d	I/I_1
9.85	1.00
5.0	0.02
3.95	0.02
3.80	0.02
3.30	0.03
3.05	0.50
2.92	0.40
2.76	0.02
2.68	0.10
2.57	0.05
2.46	0.40
2.32	0.02
2.21	0.40
2.03	0.30
1.97	0.40
1.85	0.02
1.80	0.02
1.71	0.05
1.64	0.30
1.58	0.02
1.53	0.02
1.48	0.02
1.45	0.04
1.41	0.05
1.28	0.02

C_3, Silver Propionate

d	I/I_1
12.5	1.00
6.3	0.80
4.25	0.05
3.98	0.03
3.53	0.60
3.37	0.60
3.14	0.70
3.02	0.80
2.87	0.25
2.80	0.02
2.73	0.05
2.63	0.10
2.57	0.70
2.45	0.80
2.21	0.80
2.15	0.05
2.11	0.10
2.06	0.02
2.02	0.02
1.93	0.10
1.85	0.05
1.81	0.10
1.75	0.02
1.73	0.02
1.66	0.02
1.63	0.04
1.59	0.05
1.57	0.02
1.49	0.02
1.41	0.10
1.38	0.02
1.35	0.02
1.33	0.02
1.31	0.02
1.29	0.02
1.23	0.02
1.22	0.02
1.13	0.02

C_3, Silver Propionate

d	I/I_1
1.125	0.02
1.09	0.02
1.04	0.02
1.01	0.02

C_4, Silver n-Butyrate

d	I/I_1
15.0	1.00
7.5	0.80
5.0	0.10
3.78	0.10
3.66	0.10
3.48	0.15
3.36	0.15
3.20	0.15
3.15	0.10
3.10	0.10
3.05	0.10
2.92	0.60
2.72	0.50
2.65	0.50
2.61	0.60
2.54	0.30
2.46	0.05
2.31	0.20
2.27	0.10
2.23	0.60
2.14	0.05
1.87	0.05
1.83	0.05
1.68	0.05
1.49	0.05
1.36	0.05

C_4, Silver Isobutyrate

d	I/I_1
13.2	1.00
7.2	0.90
6.4	0.80
5.6	0.40
5.5	0.30
5.0	0.20
4.43	0.50
4.27	0.20
3.93	0.60
3.84	0.10
3.72	0.10
3.61	0.05
3.29	0.80
3.08	0.20
2.98	0.10
2.92	0.15
2.85	0.15
2.72	0.30
2.65	0.10
2.62	0.10
2.54	0.10
2.51	0.10
2.46	0.10
2.38	0.70
2.22	0.10
2.16	0.20
2.08	0.15
2.04	0.15

C_4, Silver Isobutyrate

d	I/I_1
1.94	0.10
1.93	0.10
1.82	0.05
1.69	0.10
1.63	0.03
1.60	0.02
1.56	0.02
1.51	0.02
1.49	0.02
1.47	0.02
1.45	0.02
1.41	0.02
1.36	0.02

C_5, Silver n-Valerate

d	I/I_1
8.9	1.00
5.9	0.60
4.0	0.10
3.84	0.15
3.49	0.10
3.24	0.45
3.13	0.50
2.93	0.05
2.77	0.02
2.73	0.03
2.65	0.02
2.55	0.05
2.47	0.05
2.41	0.03
2.34	0.03
2.25	0.02
2.21	0.10
2.08	0.02
2.00	0.01
1.74	0.01
1.61	0.03
1.48	0.02
1.36	0.02

C_5, Silver Isovalerate

d	I/I_1
12.1	1.00
5.9	0.90
5.2	0.03
4.41	0.80
4.25	0.80
4.05	0.15
3.97	0.70
3.51	0.60
3.47	0.40
3.23	0.30
3.12	0.40
2.85	0.20
2.81	0.20
2.65	0.40
2.57	0.40
2.52	0.40
2.46	0.10
2.32	0.10
2.25	0.05
2.19	0.15
2.12	0.02
2.09	0.02
2.03	0.02

C_5, Silver Isovalerate

d	I/I_1
1.95	0.02
1.92	0.02
1.90	0.02
1.69	0.02
1.68	0.02
1.67	0.02
1.65	0.02

C_5, Silver α-Methyl Butyrate

d	I/I_1
13.0	1.00
8.9	0.90
6.4	0.50
4.6	0.01
3.89	0.01
3.48	0.01
3.03	0.05
2.74	0.10
2.64	0.10
2.47	0.03
2.05	0.01

C_5, Silver Trimethyl Acetate

d	I/I_1
12.0	1.00
8.9	0.90
8.1	0.90
6.4	0.10
6.0	0.10
5.6	0.10
4.50	0.20
4.44	0.20
4.03	0.40
3.86	0.30
3.57	0.02
3.43	0.02
3.37	0.02
3.21	0.20
3.01	0.02
2.95	0.05
2.81	0.02
2.72	0.20
2.66	0.02
2.60	0.05
2.50	0.02
2.34	0.02
2.25	0.02
2.20	0.02
2.09	0.02
1.92	0.02
1.86	0.02
1.82	0.02
1.65	0.01
1.62	0.01
1.59	0.01

C_6, Silver n-Caproate

d	I/I_1
9.7	1.00
6.5	0.80
4.9	0.02

C_6, Silver n-Caproate

d	I/I_1
4.32	0.05
4.24	0.05
3.85	0.10
3.67	0.02
3.60	0.02
3.44	0.08
3.24	0.90
3.17	0.25
3.05	0.05
2.82	0.05
2.74	0.25
2.62	0.02
2.54	0.05
2.50	0.05
2.46	0.05
2.37	0.02
2.30	0.05
2.25	0.10
2.22	0.15
2.06	0.02
2.02	0.02
1.88	0.02
1.63	0.02
1.62	0.20
1.52	0.05
1.51	0.05
1.40	0.10
1.37	0.05
1.30	0.05
1.04	0.05

C_6, Silver Isocaproate

d	I/I_1
13.8	1.00
6.9	0.90
5.2	0.05
4.9	0.05
4.6	0.70
4.29	0.60
4.13	0.60
3.82	0.02
3.56	0.55
3.42	0.55
3.21	0.10
3.16	0.10
3.10	0.10
2.96	0.08
2.86	0.08
2.66	0.10
2.62	0.10
2.57	0.10
2.52	0.10
2.48	0.02
2.37	0.02
2.29	0.08
2.18	0.02
2.03	0.01
1.97	0.01

C_7, Silver Enanthate

d	I/I_1
11.1	1.00
7.4	0.90
5.6	0.02

C_7, Silver Enanthate

d	I/I_1
4.39	0.35
4.15	0.35
3.86	0.35
3.49	0.10
3.25	0.80
3.15	0.65
2.87	0.40
2.73	0.30
2.61	0.10
2.56	0.10
2.43	0.05
2.36	0.05
2.23	0.05
2.14	0.05

C_8, Silver Caprylate

d	I/I_1
12.1	1.00
8.1	0.90
6.1	0.35
4.9	0.30
4.33	0.30
4.06	0.02
3.73	0.20
3.50	0.05
3.25	0.80
3.15	0.10
3.02	0.10
2.88	0.10
2.70	0.10
2.45	0.10
2.21	0.10
2.11	0.05
2.04	0.05
1.88	0.08
1.63	0.02
1.57	0.02
1.53	0.05

C_9, Silver Pelargonate

d	I/I_1
13.6	1.00
9.1	0.90
6.8	0.40
5.5	0.30
4.6	0.30
4.36	0.30
3.95	0.20
3.78	0.30
3.48	0.10
3.31	0.80
3.25	0.20
2.97	0.05
2.73	0.30
2.56	0.30
2.34	0.30
2.19	0.30
2.10	0.10
1.96	0.20
1.83	0.05
1.80	0.03
1.74	0.02
1.71	0.05
1.60	0.03
1.52	0.02

Table II. X-Ray Diffraction Data on Silver Salts (*Continued*)

C_{10}, Silver Caprate		C_{11}, Silver Undecylate		C_{13} Silver Tridecylate		C_{16}, Silver Palmitate		C_{18}, Silver Stearate		C_{20}, Silver Arachidate	
d	I/I_1	*d*	I/I_1	*d*	I/I_1	*d*	I/I_1	*d*	I/I_1	*d*	I/I_1
14.8	0.80	2.07	0.02	2.23	0.10	11.0	0.60	16.3	1.00	2.39	0.05
9.8	0.90	2.00	0.05	2.17	0.10	8.8	0.60	12.2	0.60	2.34	0.05
7.4	0.75	1.88	0.02			7.3	0.20	9.7	0.60	2.22	0.20
5.9	0.05	1.68	0.02	C_{14}, Silver Myristate		...	...	8.1	0.40	2.19	0.05
4.43	0.03	1.60	0.02			6.3	0.20	7.0	0.40	2.13	0.10
4.22	0.02			13.0	1.00	5.6	0.02	6.1	0.02		
3.98	0.03	C_{12}, Silver Laurate		9.7	0.80	5.04	0.02	5.4	0.02	C_{22}, Silver Behenate	
3.76	0.05			7.8	0.80	4.54	0.50	4.55	0.60		
3.59	0.02	17.0	1.00	6.6	0.02	4.48	0.50	4.48	0.60	19.5	1.00
3.45	0.03	11.4	1.00	5.6	0.02	3.82	0.50	3.81	0.50	14.7	0.60
3.33	1.00	8.5	0.90	4.5	0.85	3.70	0.02	3.42	0.60	11.7	0.60
3.18	0.20	6.8	0.90	4.25	0.02	3.47	0.10	3.38	0.70	9.7	0.40
3.05	0.03	5.7	0.05	3.80	0.60	3.22	0.15	2.72	0.05	8.3	0.40
2.96	0.05	4.9	0.02	3.37	0.90	2.74	0.25	2.71	0.05	7.3	0.20
2.75	0.03	4.44	0.70	3.18	0.02	2.70	0.25	2.65	0.20	6.5	0.20
2.70	0.02	3.78	0.03	2.68	0.50	2.55	0.02	2.53	0.05	5.85	0.05
2.63	0.02	3.61	0.02	2.46	0.02	2.27	0.02	2.43	0.05	5.3	0.05
2.54	0.03	3.34	0.80	2.23	0.05	2.23	0.02	2.22	0.10	4.56	0.30
2.47	0.03	2.67	0.02	2.08	0.02	2.08	0.02	C_{20}, Silver Arachidate		4.51	0.30
2.38	0.03	2.45	0.02			2.03	0.02			3.82	0.30
2.21	0.03	2.32	0.02	C_{15}, Silver Pentadecylate		1.93	0.02	17.9	1.00	3.75	0.05
2.17	0.03	2.21	0.02					13.35	0.40	3.61	0.05
		2.08	0.02	14.1	1.00			10.75	0.40	3.45	0.20
C_{11}, Silver Undecylate		2.01	0.02	10.6	0.90	C_{17}, Silver Margarate		8.9	0.20	3.43	0.20
				8.5	0.90			7.65	0.20	3.34	0.02
16.0	0.80	C_{13}, Silver Tridecylate		7.1	0.10	16.0	0.80	6.7	0.10	3.21	0.05
10.5	1.00			6.0	0.10	12.0	0.90	5.9	0.10	3.10	0.02
7.9	0.80	18.4	1.00	5.3	0.02	9.5	1.00	4.56	0.15	3.00	0.02
6.4	0.80	12.3	1.00	4.53	0.80	8.0	0.50	4.49	0.15	2.96	0.02
5.35	0.02	9.2	0.95	3.89	0.70	6.8	0.50	4.32	0.02	2.90	0.02
4.52	0.10	7.4	0.95	3.39	0.50	6.0	0.02	4.28	0.02	2.86	0.02
3.98	0.05	6.1	0.40	2.68	0.10	5.35	0.02	3.81	0.20	2.71	0.05
3.74	0.02	5.3	0.40	2.23	0.02	4.57	0.90	3.75	0.02	2.64	0.20
3.30	0.25	4.46	0.70			3.90	0.30	3.63	0.02	2.55	0.05
3.04	0.05	4.14	0.05	C_{16}, Silver Palmitate		3.44	0.02	3.45	0.10	2.46	0.05
2.84	0.02	3.74	0.05			3.24	0.02	3.06	0.05	2.37	0.10
2.73	0.02	3.33	0.90	22.1	1.00	2.70	0.20	2.92	0.05	2.29	0.10
2.50	0.02	2.72	0.20	14.8	1.00	2.23	0.01	2.80	0.05	2.22	0.20
2.29	0.02	2.65	0.20					2.72	0.05	2.15	0.10
2.18	0.03	2.30	0.05					2.69	0.05	2.08	0.10

This material has very low x-ray absorption and gives a cubic pattern which provides check lines for the alignment of patterns for comparison purposes. These lines occur at sufficiently high angles not to interfere with the predominantly long spacings of organic compounds.

PREPARATION OF AMIDES

In general, the amides were prepared from the corresponding acid through the acid chloride (*4*).

To about 10 grams of the acid, approximately twice the stoichiometric amount of thionyl chloride was added. The mixture was warmed on a steam bath under reflux for 0.5 hour and allowed to cool. It was then slowly dripped into aqueous ammonia (28%), and the mixture was cooled to below 0° C. The precipitated amide was filtered off and extracted with hot benzene. Recrystallizations, followed by vacuum drying, were repeated until the melting point remained constant within 0.2° C. A few of the commercially available amides were also used, after recrystallization.

Acetamide was found to be extremely hygroscopic and for this reason the following method of purification was employed. A large sample was melted and allowed to cool slowly. After half the sample had crystallized, the remaining melt was discarded. The crystals were then recrystallized from benzene. Chloroform was found to be a most efficient recrystallization solvent for stearamide. Removal of the solvent from pentadecylamide was difficult but was accomplished by heating in a vacuum drying pistol. α-Methylbutyramide was found to be very soluble in water. The aqueous solution was evaporated and the amide extracted from the residue with benzene and filtered to remove impurities such as ammonium chloride. Melting points reported in Table IV were determined in capillary tubes using certified thermometers; the temperatures were corrected for stem exposure.

PREPARATION OF SILVER SALTS

To the corresponding acid an excess of concentrated aqueous ammonia was added. The mixture was warmed and the excess ammonia was evaporated. To this aqueous solution a slight excess of 0.1 *N* silver nitrate was added with stirring. The floc was allowed to settle, filtered using suction, and washed with water until no silver could be detected in the washings. The silver salt was then washed with alcohol and ether, dried under vacuum, and stored in a dark bottle. The purity of the silver salt was determined by igniting a portion to 600° C. and weighing

Table III. X-Ray Diffraction Data on Anilides

C_{13}, Tridecylanilide		C_{15}, Pentadecylanilide		C_{17}, Margaranilide	
d	I/I_1	*d*	I/I_1	*d*	I/I_1
20.7	0.25	11.15	0.35	12.1	0.25
10.1	0.35	7.4	0.20	8.1	0.15
6.75	0.10	5.55	0.05	6.1	0.05
5.0	0.10	4.46	0.15	4.85	0.05
4.48	0.10	4.28	0.45	4.45	0.10
4.30	0.40	4.07	1.00	4.22	0.40
4.06	1.00	3.97	0.15	4.06	1.00
3.64	0.30	3.66	0.40	3.94	0.25
3.46	0.15	3.47	0.15	3.80	0.05
3.17	0.05			3.63	0.35
3.09	0.05			3.48	0.10
3.06	0.05			2.45	0.05
2.45	0.05				
2.36	0.03				
2.29	0.05				
2.23	0.05				
1.88	0.25				

Table IV. Melting Points of Amides of Aliphatic Acids

Acid	No. of Carbon Atoms in Acid	Melting Point, ° C.	
		Found	Literature (*2*)
Acetic	2	81	81.5
Propionic	3	80.2	79, 81.3
n-Butyric	4	115.5	115
Isobutyric	4	129	126.8, 129
n-Valeric	5	105	105.8, 106
Isovaleric	5	136.5	135, 137
α-Methylbutyric	5	112.5	110.9, 111.4, 112, 121
Trimethylacetic	5	155	153-4, 155-7
n-Caproic	6	101	100, 101
Isocaproic	6	120.2	118.8, 119, 120-121
Enanthic	7	95	96, 96.5
Caprylic	8	105.5	105.5, 106. 105
Pelargonic	9	99.5	99
Capric	10	99.5	99, 100.1
Undecylic	11	99	99, 103
Lauric	12	100.5	99, 100
Tridecylic	13	99	98.5 (*9*)
Myristic	14	103	103
Pentadecylic	15	101	102.5 (*7*)
Palmitic	16	105.3	105.3, 106
Margaric	17	104.5	103 (*8*), 106 (*6*)
Stearic	18	108.5	108.4, 109

Table V. Assay on Silver Salts of Aliphatic Acids

Acid	No. of Carbon Atoms in Acid	% Silver Found	% Silver Calculated
Acetic	2	64.68	64.63
Propionic	3	59.81	59.95
n-Butyric	4	55.41	55.33
Isobutyric	4	55.27	55.33
n-Valeric	5	51.62	51.62
Isovaleric	5	51.70	51.62
α-Methylbutyric	5	51.66	51.62
Trimethylacetic	5	51.54	51.62
n-Caproic	6	48.37	48.37
Isocaproic	6	48.40	48.37
Enanthic	7	45.54	45.51
Caprylic	8	43.07	42.97
Pelargonic	9	40.71	40.69
Capric	10	38.58	38.65
Undecylic	11	36.70	36.80
Lauric	12	35.16	35.12
Tridecylic	13	33.68	33.58
Myristic	14	32.04	32.18
Pentadecylic	15	30.80	30.89
Palmitic	16	29.41	29.70
Margaric	17	28.63	28.59
Stearic	18	27.53	27.57
Arachidic	20	25.77	25.72
Behenic	22	24.17	24.11
Lignoceric	24	...	22.69

Table VI. Analytical Data of Anilides

Acid	No. of Carbon Atoms	Melting Points, °C. Found	Melting Points, °C. Literature	Found, % C	Found, % H	Found, % N	Calculated, % C	Calculated, % H	Calculated, % N
Tridecylic	13	79.5	80 (*12*)	...	...	...	...	...	...
Pentadecylic	15	85.3	...	78.9	11.05	4.5	79.4	11.1	4.41
Margaric	17	90.6	...	80.2	11.55	4.1	80.0	11.3	4.06

the reduced metal. The behavior of acids higher than C_{12} indicated that acid ammonium salts were formed. The solution was for this reason kept slightly alkaline during the addition of silver nitrate. When impurities were present which tended to precipitate inorganic silver compounds, precipitation of the silver salt from alcoholic solutions (*3*) was found preferable. Table V gives the assay of the silver salts obtained.

PREPARATION OF ANILIDES

Anilides were obtained by heating equimolar proportions of acid and aniline in sealed glass tubes for 2 hours at 160° to 190° C. (*11*). The material was then dissolved in hot benzene, filtered, recrystallized, and vacuum-dried. In the case of compounds for which no melting point was found in the literature the carbon, hydrogen, and nitrogen were determined as a check of purity and identity. These data are given in Table VI.

DISCUSSION OF POWDER DIFFRACTION DATA

The tendency for a homologous series of organic compounds to form a series of crystalline compounds with homologously related crystal structures has been noted. [In a previous paper (*10*) the term "isostructural" was used to describe the similarity of structures found in the homologous anilides of fatty acids. Because in crystallography the term isostructural has a different meaning from that intended here, the authors have substituted "homologously related structures."] In the anilides previously reported (*10*), this relationship was noted in compounds having carbon chains longer than C_8. The odd members and even members formed separate series. In the amides exclusive of C_1, evidence of the homologous crystal structure is shown by the innermost line of the diffraction pattern, but no marked odd and even alternation is noted. A plot of the innermost line, shown in Figure 1, illustrates this property. The formation of such a series may be considered a disadvantage for differentiation of homologous neighbors. The stepwise change in the pattern and the detail of the other lines are, however, sufficient to make satisfactory differentiation of the members of the series. The differentiation of structural isomers is also satisfactory, as seen from the examination of the data on amides of four structural isomers of valeric acid.

The straight-line relation between the number of carbon atoms in the acid and the innermost reflection can be given by the equation: $x = 6.25 + 1.85\,(y - 2)$, where x is the innermost reflection and y is the number of carbon atoms in the acid. $(y - 2)$ gives the number of methylene groups in the chain and the factor 1.85 A. is a measure of the increment for each such group. The distance 6.25 A. is associated with the methyl and amide groups.

The silver salts similarly show a structurally homologous series with several orders of the innermost reflection present (see Figure 2). ("Orders" here refers to d spacings related in value by factors of small whole numbers. It is the value of n in Bragg's

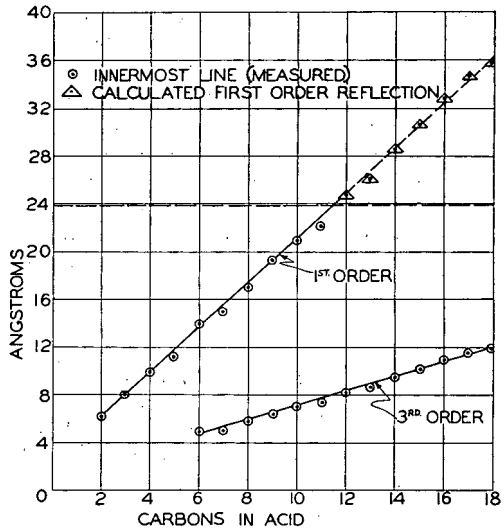

Figure 1. Amides of Normal Fatty Acids

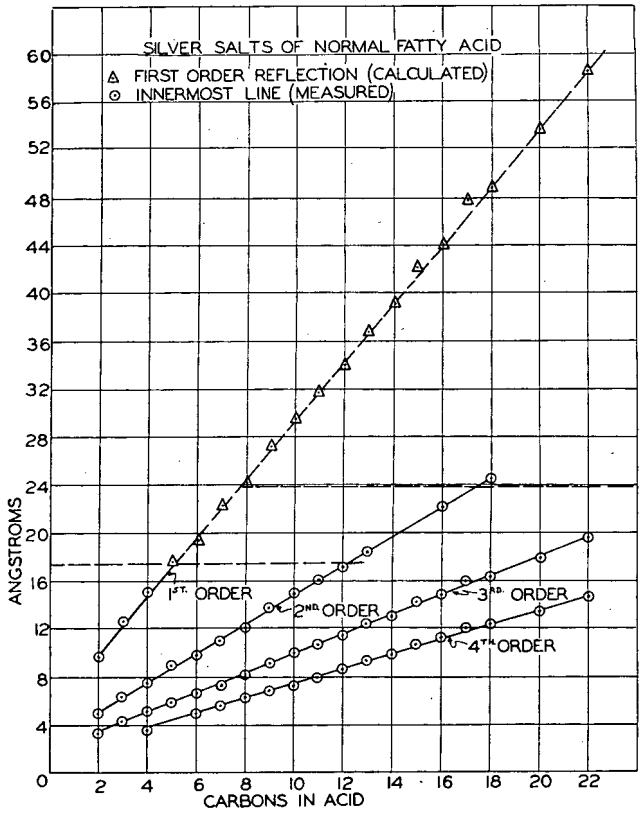

Figure 2

Table VII. Inner Lines of Silver Stearate Pattern

d, A.	Order	1st Order
48.9	1	48.9
24.3	2	48.6
16.3	3	48.9
12.2	4	48.8
9.65	5	48.3
8.16	6	49.0
		Av. 48.8 ± 0.2

law, $n\lambda = 2d \sin \phi$, which expresses the relation between the wave length of an x-ray beam, λ, and the angle of diffraction, ϕ, from crystallographic planes of spacing d.) Using the measurement of several lines to calculate the innermost spacing, the scatter of the points on the curve was improved over the measurements made from the innermost line alone. This spacing provides an excellent check on the authenticity and purity of the salts. A small amount of a lower or higher acid added to pure material will shift the measurement of the line in the direction of the value of the impurity. This is in agreement with the findings of Hess and Kiessig (*1*) in their study of mixtures of potassium salts of fatty acids. (This shift, however, may or may not be proportional to the impurity in the acid. Experiments to check this point showed that the relative solubilities of the silver salts may vary with composition.)

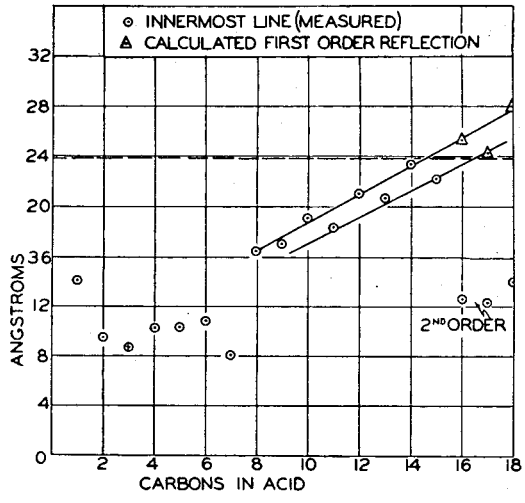

Figure 3. Anilides of Normal Fatty Acids

The relation between the innermost reflection of the silver salt and the number of carbon atoms in the acid is given by the equation, $x = 9.85 + 2.44(y - 2)$, where x and y have the same significance as the previous equation. Using this relation, the values were extrapolated to C_{24} and gave a good check with an acid which, from the neutralization equivalent and melting point, was identified as lignoceric acid.

Data in addition to those given in the previous paper (*10*) have been obtained for the anilide series. The data for the odd numbered members of the series C_{13} to C_{17} confirm the existence of the odd and even series in these compounds. The innermost reflection of undecylanilide was redetermined and found to be 18.3 A. (previously reported as 17.4 A.). Data for the silver salts of acids C_2 to C_{22}, of amides of C_2 to C_{18}, and of anilides of C_{13}, C_{15}, and C_{17} are given in Tables VIII to X.

The cutoff of the powder camera used (143.2 mm. in diameter) was 17 A. for copper radiation and 24 A. for chromium radiation. In the patterns of the higher members of the series, the innermost reflections are missing because of this cutoff of the camera. In these cases, the spacing of the innermost reflection was calculated as a simple multiple of the higher orders obtained. Graphs of the innermost reflections in the three series are given in Figures 1 to 3. A pattern of silver stearate taken with a flat plate transmission powder camera (crystal to plate distance, 17 cm.) shows six orders of the innermost reflection (Table VII).

For accurate data on acids higher than C_{12} it is advisable to use a technique designed to record long spacings. Satisfactory results were obtained on the C_{24} acids by the use of chromium

Table VIII. Index Lines of Amides on Fatty Acids

No.	Name	Strongest Lines 1st	2nd	3rd	4th	Innermost Line
C_2	Acetamide	3.55 (1.00)	5.7 (0.90)	2.87 (0.50)	3.31 (0.40)	6.25 (0.02)
C_3	Propionamide	4.8 (1.00)	8.2 (0.90)	4.7 (0.80)	4.42 (0.50)	8.2 (0.90)
C_4	*n*-Butyramide	9.8 (1.00)	3.77 (1.00)	4.6 (0.90)	4.9 (0.20)	9.8 (1.00)
C_4	Isobutyramide	5.1 (1.00)	4.55 (0.50)	9.7 (0.30)	4.7 (0.30)	9.7 (0.30)
C_5	*n*-Valeramide	4.8 (1.00)	11.1 (0.60)	4.06 (0.50)	4.02 (0.50)	11.1 (0.60)
C_5	Isovaleramide	11.4 (1.00)	4.7 (0.90)	4.22 (0.40)	4.04 (0.40)	11.4 (1.00)
C_5	α-Methylbutyramide	5.55 (1.00)	10.5 (0.50)	3.08 (0.40)	5.2 (0.30)	11.5 (0.02)
C_5	Trimethylacetamide	5.1 (1.00)	10.2 (0.90)	3.83 (0.80)	5.0 (0.60)	10.9 (0.02)
C_6	*n*-Caproamide	13.9 (1.00)	4.8 (0.80)	4.44 (0.50)	4.29 (0.30)	13.9 (1.00)
C_6	Isocaproamide	13.7 (1.00)	4.9 (0.70)	4.5 (0.50)	5.0 (0.40)	13.7 (1.00)
C_7	Enanthamide	4.9 (1.00)	14.9 (0.90)	3.71 (0.60)	3.67 (0.60)	14.9 (0.90)
C_8	Caprylamide	17.2 (1.00)	4.00 (0.90)	4.9 (0.80)	4.3 (0.50)	17.2 (1.00)
C_9	Pelargonamide	19.3 (1.00)	3.87 (0.80)	4.9 (0.50)	4.39 (0.50)	19.3 (1.00)
C_{10}	Capramide	20.8 (1.00)	3.76 (0.90)	4.9 (0.80)	4.40 (0.80)	20.8 (1.00)
C_{11}	Undecylamide	22.0 (1.00)	3.91 (0.60)	4.9 (0.50)	4.40 (0.40)	22.0 (1.00)
C_{12}	Lauramide	25.2 (1.00)	4.9 (0.60)	3.64 (0.50)	4.47 (0.45)	25.2 (1.00)
C_{13}	Tridecylamide	3.75 (1.00)	4.45 (0.80)	4.9 (0.70)	4.26 (0.40)	8.6 (0.05)
C_{14}	Myristamide	3.93 (1.00)	4.46 (0.60)	4.8 (0.50)	9.4 (0.40)	13.9 (0.02)
C_{15}	Pentadecylamide	3.84 (1.00)	4.5 (0.80)	4.9 (0.50)	4.8 (0.50)	10.0 (0.20)
C_{16}	Palmitamide	3.70 (1.00)	4.47 (0.50)	4.39 (0.50)	10.9 (0.30)	10.9 (0.30)
C_{17}	Margaramide	3.88 (1.00)	4.33 (0.50)	4.92 (0.20)	10.3 (0.10)	11.5 (0.10)
C_{18}	Stearamide	4.46 (1.00)	4.37 (1.00)	3.70 (0.90)	4.09 (0.30)	11.9 (0.10)

Table IX. Index Lines of Silver Salts of Fatty Acids

No.	Silver Salt	Strongest Lines 1st	2nd	3rd	4th	Innermost Line
C_2	Acetate	9.85 (1.00)	3.05 (0.50)	2.92 (0.40)	2.46 (0.40)	9.85 (1.00)
C_3	Propionate	12.5 (1.00)	6.3 (0.80)	3.02 (0.80)	2.45 (0.80)	12.5 (1.00)
C_4	*n*-Butyrate	15.0 (1.00)	7.5 (0.80)	2.92 (0.60)	2.59 (0.60)	15.0 (1.00)
C_4	Isobutyrate	13.2 (1.00)	7.2 (0.90)	6.4 (0.80)	3.29 (0.80)	13.2 (1.00)
C_5	*n*-Valerate	8.9 (1.00)	5.9 (0.60)	3.13 (0.50)	3.24 (0.45)	8.9 (1.00)
C_5	Isovalerate	12.1 (1.00)	5.9 (0.90)	4.41 (0.80)	4.25 (0.80)	12.1 (1.00)
C_6	α-Methylbutyrate	13.0 (1.00)	8.9 (0.90)	6.4 (0.50)	2.74 (0.10)	13.0 (1.00)
C_5	Trimethyl acetate	12.0 (1.00)	8.9 (0.90)	8.1 (0.90)	4.03 (0.40)	12.0 (1.00)
C_6	*n*-Caproate	9.7 (1.00)	3.24 (0.90)	6.5 (0.80)	3.17 (0.25)	9.7 (1.00)
C_6	Isocaproate	13.8 (1.00)	6.9 (0.90)	4.6 (0.70)	4.29 (0.60)	13.8 (1.00)
C_7	Enanthate	11.1 (1.00)	7.4 (0.90)	3.25 (0.80)	3.15 (0.65)	11.1 (1.00)
C_8	Caprylate	12.1 (1.00)	8.1 (0.90)	3.29 (0.80)	6.1 (0.35)	12.1 (1.00)
C_9	Pelargonate	13.6 (1.00)	9.1 (0.90)	3.31 (0.80)	6.8 (0.40)	13.6 (1.00)
C_{10}	Caprate	3.33 (1.00)	9.8 (0.90)	14.8 (0.80)	7.4 (0.75)	14.8 (0.80)
C_{11}	Undecylate	10.5 (1.00)	16.0 (0.80)	7.9 (0.80)	6.4 (0.80)	16.0 (0.80)
C_{12}	Laurate	17.0 (1.00)	11.4 (1.00)	8.5 (0.90)	6.8 (0.90)	17.0 (1.00)
C_{13}	Tridecylate	18.4 (1.00)	12.3 (1.00)	9.2 (0.95)	7.4 (0.95)	18.4 (1.00)
C_{14}	Myristate	13.0 (1.00)	3.37 (0.90)	4.5 (0.85)	9.7 (0.80)	13.0 (1.00)
C_{15}	Pentadecylate	14.1 (1.00)	10.6 (0.90)	8.5 (0.90)	4.53 (0.80)	14.1 (1.00)
C_{16}	Palmitate	22.1 (1.00)	14.8 (1.00)	11.0 (0.60)	8.8 (0.60)	22.1 (1.00)
C_{17}	Margarate	9.5 (1.00)	12.0 (0.90)	4.57 (0.90)	16.0 (0.80)	16.0 (0.80)
C_{18}	Stearate	16.3 (1.00)	3.38 (0.70)	12.2 (0.60)	9.7 (0.60)	16.3 (1.00)
C_{20}	Arachidate	17.9 (1.00)	13.35 (0.40)	10.75 (0.40)	8.9 (0.20)	17.9 (1.00)
C_{22}	Behenate	19.5 (1.00)	14.7 (0.60)	11.7 (0.60)	9.7 (0.40)	19.5 (1.00)

Table X. Index Lines of Anilides of Fatty Acids

No.	Name	Strongest Lines 1st	2nd	3rd	4th	Innermost Line
C_{13}	Tridecylanilide	4.06 (1.00)	4.30 (0.40)	10.1 (0.35)	3.64 (0.30)	20.7 (0.25)
C_{15}	Pentadecylanilide	4.07 (1.00)	4.28 (0.45)	3.66 (0.40)	11.15 (0.35)	11.15 (0.35)
C_{17}	Margaranilide	4.06 (1.00)	4.22 (0.40)	3.63 (0.35)	12.1 (0.25)	12.1 (0.25)

radiation with a powder camera (diameter 143.2 mm.). The significance of the innermost reflection in the powder pattern with respect to the structure of these acids is under investigation and will be reported at a later date.

CONCLUSION

X-ray powder diffraction data on three series of derivatives of the fatty acids—anilides, amides, and silver salts—have been determined for use as a means of identification of the acids, C_2 to C_{22}. Differentiation of the acids is possible in all three series.

Melting point data are available for most of the anilides and amides, although there is considerable variation in the published values for the higher members. Differentiation on this basis, however, requires careful purification before reliable results can be obtained. The silver salts are easy to prepare and their silver content may be readily determined and compared to a calculated value.

Homologously related crystal structures are found throughout the amides and silver salt series and in the anilides of acids C_8 and longer. The latter show two separate homologous series, the odd or even numbers. This factor may favor the use of anilides in certain instances. The increment in the longest d spacing is greatest in the silver salts. This factor, coupled with its ease of preparation and analysis, favors the use of this derivative for the identification of a fatty acid.

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X-Ray Identification of Alkyl Halides

As Alkyl 6-Nitrobenzothiazolyl-2-sulfides and Sulfones

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Using chromium target x-radiation, the powder diffraction patterns for the alkyl 6-nitrobenzothiazolyl-2-sulfides and the alkyl 6-nitrobenzothiazolyl-2-sulfones were shown to be sufficiently characteristic to enable individual identification and thus identification of the alkyl halides from which the sulfides and sulfones were prepared. Extreme purity of the crystalline substance was unnecessary to obtain characteristic patterns.

IDENTIFICATION of alkyl halides is one of the more difficult problems of the organic chemist, because there are few entirely suitable derivatives. The recently proposed (*3*) method of identification through the formation of alkyl 6-nitrobenzothiazolyl-2-sulfides from the alkyl halide and 6-nitromercaptobenzothiazole has the advantage that it serves for primary and secondary alkyl chlorides, bromides, or iodides and that two crystalline derivatives are readily formed from each alkyl halides—i.e., the sulfide and the sulfone. Small amounts of impurities cause lowering of the melting points of derivatives. It has been shown (*2*, *6*, *7*) that the x-ray powder diffraction patterns of the derivatives are useful aids in the identification of mixtures. In this paper the x-ray powder diffraction patterns of a number of these derivatives of alkyl halides are reported.

EXPERIMENTAL

The compounds used in this study were prepared and furnished by Harold B. Cutter and Harold R. Golden of Wayne University. The alkyl 6-nitrobenzothiazolyl-2-sulfides were prepared from alkyl halides (except tertiary alkyls) and 6-nitro-2-mercaptobenzothiazole dissolved in butyl Carbitol (diethylene glycol monobutyl ether) and 2 N sodium hydroxide. After refluxing, the mixtures were cooled to room temperature and poured into ice water. The crude product was recrystallized from methanol (*3*).

The alkyl 6-nitrobenzothiazolyl-2-sulfones were prepared from the sulfides by solution of the sulfide in glacial acetic acid and oxidation with a 50% excess of 7.5% potassium permanganate solution. The manganese dioxide was removed by addition of sulfurous acid. The sulfones were precipitated by adding ice water to the solution, and after filtration were recrystallized from water–ethyl alcohol solutions. Complete details of the preparations are given by Cutter and Golden (*3*).

The Hayes diffraction unit was used for recording the powder patterns. Increased dispersion was accomplished by the use of chromium K_α (λ = 2.28962 A.) radiation (*1*, *5*). The source of chromium radiation was a Machlett Type A-2 tube with beryllium metal windows. The tube was operated at a potential of 35 kv. and a current of 15 ma.

Exposures were made with powder cameras of 6.95-cm. radius, and an 0.06-inch pinhole was used as the slit for the incident x-rays. A conically machined supporting tube holding the camera to the Machlett tube assured positive alignment with the x-ray beam. A small beam trap and central mounting of the specimen rotated by a motor permitted the registration of spacings of less than 20 A. and measurement on both sides of the central beam. The radii of the cameras were determined from the diffraction patterns of pure sodium chloride. The samples used were carefully ground in a Mullite mortar and were then mounted on a thin glass fiber which was coated with vaseline (*8*, *9*).

Using Eastman Blue Brand film, the exposure time was about 4 hours for the organic compounds. Films were developed in East-

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Table I. X-Ray Diffraction Data for Alkyl 6-Nitrobenzothiazolyl-2-sulfides

Methyl		Ethyl		*n*-Propyl		Isopropyl	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
5.42	10	3.42	10	3.45	10	3.74	10
3.43	9	5.25	9	6.25	8	8.22	7
4.88	8	3.24	8	9.12	6	5.11	6
4.40	3	3.06	2	3.57	4	10.23	5
3.19	1	...	..	4.03	3	3.13	4
3.28	0.5	...	..	3.74	1	...	..
n-Butyl		Isobutyl		*n*-Amyl		*n*-Hexyl	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
3.39	10	3.62	10	3.91	10	3.65	10
3.60	9	5.60	9	3.38	9	5.31	9
4.05	8	3.45	3	4.26	8	3.35	7
5.81	7	11.29	2	3.70	8	10.68	6
5.09	7	...	..	9.65	7	3.87	6
8.95	6	...	..	7.38	7	4.00	5
7.36	6	...	..	5.50	6	9.13	3
4.62	6	...	..	...	..	4.68	2
n-Heptyl		Cyclohexyl		Benzyl		Isoamyl	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
3.67	10	6.93	10	4.19	10	3.80	10
5.57	9	9.37	9	3.58	9	3.37	9
11.07	8	4.94	7	5.79	8	4.78	8
3.38	4	3.55	5	10.83	4	7.51	7
4.70	2	3.32	2	8.40	4	10.95	2
3.87	2	4.46	1	3.25	1	...	..
4.03	1	...	..	...	..	...	..

man Kodak x-ray developer for 5 minutes at 20° C. The arcs on the film were measured on the centimeter scale of a comparator. The intensities recorded were estimated from a visual examination of the film and are noted on a scale of one to ten, ten being the most intense line of the pattern. If two or more arcs appeared to be equally intense to the eye, the innermost—the one with the greatest spacing—was recorded as being the most intense.

The filter used to pass essentially the K_α wave length was made from vanadium pentoxide ground in cellulose acetate or nitrate cement (*4*, *5*). The concentration found by Matthews and Michell to give satisfactory removal of the chromium K_β lines was 15 mg. of vanadium pentoxide per square centimeter (*7*).

Table II. X-Ray Diffraction Data for Alkyl 6-Nitrobenzothiazolyl-2-sulfones

Methyl		Ethyl		*n*-Propyl		Isopropyl	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
3.61	10	5.74	10	3.54	10	5.52	10
9.23	9	3.25	9	3.99	9	3.64	9
5.41	8	5.03	8	5.64	8	7.64	8
4.67	4	3.89	7	5.15	7	3.32	7
2.98	3	3.11	6	10.19	5	3.95	3
3.90	1	2.64	2	2.89	3	10.65	2
...	..	..	..	3.19	1	...	..
n-Butyl		Isobutyl		*sec*-Butyl		*n*-Amyl	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
5.77	10	3.47	10	3.49	10	5.79	10
3.96	9	5.22	9	5.36	9	3.33	9
3.71	8	4.05	8	11.48	7	3.48	8
3.26	7	2.93	4	9.44	6	3.78	6
12.36	5	..	..	6.90	3	3.16	6
3.44	5	..	..	4.15	3	3.95	5
9.17	4	..	..	2.90	2	...	..
6.96	2	..	..	4.50	1	...	..
5.01	1	..	..	2.79	1	...	..
4.51	1	..	..	...	..	...	..
Isoamyl		*n*-Hexyl		*n*-Heptyl		Cyclohexyl	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*
12.09	10	5.57	10	16.41	10	5.41	10
5.17	9	3.50	9	3.31	9	3.61	9
3.53	8	3.16	8	5.57	8	3.98	8
3.94	5	4.91	7	4.09	7	6.94	7
...	..	4.16	6	3.88	6	3.40	7
...	..	3.94	6	3.56	6	4.20	3
...	..	3.75	6	3.02	4	3.03	2
...	..	..	..	4.96	1	2.88	1

The powder diffraction data (an average of two films) for the alkyl 6-nitrobenzothiazolyl-2-sulfides are listed in Table I, and those for the alkyl 6-nitrobenzothiazolyl-2-sulfones are listed in Table II. Table III contains the data for four mixtures made up from some of the compounds listed in Tables I and II.

DISCUSSION

Examination of the powder diffraction data for unique characteristics by which identity of the compounds can be established shows that the patterns of the alkyl 6-nitrobenzothiazolyl-2-sulfides and the alkyl 6-nitrobenzothiazolyl-2-sulfones may be readily distinguished by the three strongest reflection lines of their patterns (see Table IV). The pattern of a straight-chain derivative can be readily distinguished from that of its structural isomer.

The method would not be acceptable for the determination of mixtures unless the two components were present in essentially equal amounts. It was possible to distinguish the two components of mixtures 1 and 2 where the compounds were present in equal amounts, but in mixtures 3 and 4 the only lines of the minor component appearing are those near one of the diffraction lines of the major component (see Table III). This is true even in mix-

Table III. X-Ray Diffraction Data for Mixtures of Alkyl 6-Nitrobenzothiazolyl-2-sulfides

Mixture 1[a]		Ethyl		*n*-Butyl	
d	*I*	*d*	*I*	*d*	*I*
3.41	10	3.42	10	3.39	10
5.23	9	5.25	9	..	..
3.60	8	..	..	3.60	9
7.41	4	..	..	7.36	6
3.25	4	3.24	8	..	..
4.03	2	..	..	4.05	8
5.83	1	..	..	5.81	7
Mixture 2[b]		*n*-Butyl		*n*-Amyl	
d	*I*	*d*	*I*	*d*	*I*
3.78	10	..	..	3.70	8
5.50	7	..	..	5.50	6
3.41	7	3.39	10	..	..
3.61	5	3.60	9	..	..
3.95	4	4.05	8	3.91	10
Mixture 3[c]		Ethyl		*n*-Butyl	
d	*I*	*d*	*I*	*d*	*I*
3.40	10	3.42	10	3.39	10
3.61	9	..	..	3.60	9
4.04	8	..	..	4.05	8
7.38	5	..	..	7.36	6
4.67	4	..	..	4.62	6
5.86	3	..	..	5.81	7
9.04	2	..	..	8.95	6
Mixture 4[d]		*n*-Butyl		*n*-Amyl	
d	*I*	*d*	*I*	*d*	*I*
3.89	10	..	..	3.91	10
3.39	9	3.39	10	3.38	9
3.64	8	3.60	9	3.64	8
7.37	7	..	..	7.38	7
4.23	6	..	..	4.26	8
9.58	2	..	..	9.65	7
5.46	1	..	..	5.50	6

[a] 50% by weight ethyl sulfide and *n*-butyl sulfide.
[b] 50% by weight *n*-butyl sulfide and *n*-amyl sulfide.
[c] 25% ethyl sulfide and 75% *n*-butyl sulfide.
[d] 25% *n*-butyl sulfide and 75% *n*-amyl sulfide.

Table IV. Data Arranged in Order of Strongest Line of Diffraction Pattern

1st Line	2nd Line	3rd Line	Compound
3.39	3.60	4.05	*n*-Butyl sulfide
3.42	5.25	3.24	Ethyl sulfide
3.45	6.25	9.12	*n*-Propyl sulfide
3.47	5.22	4.05	Isobutyl sulfone
3.49	5.36	11.48	*sec*-Butyl sulfone
3.54	3.99	5.64	*n*-Propyl sulfone
3.61	9.23	5.41	Methyl sulfone
3.62	5.60	3.45	Isobutyl sulfide
3.65	5.31	3.35	*n*-Hexyl sulfide
3.67	5.57	11.07	*n*-Heptyl sulfide
3.74	8.22	5.11	Isopropyl sulfide
3.80	3.37	4.78	Isoamyl sulfide
3.91	3.38	4.26	*n*-Amyl sulfide
4.19	3.58	5.79	Benzyl sulfide
5.41	3.61	3.98	Cyclohexyl sulfone
5.42	3.43	4.88	Methyl sulfide
5.52	3.64	7.64	Isopropyl sulfone
5.57	3.50	3.16	*n*-Hexyl sulfone
5.74	3.25	5.03	Ethyl sulfone
5.77	3.96	3.71	*n*-Butyl sulfone
5.79	3.33	3.48	*n*-Amyl sulfone
6.93	9.37	4.94	Cyclohexyl sulfide
12.09	5.17	3.53	Isoamyl sulfone
16.41	3.31	5.57	*n*-Heptyl sulfone

ture 3, where ethyl 6-nitrobenzothiazolyl-2-sulfide is the minor component. The only line recorded that might belong to the ethyl derivative is 3.41, but this also corresponds to the major line of the *n*-butyl derivative, the major component. It is safe to assume that if the line was due to the ethyl derivative there would, also, be present in the pattern a line equivalent to the 5.25 spacing which is a very intense line, as can be seen from Table I. It may be concluded from the data that extreme purity of the crystalline samples was not necessary to obtain distinctive diffraction patterns. With improved techniques, it is possible that 25% of a second phase might be detected.

The error in measurement of d increases from ±0.05 A. at 3.0 A. to ±0.20 A. at 16.0 A.

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Polarography of Chloroform and Carbon Tetrachloride

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Both carbon tetrachloride and chloroform can be polarographically reduced. Carbon tetrachloride gives two 2-electron reduction waves, the first corresponding to a reduction to chloroform and the second to a reduction to methylene chloride. Chloroform gives one wave which coincides with the second reduction wave of carbon tetrachloride. The height of the waves was found to be proportional to the concentration of the halogenated methane. Procedures are given for the determination of chloroform and carbon tetrachloride separately and in mixtures of the two. A solvent composed of 2 volume parts of methanol and 1 volume part of water with a supporting electrolyte of 0.1 *M* tetramethylammonium bromide was found to be most satisfactory.

NO systematic study of the reduction of halogenated methanes at the dropping mercury electrode has previously been made (*9*). Statements made by Matheson and Nichols (*6*) concerning carbon tetrachloride and by Stone (*8*) concerning carbon tetrabromide indicate that these compounds are polarographically reducible. In the investigation described below it was found that carbon tetrachloride is reduced at the dropping mercury electrode to chloroform, and chloroform is reduced to methylene chloride. Thus carbon tetrachloride yields two polarographic waves, the second of which is similar to the single wave given by chloroform. The dependence of the height of the polarographic waves on concentration and the dependence of the half-wave potentials on concentration and pH were studied. The results of this investigation lead to the conclusion that the polarographic method provides a simple and reliable means of identifying and determining carbon tetrachloride and chloroform. The polarographic method was used to determine the solubility of these two compounds in pure water and to determine small amounts of carbon tetrachloride in the presence of large amounts of chloroform.

As will be shown in a subsequent publication, other halogenated methanes are also reducible at the dropping mercury electrode. The ease of reduction is in the order: iodinated methanes > brominated methanes > chlorinated methanes. The ease of reduction also increases with the number of halogen atoms joined to the carbon atom—e.g., carbon tetrachloride is more easily reduced than chloroform.

EXPERIMENTAL

Apparatus. A Sargent Model XII Heyrovský polarograph was used to record polarographic waves. The measurements of diffusion current constants and the determinations of carbon tetrachloride and chloroform were made with a manual polarograph (*5*).

Two capillaries were used in the investigation. The value of $m^{2/3}t^{1/6}$ of capillary A under the experimental conditions was 2.060 mg.$^{2/3}$ sec.$^{-1/2}$ at −0.5 volt *vs.* S.C.E., 2.030 at −1.2 volts, and 1.870 at −2.0 volts. The value of $m^{2/3}t^{1/6}$ of capillary B was 1.791 at −0.5 volt, 1.770 at −1.2 volts, and 1.625 at −2.0 volts.

All mercury electrode potentials were measured against an external saturated calomel reference electrode.

In the experiments carried out at 25° C. the polarographic cell was immersed in a thermostated (±0.1°) water bath. For experiments at 0° a bath of water and cracked ice was used.

Reagents. Mallinckrodt's reagent grade carbon tetrachloride and Merck's reagent grade chloroform were used without further purification. In the early experiments the chloroform and carbon tetrachloride were purified by fractional distillation. However, the purified and the untreated reagent grade compounds gave identical results in polarographic experiments. (Reagent grade chloroform usually contains about 0.7% ethanol as an inhibitor for decomposition.)

Reagent grade methanol was used. The tetramethylammonium bromide and calcium chloride used for supporting electrolytes were both polarographically pure.

Procedure. Because carbon tetrachloride and chloroform are only slightly soluble in water, a solvent consisting of 2 volume parts of methanol and 1 volume part of water was used.

Inasmuch as oxygen is easily reduced at the dropping mercury electrode, it was necessary to remove dissolved oxygen from the solutions under investigation. Sodium sulfite, which is sometimes used for this purpose, was not effective because the alcohol greatly retarded the reaction of sulfite with oxygen. It is not feasible to remove dissolved oxygen by bubbling nitrogen directly through the solutions of the halogenated methanes because of the high volatility of these compounds. The following technique was therefore adopted:

Purified nitrogen previously saturated with the solvent was bubbled for 30 minutes through a polarographic cell, which contained the alcohol-water solvent and the supporting electrolyte. The flow of nitrogen was then interrupted and the nitrogen was allowed to pass slowly over the surface of the solution. A small volume of a methanol solution of the halogenated methane was added from a pipet or microburet. The contents of the polarographic cell were stirred with a glass rod and the polarographic measurements were made immediately.

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Table I. Characteristics of Polarographic Waves of Carbon Tetrachloride and of Chloroform (at 25° C.)

Compound	Concn., Millimolar	$(\pi_{1/2})_1$	$(\pi_{1/2})_2$	$\frac{i_d}{Cm^{2/3}t^{1/6}}$	$\frac{i_{d1}+i_{d2}}{Cm^{2/3}t^{1/6}}$
CCl_4[a]	0.35	...	...	4.07[b]	7.47
	0.695	−0.75	−1.70	4.23	8.10
	1.38	−0.75	−1.70	4.24	8.28
	2.06	−0.75	−1.73	4.23	8.17
$CHCl_3$[c]	0.33	−1.69	..	4.35	..
	0.665	−1.67	..	4.37	..
	1.33	−1.68	..	4.29	..

[a] Capillary A used.
[b] All values of diffusion current corrected for residual current.
[c] Capillary B used.

Table II. Dependence of Diffusion Current on Concentration (at 0° C.)

Compound	Concn., Millimolar	i_d[a], μa.	i_d/C, μa./millimole
CCl_4 (first wave)	0.443	2.28[b]	5.15
	0.882	4.54	5.14
	1.32	6.70	5.08
	1.75	8.92	5.09
	2.18	11.06	5.07
			Av. 5.11
$CHCl_3$	0.632	2.90[c]	4.59
	1.26	6.06	4.82
	1.88	9.14	4.85
	2.50	12.18	4.87
	3.11	14.80	4.75
	3.73	17.70	4.74
			Av. 4.77

[a] All values of diffusion current corrected for residual current. Capillary A used.
[b] Measured at −1.2 volts *vs.* S.C.E.
[c] Measured at −2.0 volts *vs.* S.C.E.

In the determination of chloroform and carbon tetrachloride the volume of methanol solution added should be less than 2 ml. (per 50 ml. of solvent) in order to have a negligible error due to oxygen. (Air-saturated methanol at 25° C. is about 0.002 *M* in oxygen.) Calibration curves are recommended in the determination of chloroform and carbon tetrachloride. This procedure effectively eliminates any error that might otherwise result from the presence of oxygen. An alternative procedure would be to apply a correction for the amount of oxygen introduced with the methanol solution. The correction can be found from a "blank" experiment, in which pure methanol is substituted for the methanol solution of carbon tetrachloride or chloroform.

Great care must be taken in handling samples and solutions containing carbon tetrachloride and chloroform, to avoid serious loss by volatilization.

RESULTS AND DISCUSSION

Carbon Tetrachloride. In Figure 1 (curve I) is shown a polarogram of carbon tetrachloride in the methanol-water solvent with tetramethylammonium bromide as supporting electrolyte. Carbon tetrachloride yields two waves of nearly equal height. The half-wave potentials of the two waves are −0.75 and −1.70 volts *vs.* the saturated calomel electrode. The waves are not nearly so steep as the wave for a reversible reduction, as can be seen by comparing the polarographic wave of lead in aqueous solution (curve IV) with the carbon tetrachloride waves. The equation of the wave is (*4*)

$$\pi = \pi_{1/2} + \frac{RT}{\alpha F} \ln \frac{i_d - i}{i}$$

where α has the value 0.23 instead of the theoretical value 2 for a reversible 2-electron reduction

In Figure 2 are shown polarograms of carbon tetrachloride solutions of varying concentrations. It can be seen that the half-wave potentials of the first and second waves are independent of the carbon tetrachloride concentration. The dependence of wave height on concentration is shown in Tables I and II. The experiments of Table I were carried out at 25° C., and although

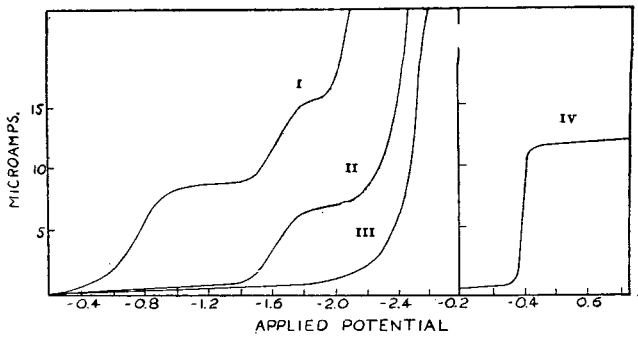

Figure 1. Polarogram of Carbon Tetrachloride and Chloroform

I. 1.1 millimolar carbon tetrachloride
II. 1.0 millimolar chloroform
III. Residual current. Solvent 2 volume parts of methanol, 1 volume part of water, supporting electrolyte 0.1 *M* tetramethylammonium bromide
IV. 1.53 millimolar lead nitrate in 0.1 *M* potassium nitrate

Temperature, 25° C.
Capillary A used

a small error in the value of the diffusion current, i_d, undoubtedly resulted from volatilization and loss of carbon tetrachloride, it is evident that the diffusion current is proportional to concentration. The value of the polarographic constant, $i_d/Cm^{2/3}t^{1/6}$, at 25° C. is about 4.2 μa. per millimole mg.$^{2/3}$ sec.$^{-1/2}$, compared with about 3.6 for benzoquinone in the same solvent. Inasmuch as the reduction of benzoquinone involves two electrons and the diffusion coefficient of carbon tetrachloride is somewhat larger than that of benzoquinone, it can be concluded that two electrons are involved in the first step of the reduction of carbon tetrachloride. The value of the polarographic constant of the second wave of carbon tetrachloride is about 4.0, close to the value for the first wave; therefore, the second wave also corresponds to a reduction involving two electrons.

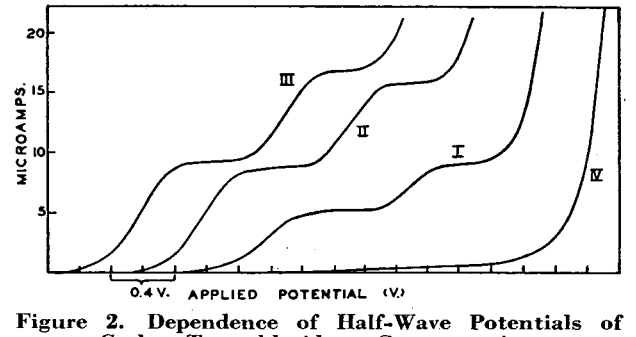

Figure 2. Dependence of Half-Wave Potentials of Carbon Tetrachloride on Concentration

Solvent 2 to 1 methanol–water. Electrolyte 0.1 *M* tetramethylammonium bromide. Temperature 25° C. Waves start at − 0.20 volt

I. 0.675 millimolar, sensitivity 1/100
II. 1.35 millimolar, sensitivity 1/100
III. 2.01 millimolar, sensitivity 1/150
IV. Blank, sensitivity 1/70

The proportionality of diffusion current of the first carbon tetrachloride wave to the concentration is also demonstrated in Table II. These experiments were carried out at 0° C. and the loss by volatilization was negligible.

The effect of pH on the first carbon tetrachloride wave is shown in Figure 3. [The solutions for these experiments were prepared by adding 2 volumes of methanol to 1 volume of aqueous Britton-Robinson buffer solution (*2*). The values of pH given in Figure 3 refer to the pH of the aqueous solution before addition of methanol.] The half-wave potential and the wave height do not change with pH in the range pH 4.6 to 11. In solutions of low pH (4 or less) the reduction of hydrogen ion interferes with the carbon tetrachloride wave. Consequently,

the polarographic determination of carbon tetrachloride cannot be carried out in a solution more acid than pH 4.

Chloroform. In Figure 1, curve II, is shown the polarogram of chloroform in a methanol-water solution of tetramethylammonium bromide. The half-wave potential of chloroform is −1.70 volts, the same as that of the second carbon tetrachloride wave. The dependence of the half-wave potential of the chloroform wave on concentration is shown in Figure 4 and Table I. It can be seen that the half-wave potential is independent of concentration of chloroform. The dependence of the height of the wave on concentration is shown in Tables I and II. The data of Table II are more reliable because of the relatively low volatility of chloroform from the solution at 0° C. The height of the wave is, within experimental error, proportional to the concentration.

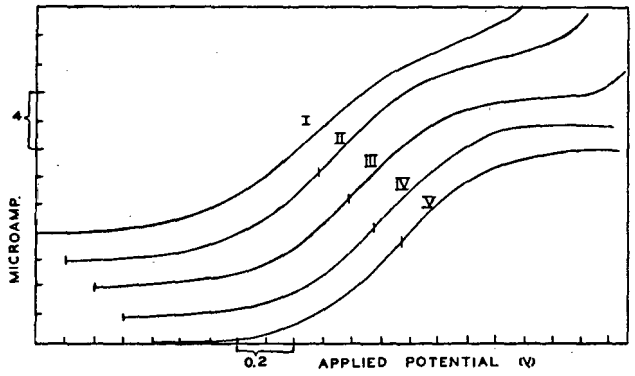

Figure 3. Effect of pH on First Carbon Tetrachloride Wave

Solvent 2 to 1 methanol–water. Electrolyte 0.1 *M* tetramethylammonium bromide. 2 millimolar carbon tetrachloride. Capillary B. Curves start at +0.1 volt

I. pH 3.9
II. pH 4.6
III. pH 5.9
IV. pH 8.8
V. pH 11.0

Under certain conditions the chloroform wave exhibits a maximum in the region of greatest slope—i.e., in the middle of the wave—which is most pronounced if the concentration of chloroform is high. The maximum also appears to be dependent on the capillary used, some capillaries yielding a maximum and others not yielding one. The maximum can be suppressed by addition to the solution of an electrolyte containing a divalent cation such as calcium. In Figure 5 are shown the polarograms of chloroform in solutions containing various amounts of calcium chloride. It can be seen that in a solution 0.05 *M* in calcium chloride the maximum is largely suppressed. However, the calcium ion itself yields a wave beginning at about −2.1 volts, and thus makes it difficult to find accurately the height of the chloroform wave. Nevertheless, even in the presence of calcium, the concentration of chloroform can be found from the wave height with an accuracy of about 2%.

The dependence of the half-wave potential of chloroform on pH was not investigated because of the relatively negative value of the chloroform half-wave potential.

The diffusion currents of carbon tetrachloride and chloroform were found to be proportional to the 0.5 power of the height of the mercury column, as would be expected from the Ilkovič equation. It can be concluded that the reduction of these compounds at the dropping mercury electrode is diffusion-controlled.

Electrode Reactions. The experimental results given above make it apparent that carbon tetrachloride is reduced at the electrode to chloroform and that two electrons are involved in the reaction. The over-all electrode reaction is therefore probably:

$$CCl_4 + H^+ + 2e \longrightarrow CHCl_3 + Cl^-$$

or $$CCl_4 + H_2O + 2e \longrightarrow CHCl_3 + Cl^- + OH^-$$

If the potential of the mercury electrode is sufficiently negative, chloroform is also reduced. This reduction also involves two electrons. The over-all reaction is probably:

$$CHCl_3 + H^+ + 2e \longrightarrow CH_2Cl_2 + Cl^-$$

or $$CHCl_3 + H_2O + 2e \longrightarrow CH_2Cl_2 + Cl^- + OH^-$$

Inasmuch as the half-wave potentials of the carbon tetrachloride and chloroform waves are independent of pH, the electrode reactions cannot be reversible. Although the mechanisms of the electrode reactions are not known, it is probable that the reaction step involving the proton occurs subsequent to the rate-determining reaction step.

Determination of Carbon Tetrachloride and Chloroform. The recommended procedure is the following:

Mix 2 volumes of methanol with 1 volume of 0.3 *M* tetramethylammonium bromide solution in water and bring the temperature of the mixture to 25° C. Place 50 ml. of the mixture in the polarographic cell, cool to 0° C., and pass nitrogen, previously saturated with solvent at 0° C., through the cell. After 30 minutes add exactly 1 ml. of a pure methanol solution of the sample to the cell as recommended in the procedure above. Measure the diffusion current at −1.2 volts *vs.* S.C.E. (carbon tetrachloride) or at −2.0 volts (chloroform). Compare the value of diffusion current with a calibration curve that is established by treating known amounts of carbon tetrachloride or chloroform in the same manner.

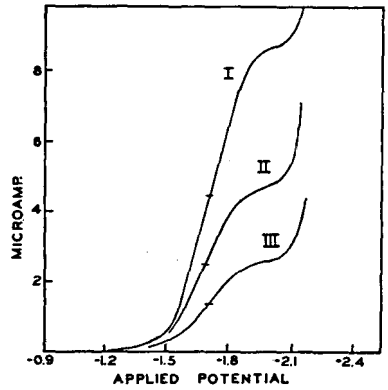

Figure 4. Dependence of Half-Wave Potential of Chloroform on Concentration

Solvent 2 to 1 methanol–water. Electrolyte 0.05 *M* calcium chloride. Temperature 25° C. Capillary B

I. 1.33 millimolar
II. 0.665 millimolar
III. 0.33 millimolar

In the recommended procedure the loss by volatilization of carbon tetrachloride or chloroform is minimized. Moreover, because in each experiment 1 ml. of air-saturated methanol solution is used, the amount of dissolved oxygen introduced is constant. A convenient alternative procedure can sometimes be used, in which pure carbon tetrachloride or chloroform is dissolved in methanol, which has previously been rendered air-free by bubbling nitrogen through it. The data for the calibration curve are readily obtained by adding successive increments of the air-free standard solution from a microburet to 50 ml. of 0.1 *M* tetramethylammonium bromide in 2 to 1 methanol-water solution at 0° C. If the calibration curve is prepared in this way, the sample must also be dissolved in air-free methanol. This procedure cannot be used if the sample before dilution contains less than about 10% carbon tetrachloride or chloroform.

The concentration of carbon tetrachloride or chloroform in the methanol solution should be 0.02 to 0.2 *M*. The methanol of the original solution could undoubtedly be replaced by other common solvents such as ethanol, dioxane, or ethylene chloride. The calibration "curves" are plots of the observed diffusion cur-

rent (not corrected for residual current) *vs.* the amount or concentration of compound taken. The calibration curves are, within experimental error, straight lines.

The accuracy of the recommended procedure can be seen from the results of Table II, which correspond to an average deviation of less than 1% in the determination of carbon tetrachloride and less than 2% in the determination of chloroform. The presence of substances which are reducible at the mercury electrode, such as aldehydes, organic nitro compounds, and many metal cations, interferes in the determination.

The recommended procedure was applied to the determination of the solubilities of carbon tetrachloride and chloroform in water. The solubilities at 25° C. were found to be 0.0053 *M* and 0.077 *M*, respectively. These values may be compared with the values 0.0050 *M* at 25° C. (carbon tetrachloride) and 0.0646 *M* at 30° C. (chloroform) found by Gross and Saylor (*3*) and independently by van Arkel and Vles (*1*).

Analysis of Mixtures of Carbon Tetrachloride and Chloroform. The polarographic method is also useful for the analysis of mixtures of the two halogenated methanes. Moderate amounts of chloroform do not interfere in the determination of carbon tetrachloride. On the other hand, carbon tetrachloride does make a contribution to the chloroform wave and it must be taken into account in the calculation of the amount of chloroform present. The total diffusion current at −2.0 volts *vs.* S.C.E. in the mixture is composed of the total diffusion current of carbon tetrachloride and the diffusion current of chloroform. The contribution made by carbon tetrachloride is found by multiplying the first diffusion current at −1.2 volts *vs.* S.C.E. by 0.925 × 1.93 = 1.79. The factor 0.925 accounts for the change of $m^{2/3}t^{1/6}$ between −1.2 and −2.0 volts, while 1.93 is the ratio of the total diffusion current constant to the first diffusion current constant of carbon tetrachloride (see Table I).

The following procedure is recommended for a mixture of carbon tetrachloride and chloroform. Measure the diffusion current at −1.2 volts (i_{d_1}) and at −2.0 volts (i_{d_t}). Multiply i_{d_1} by 1.79 and subtract this from i_{d_t}. Compare the value thus obtained with the calibration "curve" to find the concentration of chloroform present. In a synthetic mixture composed of 25 parts of carbon tetrachloride and 75 parts of chloroform the results were accurate to within 2%.

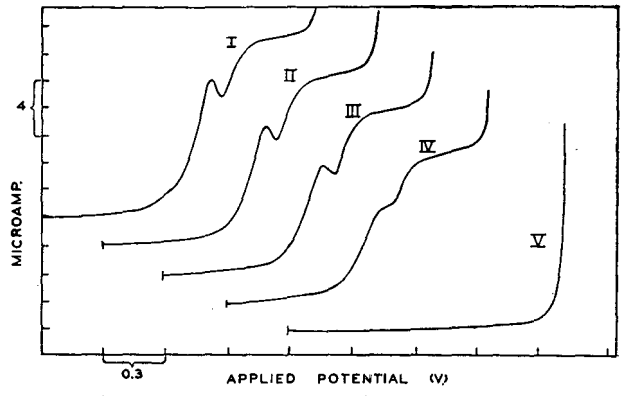

Figure 5. Effect of Calcium Ion on Maximum in Chloroform Wave

Solvent 2 to 1 methanol–water. Electrolyte 0.15 *M* tetramethylammonium bromide. Chloroform 2 millimolar. Temperature 25° C. Capillary B. Curves start at −0.9 volt

I. 0.005 *M*
II. 0.010 *M*
III. 0.015 *M*
IV. 0.03 *M*
V. 0.005 *M*, no chloroform

The polarographic method has also been applied to the determination of carbon tetrachloride in the presence of a large amount of chloroform. In Figure 6 is shown a polarogram of a mixture of carbon tetrachloride and chloroform (curve I), as well as a polarogram of a solution containing the same amount of chloroform but no carbon tetrachloride (curve II). The true diffusion current due to carbon tetrachloride is represented in Figure 6 by i_d and is obtained by subtracting from the current of curve I (at −1.3 volts) the current of curve II. For comparison purposes is shown a polarogram of a solution containing carbon tetrachloride only (curve III).

Table III. Characteristics of Carbon Tetrachloride Waves in Solutions of High Chloroform Concentrations

(Temp. 25° C., solvent 2 to 1 methanol-water, 0.1 *M* in tetramethylammonium bromide)

Concn. of CCl_4[a], Millimolar	Concn. of $CHCl_3$[a], Millimolar	$\pi_{1/2}$ of CCl_4 (First Wave)	i_d/C (at −1.3 Volts)
2.0	0	0.75	7.5[b]
2.0	200	0.80	7.5
6.6	200	0.80	7.3
6.6	400	0.85	7.3
6.6	800	0.90	7.3

[a] Concentration of solution in polarographic cell.
[b] Measurements made with capillary B. Diffusion current corrected for current due to chloroform.

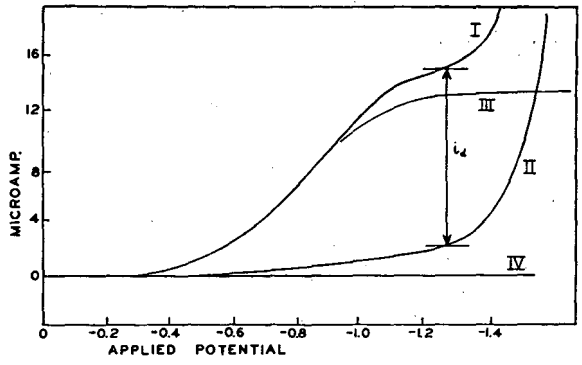

Figure 6. Polarogram of Mixture of Carbon Tetrachloride and Chloroform

Solvent 2 to 1 methanol–water. 0.08 *M* calcium chloride. Temperature 25° C. Capillary B

I. 0.002 *M* carbon tetrachloride and 0.2 *M* chloroform
II. 0.2 *M* chloroform
III. 0.002 *M* carbon tetrachloride
IV. Blank

In Table III are given the results of the determination of i_d/C of the first carbon tetrachloride wave in mixtures of varying composition. The diffusion current is proportional to the concentration of carbon tetrachloride and is practically independent of the concentration of chloroform. From Table III it also appears that the half-wave potential of the carbon tetrachloride wave is slightly more negative in solutions containing a large amount of chloroform than in solutions containing no chloroform. The change in half-wave potential is ascribed to the change in the nature of the solvent. Thus, in the last experiment of Table III the solvent contained about 6 volume % chloroform.

The polarographic method therefore provides a means of determining a small amount (down to 1%) of chloroform in carbon tetrachloride. From the results of Table III it appears that an accuracy of 2 to 3% is attainable.

SUMMARY

Carbon tetrachloride is reduced at the dropping mercury electrode, yielding two waves for which the values of $\pi_{1/2}$ are −0.75 and −1.70 volts *vs.* S.C.E., respectively. Chloroform yields one wave, for which the $\pi_{1/2}$ value is −1.70 volts.

The diffusion currents given by carbon tetrachloride and chloroform are proportional to concentration. Procedures for the polarographic determination of carbon tetrachloride and of chloroform yield results accurate to within 2%. Mixtures of the two chlorinated methanes can also be analyzed.

ACKNOWLEDGMENT

Acknowledgment is made to the Graduate School of the University of Minnesota for a grant which enabled the authors to carry out this investigation.

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RECEIVED November 10, 1949. After this manuscript was submitted, a publication by Stackelberg and Straeke appeared (*7*) in which the polarographic behavior of numerous halogenated hydrocarbons was studied briefly.

Polarography of Reduced Glutathione and Glutathione–Ascorbic Acid Mixtures

Amperometric Method for Determination of Ascorbic Acid

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In oxygen-free solutions buffered at pH values between 3 and 4, glutathione alone or in glutathione–ascorbic acid mixtures at concentrations from 10 to 300 micrograms per ml. can be determined with an accuracy of ±4%. In the mixtures the character of the ascorbic acid wave is influenced markedly by the glutathione. In solutions containing 20 to 40 micrograms of glutathione and 9 to 80 micrograms of ascorbic acid per milliliter a method of measuring ascorbic acid wave height is described which yields results within 0 to 2% of the weight value. Glutathione is found to be present in certain orange, guava, and potato samples. In most citrus fruit juices the content of glutathione and interfering materials is not high enough to affect the ascorbic acid wave seriously. An amperometric method for determining ascorbic acid is described and used in comparing polarographic with dye method results.

IN THE determination of ascorbic acid in fruits and vegetables the highest specificity is probably obtained by methods involving the use of 2,6-dichlorophenolindophenol dye and by those based on polarographic oxidation. When the solutions are too highly colored to permit direct titration with the dye solution, various potentiometric methods have been employed. Of these, that of Ramsey and Colichman (*8*) has the advantage of requiring only a stable potassium iodate solution as a standard oxidant, thus eliminating the necessity of frequent standardization of the dye solution. In the present work the authors have used an amperometric method which has several advantages over the potentiometric procedure.

The polarographic method has been employed by several workers (*1–4, 6, 7, 9*) with varying degrees of success. Results were satisfactory with certain fruits and vegetables, but there was indication of interference by other reducing agents in some cases. Recently Gillam (*2*) has made an extended study of the method in the determination of ascorbic acid in a number of fruits and vegetables and has developed a technique applying to quantities ranging from 4 to 85 micrograms per ml. with an accuracy of 3.3 to 4.3%. However, he noted that in certain materials interfering substances prevented the formation of a well defined limiting current. He also stated that the nature of the polarograms should show whether or not other reducing materials are present, and mentioned glutathione as a reductant that might have to be considered. No data appear in the literature regarding a study of the polarographic oxidation of glutathione or its effect on the polarographic determination of ascorbic acid. It was the purpose of the present investigation to make such a study, to consider the practicability of making a polarographic determination of glutathione, and to compare results of ascorbic acid determinations obtained by polarographic, potentiometric, and amperometric methods.

MATERIALS, APPARATUS, AND PROCEDURES

Materials. The glutathione was Eastman's No. 2585. An iodate titration of a vacuum desiccator–dried sample on the basis of oxidation to the disulfide showed a calculated value of 102% glutathione. A comparison of the glutathione polarograms with those of cysteine reported by Kolthoff and Barnum (*5*) indicated that no appreciable amount of cysteine was present.

The ascorbic acid was Merck's U.S.P. grade. An iodate titration of a dried sample showed 99.8% ascorbic acid.

The indophenol dye was Eastman's No. P3463.

The buffer solutions were 0.2 *M* when all constituents had been added preparatory to analysis. At pH values from 2 to 3 and 6 to 7 they were prepared by partially neutralizing 0.8 *M* orthophosphoric acid with saturated sodium hydroxide solution. At pH values from 4 to 6 they were prepared by partially neutralizing 0.8 *M* acetic acid with the base.

The natural products analyzed consisted of oranges, lemons, grapefruit, canned orange juice, guavas, and potatoes.

Apparatus. In the potentiometric method, a Leeds & Northrup student's potentiometer was used. In the polarographic work a Fisher Elecdropode was employed. A saturated calomel electrode was connected to the dropping mercury anode compartment by means of a 1 *M* sodium acetate agar bridge. For the amperometric method either a rotating platinum cathode or a fixed platinum cathode accompanied by constant stirring was found to be satisfactory. The anode consisted of a saturated calomel electrode which made connection with the titrated solution by means of a saturated potassium chloride agar bridge. Current measurements were made by means of the Elecdropode galvanometer.

pH measurements were made by means of a Model H Beckman pH meter.

All polarographic measurements were made at 25° ± 0.1° C. in a water bath.

Nitrogen was maintained oxygen-free by passage through a chromous chloride tower.

Procedures. AMPEROMETRIC TITRATIONS. Solution 1 consisted of 75 ml. of 0.3 *N* hydrochloric acid plus 10 ml. of 0.1 *M* potassium iodide solution and 10 ml. of ascorbic acid solution or unknown extract. Solution 2 was the same as 1 plus sufficient

excess indophenol dye solution containing 0.5 to 1 mg. per ml. to produce a recognizable color of the unreduced dye. In experiments on synthetic mixtures involving glutathione, 5 ml. of its aqueous solution were added to each titration mixture and the solutions were run into separate titration beakers. For each titration the electrodes were inserted and connected in series with the galvanometer. With a uniform rate of stirring, approximately 0.01 N potassium iodate solution was added at a convenient rate when no dye was present and about one drop every 5 seconds when the dye was present; readings were taken every milliliter until the addition of a drop produced a sudden rise in current. The rate of addition when the dye is present should not be much faster than that stated, for high local concentrations of iodine may cause oxidation of the reduced dye. The dropwise addition of iodate solution was continued past the equivalence point until four or five readings were obtained.

The end point was taken as the intersection of the straight lines resulting from plotting the volumes of reagent against currents read. The preliminary stage in which oxidation takes place is indicated by a straight line at practically zero current. With excess iodate an abrupt rise in current occurs and another straight line at an angle to the line of the first stage results. The sharp intersection of the two lines makes it possible to obtain an accurate measure of the reagent volume used. During the second stage the maximum current values were plotted and these were reached within less than a minute. It is not necessary to measure the current exactly at the end point, because points within a few drops on either side will be sufficient to form the two intersecting lines. The amount of ascorbic acid in the samples was measured by the difference between the iodate titrations of solutions 1 and 2.

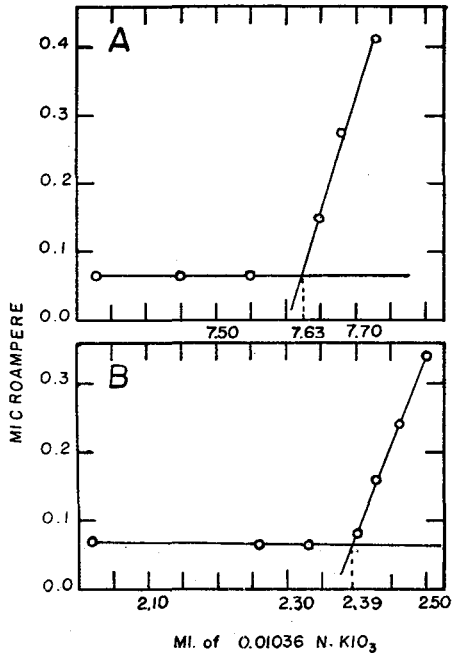

Figure 1. Amperometric Titration of Ascorbic Acid and Glutathione Mixtures

A. **Without dye addition**
B. **With dye addition**

Potentiometric Method. The composition of the solutions was essentially the same as in the amperometric method and the procedure of Ramsey and Colichman was closely followed.

Polarographic Experiments. About 10 ml. of solution consisting of suitable volumes of the unknown and buffer solutions to be run were introduced into a cylindrical vessel of about 15-ml. capacity, provided with a rubber stopper through which were inserted one arm of the salt bridge, the mercury capillary tube, a nitrogen bubbler tube, a gas exit tube, and a 10-ml. buret tip. The vessel was placed in the constant temperature bath, and nitrogen was bubbled through the solution for 15 to 20 minutes, after which current-voltage points were obtained from readings on the galvanometer scale and Elecdropode dial. From these data, the polarograms were plotted and the half-wave potentials determined. The mass of mercury per second, m, and drop time, t, of the mercury capillary were obtained in the phosphate buffer at pH 2.98, which was the value used in most of the determinations of ascorbic acid and glutathione, inasmuch as the pH of the solutions should not be much less than 3 or greater than 4. If the pH is much less than 3, there may be interference due to the dissolution of mercury at the anode, and at pH values much greater than 4 the ascorbic acid becomes less stable. In ascorbic acid the value of m was 1.29 mg. of mercury per second and that of t was 4.25 seconds per drop at +0.20 volt *vs.* the saturated calomel electrode. The corresponding values for glutathione were 1.29 mg. of mercury per second for m and 4.60 seconds for t at 0.00 volt *vs.* S.C.E. The diffusion current constants ($i_d/Cm^{2/3}t^{1/6}$), where i_d is the diffusion current in microamperes and C the concentration in millimoles per liter, were calculated for ascorbic acid and glutathione. The value of the diffusion current constant for ascorbic acid was 3.08 and that for glutathione was 1.39.

The slide wire on the Elecdropode drum was calibrated against a Leeds & Northrup student potentiometer. The galvanometer scale was checked by applying a known potential across a standard resistance in series with the galvanometer and comparing the calculated currents with the corresponding galvanometer deflections.

The fresh fruit extracts were prepared by squeezing the juice from the fruit and filtering it through several layers of cheesecloth. The potato and guava extracts were obtained by cutting up the materials into small cubes, whipping them with 0.1 M sulfuric acid solution in a Waring Blendor for about 5 minutes, and filtering through cheesecloth.

EXPERIMENTAL RESULTS

Amperometric Determination of Ascorbic Acid. Table I shows data obtained in a typical run in the determination of ascorbic acid in ascorbic acid–glutathione synthetic mixtures by the amperometric method. In this run 0.0540 me. of ascorbic acid was determined in the presence of 0.0246 me. of glutathione. For comparison, results by the potentiometric method are also shown. The data in Table I are plotted in Figure 1.

The values corresponding to the intersections of the straight lines of the graphs in the titrations before and after the addition of the dye are seen to be 7.63 and 2.39 ml., respectively. These volumes can be determined within about 0.01 ml. The volume of iodate corresponding to that equivalent to the ascorbic acid present will therefore be 5.24 ml. The difference between the amperometric and potentiometric methods is not significant. Other determinations in solutions containing 350 to 700 micrograms per ml. of ascorbic acid and 90 to 770 micrograms per ml. of glutathione showed an agreement of −0.7 to +1.2% in the ascorbic acid content by the two methods.

The advantages of the amperometric method over the potentiometric method are that it is more rapid, the end point is sharper, there is little trouble due to drift, and it is unnecessary to exclude air during a titration.

Table I. Amperometric Titration of Ascorbic Acid in Mixture of Ascorbic Acid and Glutathione

Before Dye Addition		After Dye Addition	
Buret, ml.	μa.	Buret, ml.	μa.
5.00	0.074	2.02	0.074
6.00	0.067	2.26	0.063
7.01	0.063	2.33	0.063
7.55	0.067	2.40	0.081
7.65	0.152	2.43	0.154
7.68	0.275	2.46	0.247
7.73	0.412	2.50	0.342

Ml. of 0.01036N KIO_3	7.63		2.39
Me. of KIO_3	0.0791		0.0248
		Found	
	Taken	Amperometric	Potentiometric
Me. of ascorbic acid	0.0543	0.0543	0.0540
% Difference		0.0	0.6

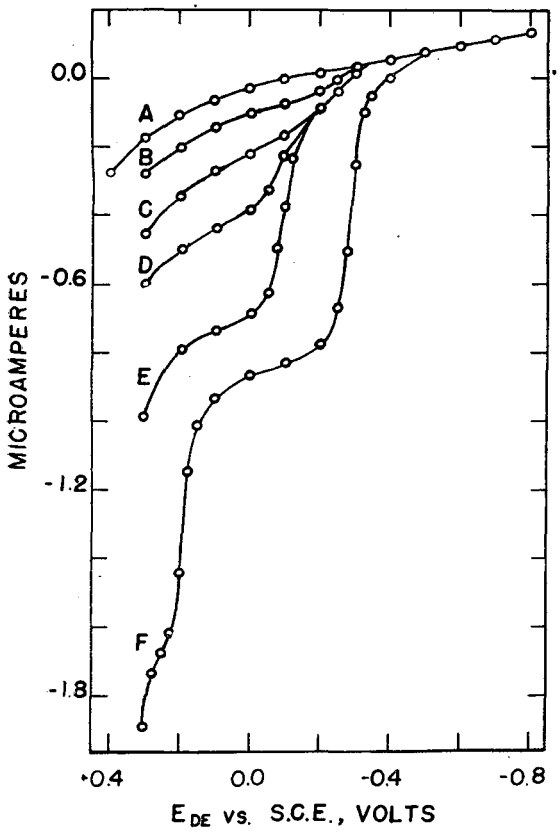

Figure 2. Polarograms for Glutathione

Concentrations *A* through *F*, 0, 11.2, 28.9, 51.5, 98.7, and 118.2 micrograms per ml., respectively. In *A* through *E* pH was 2.98 and in *F* was 6.00

Table II. Relation between Concentration of Glutathione and Current

Concn., γ/ml.	11.2	28.9	51.5	64.0	83.3	118.4	164	231
Current, μa.	0.7	0.21	0.37	0.47	0.60	0.81	1.16	1.60

Polarography of Glutathione. Figure 2 shows a set of polarograms for glutathione at different concentrations in phosphate buffers. In *A* to *E*, inclusive, the pH is 2.98, and in *F* the pH is 6.00. The features of most significance are the following: At the lowest concentrations there is a small apparently irreversible wave whose wave height is proportional to the concentration up to a concentration of approximately 20 micrograms per ml., above which there is no further increase. At concentrations above 20 micrograms per ml. a second wave develops immediately after the first one. At higher pH values a third wave becomes evident. At a pH of 6.00 the third half-wave potential is +0.20 volt *vs.* S.C.E. Probably this third wave was present in the runs at pH 2.98, but the only indication of its presence was the fact that the current near the last stage began to rise in value at a potential of +0.2 volt, which was appreciably lower than that required for the dissolution of the mercury in the supporting electrolyte.

There was a linear relationship between the concentration and the sum of the heights of the first two waves and this relation could be used as a basis for the determination of glutathione. In Table II are data showing the relation between concentration of glutathione and corresponding microamperes for a phosphate buffer at a pH of 2.98.

From the curves obtained by plotting $\log i/(i_d - i)$ values, where i is the average current, against the corresponding potentials for several waves, it was shown that the apparent value of n, the number of equivalents per mole for glutathione, was 1.2 in a buffer at pH 6.00 and 1.0 in a buffer at pH 2.98. The fact that the concentration of glutathione is proportional to the sum of the first two wave heights might lead to the assumption that both waves are due to the same type of reaction. It is possible that the behavior of glutathione is similar to that of cysteine reported by Kolthoff and Barnum (*5*), that the first wave is due to a film of difficultly soluble mercurous glutathionate, and that the second wave appears when a critical concentration and potential are reached. However, at these pH values the second wave develops at a much lower current (0.14 μa.) than in the case of cysteine (about 1 μa).

In Table III are shown values of half-wave potentials of the second wave obtained in glutathione solutions whose concentration is 139 micrograms per ml., and corresponding pH values in phosphate and acetate buffers. The slope of the uniform straight-line graph obtained by plotting these data is 0.059 volt per pH unit. Because n has been found to be 1 equivalent per mole, this indicates that the reaction involves 1 gram atom of hydrogen ion per mole of glutathione.

Polarography of Ascorbic Acid. A calibration curve for ascorbic acid in which concentration from 5 to 100 micrograms per ml. was plotted against microamperes was used. This was a uniform straight line similar to that which Gillam obtained over a range of 4 to 80 micrograms per ml. in phosphate buffer. A graph in which $\log i/(i_d - i)$ values were plotted against corresponding potentials showed that the value of n for ascorbic acid was 2.0 equivalents per mole. In Table III are also included pH values and corresponding half-wave potentials for ascorbic acid. The slope of the graph obtained by plotting these data is 0.059 volt per pH unit. Inasmuch as n in this case has been shown to be 2.0 equivalents per mole, the reaction also involves 2 gram atoms of hydrogen ion per mole of ascorbic acid.

Polarography of Ascorbic Acid and Glutathione Mixtures. In Table IV are results of determinations of ascorbic acid and glutathione in synthetic mixtures of the two by the polarographic method. In Figure 3 are polarograms for different concentrations of glutathione in a solution in which the ascorbic acid concentration is 39.4 micrograms per ml. A comparison of the half-wave potentials of the glutathione and ascorbic acid waves shown in Figures 2 and 3, *B*, would indicate that there should be no serious interference by glutathione in the development of the ascorbic acid waves. However, the curves for these mixtures in Figure 3 show a marked effect on the character of the ascorbic acid wave as the glutathione concentration increases. Not only does it become more difficult to measure the height of the ascorbic acid waves due to the merging of the ascorbic acid and third glutathione waves, but the ascorbic acid half-wave potentials shift to more positive values. The change in shape of the ascorbic acid wave begins to be marked if the glutathione concentration exceeds about 5 micrograms per ml. and if the weight ratio of glutathione to ascorbic acid is much greater than 1 to 10. If the glutathione concentration exceeds about 20 micrograms per ml., it is necessary to devise a method of measuring ascorbic

Table III. Half-Wave Potentials *vs.* pH at 25° C.

pH	2.00	2.70	3.00	4.00	5.00	6.00	6.50
$E^{1/2}$ *vs.* S.C.E., volt:							
Glutathione	...	−0.121	−0.142	...	−0.255	...	−0.340
Ascorbic acid	+0.218	...	+0.160	+0.105	+0.045	−0.015	−0.043

Table IV. Polarographic Results on Synthetic Ascorbic Acid–Glutathione Mixtures

Sample No.	Ascorbic Acid: Concn. by wt., γ/ml.	Ascorbic Acid: Concn. from polarogram, γ/ml.	Ascorbic Acid: % diff. between weight and polarogram results	Glutathione: Concn. by wt., γ/ml.	Glutathione: Concn. from polarogram, γ/ml.	Glutathione: % diff. between weight and polarogram results
1	39.4	39.4	0	8.8	8.4	−4.6
2	39.4	40.0	+1.0	18.4	19.2	+4.3
3	39.4	39.7	+0.5	31.7	30.3	−4.4
4	39.4	39.4	0	45.3	44.5	−1.8
5	39.4	39.7	+0.5	80.6	79.0	−2.0
6	26.3	26.9	+2	13.2	13.8	+4.5

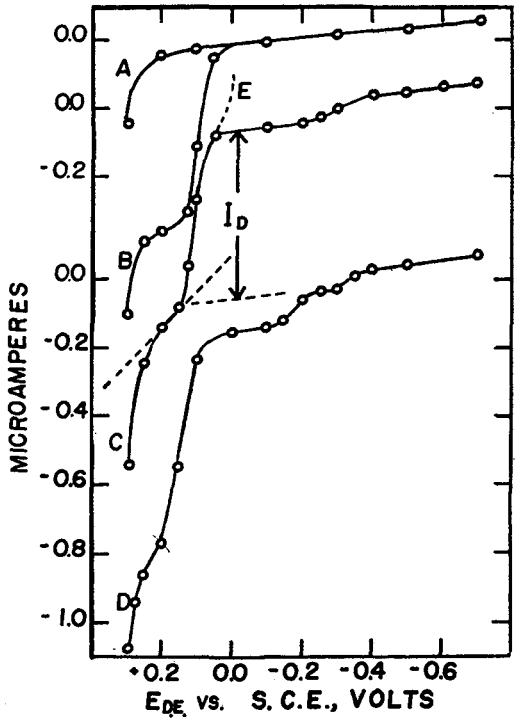

Figure 3. Polarograms of Glutathione–Ascorbic Acid Mixtures

pH 3.60. Concentrations *A* through *D*, 0, 39.4, 39.4, and 39.4 micrograms per ml. of ascorbic acid and 0, 0, 19.2, and 44.5 micrograms per ml. of glutathione, respectively. *E* is same solution as *C*, but air-saturated. I_d is ascorbic acid diffusion current

acid wave heights by which the error due to shift in half-wave potentials can be largely overcome. Several methods of measurement of wave height were tried, but the most reproducible method was found to be that shown in Figure, 3, *C*. The per cent differences between weight and polarograph concentrations of ascorbic acid are shown in Table IV and vary from 0 to 2%. The per cent differences between weight and polarograph concentrations of glutathione vary from −4.0 to +4.5%.

Figure 3, *E*, represents the change in *C* when the glutathione solutions are saturated with air. The interference of oxygen on the glutathione wave and the impracticability of measuring the heights of the ascorbic acid or glutathione waves in such a case are clearly evident. Cysteine might also offer definite ascorbic acid interference, because its second wave appears at a potential near that of ascorbic acid (*5*).

Analysis of Natural Products. In an attempt to learn if there was evidence of the presence of glutathione in certain natural products, polarograms were run on a number of samples of oranges, lemons, grapefruit, canned orange juice, guavas, and potatoes. Results of representative determinations of ascorbic acid in these samples by the polarographic and amperometric methods and of glutathione by the polarographic method are shown in Table V. Polarograms for analysis 2 of an orange sample, 7 of a potato sample, and 8 of a guava sample are shown in Figure 4. The difference between the polarographic and

Table V. Ascorbic Acid and Glutathione in Natural Products

Sample No.	Type of Sample	Ascorbic Acid, Mg./100 G. of Sample: Polarographic	Ascorbic Acid, Mg./100 G. of Sample: Amperometric	% diff. between polarographic and amperometric results	Reduced Glutathione from Polarogram, Mg./100 Grams Sample
1	Juice of freshly picked lemon	36.7	36.8	−0.3	0
2	Juice of freshly picked green orange	68.6	68.1	+0.7	4
3	Juice of freshly picked ripe orange	58.6	58.7	−0.2	0
4	Juice of storage orange	26.4	25.5	+3.5	0
5	Juice of freshly picked grapefruit	39.3	39.3	0	0
6	Canned orange juice	28.5	30.4	−6.2	0
7	Potato extracted with 0.1 *M* H_2SO_4	15.8	14.5	+8.2	9.6
8	Guava extracted with 0.1 *M* H_2SO_4	..	28	...	11

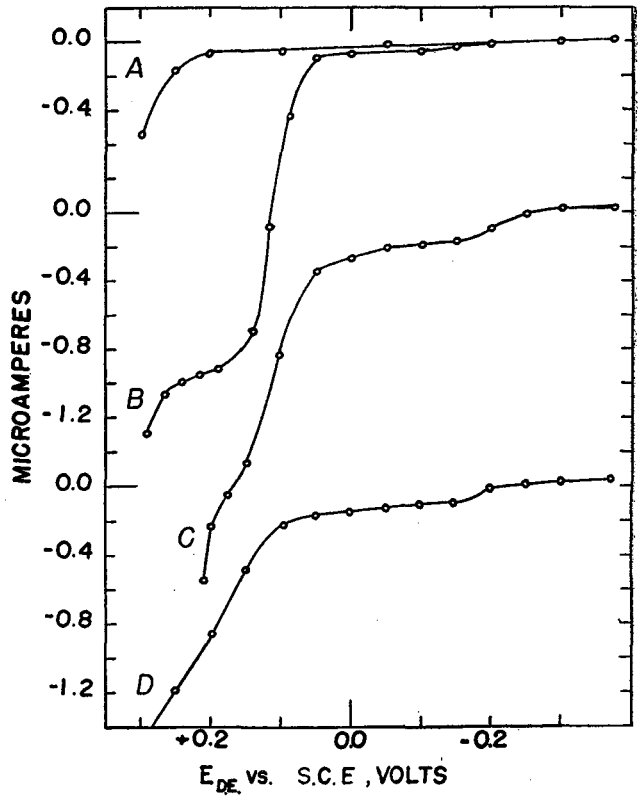

Figure 4. Polarograms of Natural Products

***A*. Buffer wave**
***B*. Orange, sample 2**
***C*. Potato, sample 7**
***D*. Guava, sample 8**
pH values for *A* and *B*, 3.60; *C* and *D*, 4.30

amperometric methods in the case of fresh citrus fruits is 0 to 1%. The storage orange shows a somewhat greater difference, which may be due to impurity which produces a wave at the ascorbic acid potential but does not react with the dye. The lower polarographic value for the canned orange juice might be due to impurity which reacts with the dye but is not indicated by the polarograph. The indication of the presence of glutathione is most striking in the cases of the potato and guava. The polarographic and amperometric ascorbic acid results in the case of the potato are in fairly close agreement. In the case of the guava it was not possible to compare results by the two methods, because it was impractical to measure the height of the ascorbic acid due to the presence of interfering material. This might be chloride if its concentration is about 10^{-5} M or greater. It could not be cysteine, because its first wave diffusion current should be 1 μa. or more before the second wave near the potential of the ascorbic acid begins to form.

The authors' results and a study of the results of others indicate that the amount of glutathione in citrus fruits is usually low. The fact that polarograms of fresh citrus fruit juices show such well developed ascorbic acid waves is due to a low content of glutathione and interfering materials. The polarograph, therefore, should prove a useful instrument in rapid routine determinations of ascorbic acid in fresh citrus fruits.

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Measurement of Radiocarbon as Carbon Dioxide inside Geiger-Müller Counters

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The measurement of radiocarbon activity as carbon dioxide admixed with carbon disulfide vapor has been studied as a quantitative procedure over the pressure range 2 to 175 cm. of mercury. The counting rate was found to be directly proportional to the quantity of active gas sample. In the region 1 to 4 cm. of carbon dioxide pressure the average deviation from the straight line drawn through the origin for eleven measurements was less than 1.2%. At a total pressure of about 50 cm. the average deviation of seven measurements from the straight line drawn for counting rate versus moles of standard active sample was 0.4%. Plateau lengths over 200 volts with slopes usually less than 2% per 100 volts are obtained over the threshold counting range of 1500 to about 3000 volts. The gas trains and apparatus for conversion of barium carbonate to carbon dioxide showed negligible memory effects and permitted precise measurement of the quantity of carbon dioxide inside the counter tube. The construction of Geiger-Müller counter tubes and auxiliary equipment is described.

MILLER and Brown (*1*, *6*) have recently reported satisfactory counting characteristics in the Geiger-Müller region at carbon dioxide pressures from 10 to 50 cm. of mercury admixed with 2-cm. pressure of carbon disulfide vapor. Skipper, Bryan, White, and Hutchison (*7*) used a voltage supply permitting counting of samples at pressures up to 35 cm. of carbon dioxide. Inasmuch as this counting method is very efficient even for relatively large samples, it was decided to study this procedure as a quantitative method of analysis for radiocarbon over as wide a pressure range as can be conveniently handled. Measurements were made in the range 2 to 10 cm. of carbon dioxide pressure. In this pressure interval, the threshold voltage range is about 1450 to 2200 volts (*2*). An advantage of operation in this range is that routinely available voltage supplies can be utilized. Measurements were also made at pressures extending up to 175 cm. At this latter pressure the threshold voltage is close to 7500 volts.

At pressures between roughly 0.5 and 2 atmospheres, the sensitivity factor with respect to even the windowless counting of barium carbonate becomes significant.

Gas trains and auxiliary apparatus provide for the routine conversion of a barium carbonate sample to carbon dioxide and quantitative transfer of the precisely measured gas to the evacuated Geiger-Müller counter tube. Memory effects, reproducibility, and constancy of measured counting rate per unit specific activity have also been studied.

EXPERIMENTAL

The gas lines and apparatus shown in Figure 1 provide for preparation and storage of purified inactive carbon dioxide, preparation of diluted active gas reservoir bulbs, conversion of a barium carbonate sample taken for analysis to carbon dioxide and measurement of the quantity of gas obtained, and quantitative transfer of the evolved carbon dioxide to a Geiger-Müller counter tube containing a suitable pressure of carbon disulfide.

Preparation and Storage of Inactive Carbon Dioxide. Sodium bicarbonate in the glass container, U, is heated to about 350° C. by the Nichrome heating element, A, after that section of the line has been evacuated. The evolved carbon dioxide is stripped of water vapor in traps E and E' surrounded by a dry ice–Cellosolve (ethylene glycol monoethyl ether) mixture. After rejection of the initial portion of evolved gas, the carbon dioxide is allowed to fill the 5-liter gas bulb, R.

Conversion of Barium Carbonate to Carbon Dioxide. With an empty container, K, in place, the conversion system is flushed with a carbon dioxide–free nitrogen stream from tank C (99.9% nitrogen), through the flowmeter capillary, B, the Ascarite-filled tube, G, and traps E, E', and F, and is vented at the mercury bubbler, D. Traps E and E' are immersed in a dry ice slurry

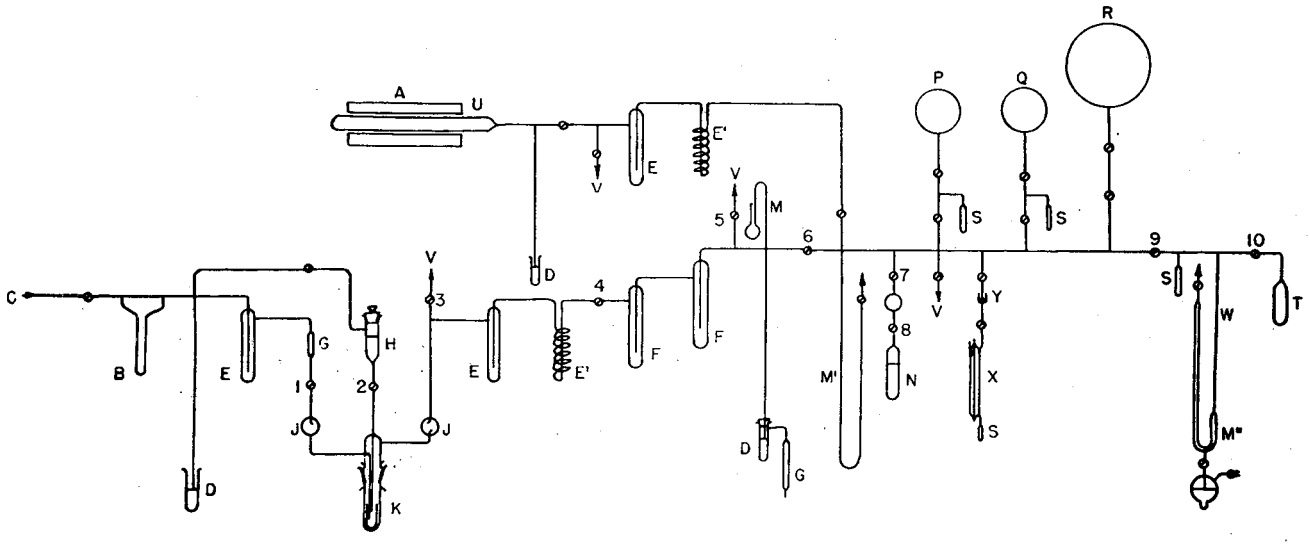

Figure 1. Gas Lines for $C^{14}O_2$ Counting

D. Mercury bubblers
G. Ascarite-containing tubes
J. Splash traps
M. Small vacuum end manometer
M'. Long vacuum end manometer
S. Cold finger for vapor condensation using liquid nitrogen
V. To high vacuum system (not shown)
Y. Grease seal standard-taper joint

while both traps labeled *F* are immersed in liquid nitrogen. After the small container or centrifuge tube holding the barium carbonate sample (usually 15 to 40 mg.) is inserted at *K*, several milliliters of 20% perchloric acid solution contained in *H* are slowly added to the sample holder. Perchloric acid solution was chosen because the barium salt is soluble. The evolved carbon dioxide is swept along by the nitrogen stream and condensed in *F*, while water vapor is removed at *E* and *E'*. In order to condense residual carbon dioxide, stopcock 1 is closed and the gas stream is slowly pumped out through stopcock 5 until the pressure is about 3 cm. Stopcock 4 is then closed and the nitrogen is completely removed from traps *F* (as checked by McLeod gage reading) by pumping for several minutes.

The quantity of carbon dioxide is measured in the constant-volume mercury manometer, *M"*, after the carbon dioxide in *F* is transferred to the cold finger, *S*, next to stopcock 9. The transfer is accomplished in less than a minute by opening stopcocks 6 and 9 after *S* is surrounded by liquid nitrogen. In order to minimize the transfer of traces of water vapor, trap *F* adjacent to stopcock 6 is immersed in a dry ice bath during the latter operation. The small volume (with stopcock 10 closed) is used when approximately 10 to 30 mg. of barium carbonate are converted. Tube *W* is made from 2-mm. capillary tubing. For samples up to several hundred milligrams of barium carbonate the larger volume includes calibrated bulb *T*. The gas sample is then quantitatively transferred to the Geiger-Müller counter tube, *X*, by condensation inside *S*. Carbon disulfide vapor inside the bulb between stopcocks 7 and 8 is similarly transferred into *X* by condensation. The carbon disulfide liquid reservoir is container *N*.

Two-liter bulbs *P* and *Q* contain active gas samples needed for study of gas counting as a quantitative procedure. The samples were prepared by conversion of active barium carbonate (as described above) and dilution with suitable quantity of inactive gas from *R*.

The stopcocks, *V*, lead to the high vacuum pumping system consisting of a Welch 2-stage Duoseal pump, mercury diffusion pump, and trap surrounded by a dry ice mixture.

Active samples are disposed of by condensation in a cold finger attached to a flask containing Ascarite (not shown in Figure 1).

Reagents. The inactive carbon dioxide used in these studies was made by heating sodium bicarbonate (Eimer and Amend, tested purity reagent) at 350° C. High specific activity carbon dioxide was prepared by addition of 20% perchloric acid (C.P., Eimer and Amend, tested purity reagent) to barium carbonate containing carbon 14. Mallinckrodt carbon disulfide (analytical reagent, 46–47° C. boiling point) was used without further purification.

Design of Geiger-Müller Counter Tubes. The principal type of tube used in the carbon dioxide counting studies is shown in Figure 2. The borosilicate glass tube has a "cold finger" extension, *A*, at the lower end to provide for condensation of tube contents when immersed in liquid nitrogen.

The chemically plated silver cathode surface, *C–D*, is coated with a thin layer (*1*) of colloidal graphite (Aquadag). The cathode lead enters at *F*. The 4-mil tungsten anode wire, *E*, is surrounded by glass shields, *B*, which extend into the volume defined by the cathode. These shields eliminate spurious pulses at the welded joint leading to the thick tungsten wire sealed through the glass and serve to define the counting volume. The tube is fitted by attachment at the ground-joint grease seal, *H*, and the precision-ground stopcock, *G*.

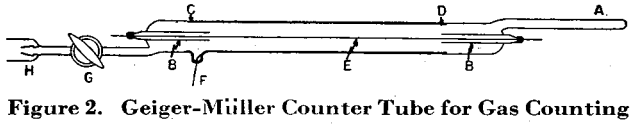

Figure 2. Geiger-Müller Counter Tube for Gas Counting

Although tubes constructed in this manner and having diameters of 10, 15.5, 32, and 55 mm. were used in some experiments the results presented in this paper were obtained using tubes that were approximately 15.5 mm. in inside diameter and about 15 to 16 cm. in cathode length. Two such tubes are referred to in this paper as tube 1 and tube 2 and have an effective volume of 29 and 32 ml., respectively. In a lead housing of 8-cm. thickness, the background count is approximately 35 counts per minute.

Electronic Equipment. The counting studies at low pressures were carried out using a scale of 64 circuit and a 2500-volt stabilized voltage supply. A modified Neher-Harper circuit containing a quenching tube and cathode follower was used. This circuit contained two 6AG5 tubes. Satisfactory quenching action and plateau lengths were obtained for all the counting tubes used in these studies by using a 6-megohm grid resistor and a grid bias voltage in the range 6 to 9 volts (extinguishing circuit 1).

The counting studies at carbon dioxide pressures over 10 cm. were carried out using a scale of 64 circuit. An electronically stabilized voltage supply (Model 1090, Nuclear Instrument and Chemical Company, Chicago, Ill.) was used in the range 2000 to 5000 volts. The high positive voltage was applied to the central wire anode. For voltages greater than 5000 and up to 8000, a suitable number of 67-volt dry cells in series were used to augment the electronic supply.

Neher-Harper Extinguishing Circuit for Higher-Voltage Counting. The Neher-Harper circuit used for counting at voltages above 2000 volts differs from the conventional Neher-Harper circuit in the specific vacuum tube used. Ordinary radio-type tubes commonly used, such as 6AG5 or 57, are not designed for large plate-filament voltage differences. It was found that an 811 transmitter type tube gave very satisfactory results even

when plate-filament voltages up to 5000 were used. A 150-volt cathode bias supply was obtained from the scaling circuit. A resistance bleeder was used to supply a negative grid bias for the 811 tube between the limits of approximately 15 and 60 volts. It was observed that a grid resistance of 10 megohms and a grid bias close to 37 volts gave satisfactory counting characteristics for the 15.5-mm. diameter tubes over a wide range of counting voltages. This range extended from approximately 3500 to 7000 volts. The plateau length is usually between 200 and 300 volts with slopes less than 1% per 100 volts. A variation of 10 volts in the grid bias at the above setting did not significantly change the counting rate or plateau characteristics. This was true over a large part of the counting range 3500 to 7000 volts. A convenient procedure for routine measurement of relative radiocarbon activity consists in bringing all gas fillings to a definite carbon dioxide pressure—e.g., 40 cm. A grid bias value is then found which, for a grid resistance of 5 or 10 megohms, furnishes satisfactory counting characteristics. This setting is used for all measurements employing this tube and filling pressure. The resolving time is measured at this setting and used for coincidence-loss corrections (extinguishing circuit 2).

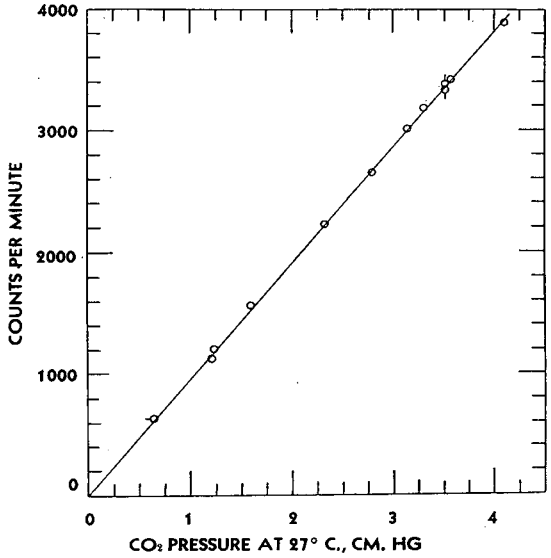

Figure 3. $C^{14}O_2$ Counting at Low Pressures

The resolving time of the tube plus circuit was measured by using two external radium sources giving approximately equal counting rates (*6*). With the circuit operating conditions used in the experiments reported here, the resolving time was close to 4×10^{-5} minute. Resolving time corrections were made for all measured counting rates following the procedure of Reid, Weil, and Dunning (*6*).

Statistical Error of Counting Results. Approximately 30,000 counts were recorded for each of the experimental points in Figures 3 to 7.

The probable error of the counting rate due to statistical variations may be calculated using the formula:

$$E\% = \frac{(100)\ (0.6745)\ \sqrt{\frac{R}{t} + \frac{R_b}{t_b}}}{R - R_b}$$

where $E\%$ = probable percentage error of the net counting rate
R = sample plus background rate
R_b = background rate
t = time of counting for sample
t_b = time of counting for background

Using the following representative data for an experimental point—$R = 1000$; $t = 30$ minutes; $R_b = 35$; $t_b = 60$ minutes—the probable percentage error is 0.41%.

RESULTS

Carbon Dioxide Counting at Low Pressures and Voltages. In Figure 3 are plotted the counts per minute (corrected for resolving time factor and background count) for twelve fillings of tube 1. Except for the point nearest the origin, the abscissa represents the total pressure of carbon dioxide present in the tube. In the case of the former point, inactive carbon dioxide was added until the total pressure was about 6 cm. The source of the carbon dioxide was an active standard gas reservoir. The open circles represent a series of fillings at a carbon disulfide pressure of 1.85 cm. The straight line in Figure 3 was drawn through these points and the origin. The fillings indicated by a circle with upper line marking contained only 0.92 cm. of carbon disulfide and fall on the line drawn.

In the case of the circle with lower line marking, carbon disulfide vapor was not added. Inasmuch as the tube and gas lines, including stopcock grease, had previously been in contact with carbon disulfide vapor, traces of the latter were undoubtedly present. When additional fillings in the absence of carbon disulfide vapor were made after prolonged pumping, it was observed that the plateau became very short (less than 50 volts) and had a poor slope. In addition, the plateaus were not reproducible. The average deviation of the points from the line in Figure 3 is less than 1.2%. Within this precision, the observed counting rate is directly proportional to the amount of active sample. Because the partial pressure of carbon dioxide in Figure 3 is varying, it is clear that this conclusion is independent of the pressure inside the counter tube over the range plotted. The results stated above, together with those for a series of fillings at carbon disulfide pressures ranging from 0.2 to 2 cm., show that the counting rate is independent of the carbon disulfide partial pressure over this range. Extinguishing circuit 1 was used for the measurements at low pressures using a 5.6-megohm grid resistor and a grid bias of 8.5 volts.

In the 15.5-mm. diameter tubes used, the threshold counting voltage at a partial pressure of 1.85 cm. of carbon disulfide and 1 cm. of carbon dioxide is about 1400 volts. The threshold voltage rises about 80 volts per cm. in an almost linear manner up to about 9 cm. of carbon dioxide. These conclusions are based upon about thirty fillings over this pressure range.

The plateau length is less than 100 volts at pressures below 2 cm. of carbon dioxide. Between 2 and 3 cm. it increases to between 100 to 200 volts, and above 3 cm. the plateau is usually greater than 200 volts. The plateau slope is, on the average, less than 2% per 100-volt interval and is frequently observed to be below 1%. As an example, the plateau obtained for a filling of 5.43 cm. of carbon dioxide and 1.85 cm. of carbon disulfide has been plotted in Figure 4.

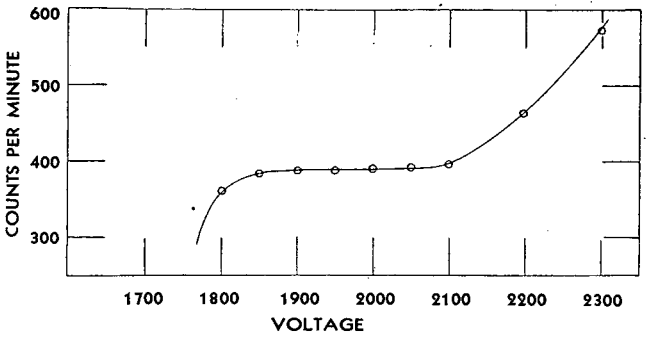

Figure 4. Counting Rate *vs.* Voltage at Low Pressures

Several counter tubes having cathode surfaces of copper gauze, stainless steel, and brass were filled with 2 cm. of carbon disulfide and 3 cm. of carbon dioxide pressure in order to observe the pulse shape and plateau length. In the case of the copper gauze cathode (18 mm. in diameter and 10 cm. long) plateaus of approximately 150 volts with slopes of about 1% per 100 volts were observed. A tube having a stainless steel cathode, 30 mm. × 15 cm., and a 5-mil stainless steel wire anode inside a glass

envelope furnished plateaus between 200 and 300 volts with slopes of less than 1% per 100 volts. A readily assembled tube consisting of a stainless steel pipe section cathode (25 mm. × 20 cm.), sealed with picein or de Khotinsky cement to flat Lucite ends, furnished plateaus between 200 and 400 volts with slopes less than 0.3% per 100 volts. The tubes with brass cylinder cathode (sealed to glass ends through a section of Kovar) had a diameter of 22 mm. and lengths of 5, 12, and 20 cm. Plateaus of 150 volts with slopes of 2% per 100 volts were observed. Extinguishing circuit 1 was used with these tubes. The oscilloscope pulses in the plateau region were free of multiple pulses or bursts.

Variation of Measured Counting Rate with Activity of Gas Sample at 50 Cm. Carbon Dioxide Pressure. The variation of measured activity as a function of moles of standard active sample was determined in the pressure interval 47 to 51 cm. of carbon dioxide. A series of seven fillings was made in which the quantity of standard active sample was varied over a threefold range.

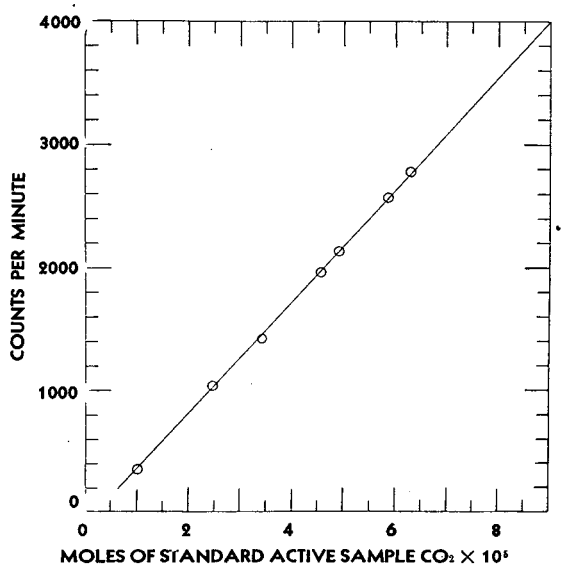

Figure 5. $C^{14}O_2$ Counting at Approximately 50 Cm. of Mercury Pressure of Carbon Dioxide

Inactive carbon dioxide was added to obtain the desired final pressure, while the carbon disulfide partial pressure was in the range 1.8 to 2.1 cm. The threshold voltage for the 15.5-mm. tube used was approximately 4000 volts. The counting rates corrected for background count and resolving time correction are plotted in Figure 5, in which a straight line has been drawn through the origin. The average deviation of the seven points from the straight line drawn is 0.4%. These data demonstrate the proportionality of measured counting rate with quantity of active sample in the higher pressure region. Extinguishing circuit 2 was used with a grid resistance of 10 megohms and grid bias of 38 volts. The plateau lengths for the points of Figure 5 ranged between 200 and 300 volts with slopes usually less than 0.5% and occasionally about 1% per 100 volts.

Two plateau curves in the voltage region 4500 to 5000 are shown in Figure 6. The upper curve refers to a filling in tube 1: 63 cm. of carbon dioxide, 1.80 cm. of carbon disulfide, 10 megohms grid resistor, and 37 volts grid bias. The lower curve refers to a filling in tube 2: 62 cm. of carbon dioxide, 2.3 cm. of carbon disulfide, 10 megohms grid resistor, and 35 volts grid bias.

Several examples of plateaus obtained at pressures close to 2 atmospheres of carbon dioxide are shown in Figure 7. The upper curve refers to tube 1: 154 cm. of carbon dioxide, 1.80 cm. of carbon disulfide. The circles with lower line markings refer to tube 2: 154 cm. of carbon dioxide, 2.27 cm. of carbon disulfide. The circles with upper line markings refer to tube 2: 171 cm. of carbon dioxide, 2.27 cm. of carbon disulfide. The grid resistor and grid bias settings of the extinguishing circuit for these curves were 10 megohms and 45 volts, respectively.

Constancy of Counting Rate over Wide Pressure Range. Gas mixtures containing the same activity of carbon dioxide (about 885 counts per minute) and successively increasing carbon dioxide partial pressures were measured over the carbon dioxide pressure range 20 to 155 cm. of mercury. In Table I is presented the measured activity at each pressure, together with the approximate length and slope of the plateau. The partial pressure of carbon disulfide was 1.80 cm. The mole percentage of carbon disulfide varied from 7.2 to 1.2 at the highest carbon dioxide pressure. The probable error of each point due to statistical variation is 3 counts per minute.

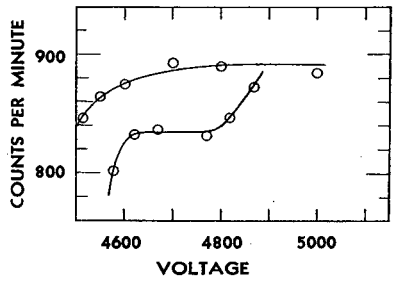

Figure 6. Counting Rate *vs.* Voltage in Neighborhood of 5000 Volts

Table I. Counting Rates over Wide Pressure Range

Carbon Dioxide Partial Pressure at 25° C., Cm.	Counts per Minute	Approx. Plateau Length, Volts	Plateau Slope, % per 100 Volts
23.7	880	150	1.3
41.0	880	200	1
63.0	882	400	<0.5
79.7	884	300	<0.5
99.8	882	300	1
118.1	882	300	1
132.9	885	200	0.5
154.5	889	300	<0.5

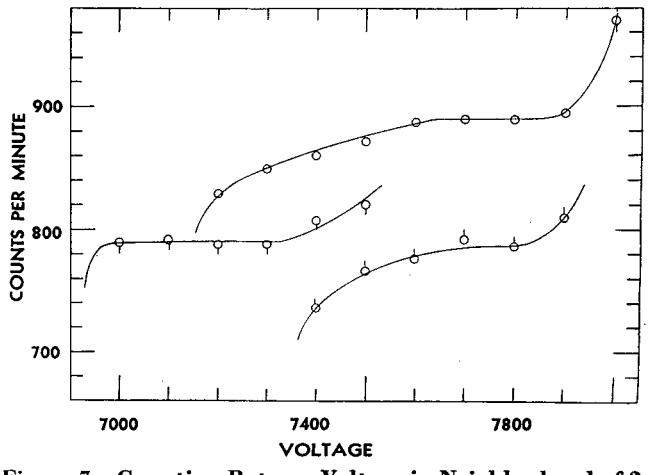

Figure 7. Counting Rate *vs.* Voltage in Neighborhood of 2 Atmospheres' Carbon Dioxide Pressure

The average value of the measured counting rate for the eight measurements is 883 counts per minute with an average deviation of 2.5. The largest deviation from the average is less than 0.7%. The measured counting rate is, within this precision, independent of the total pressure of carbon dioxide and the carbon disulfide–carbon dioxide ratio. The threshold voltage

for this series of measurements ranged from 2900 to 7400 volts. The plateau length is usually between 200 and 300 volts with slopes less than 1% per 100 volts.

Variation of Threshold Counting Voltage with Carbon Dioxide Pressure. Results obtained over a 3-month period using counting tubes 1 and 2 are plotted in Figure 8. The threshold voltage was determined by observation of pulse height equalization using a cathode ray oscilloscope. Measured amounts of carbon dioxide were added to the tubes and the pressures were calculated from the measured volume and temperature. The slight deviations from the perfect gas state were calculated using the Van der Waals constants: $a = 3.592$; $b = 0.04267$; units: moles, liters, atmospheres (*4*). At 50, 100, and 150 cm., the corrections are 0.28, 0.55, and 0.83%, respectively. The solid circle in Figure 8 is the average of six fillings for tube 1 at 50-cm. pressure. The deviations from the average value plotted are less than 50 volts. The open circles represent a series of fillings at progressively greater pressures over the range 3 to 174 cm. The circles with upper line markings represent a different series of fillings for tube 1. The circles with lower line markings represent a series of fillings for tube 2. The curve was drawn through the points for tube 1. Both tubes were approximately 15.5 mm. in diameter. The partial pressure of carbon disulfide was 2.0 cm.

Performance of Conversion Train and Gas Lines. The amount of carbon dioxide contained in the counter tube was measured using the manometric apparatus of the gas train described above. Pressure measurements are readily made with a precision error less than 0.3%. The conversion train was designed to minimize the condensation in the manometer cold finger of any vapor but carbon dioxide. To check this, three blank runs were made in which the perchloric acid was added and the conversion procedure carried through in the absence of added carbonate. In each case the blank corresponded to less than 0.1 mg. of barium carbonate. The transfer of the measured carbon dioxide to the counter tube by condensation using liquid nitrogen was observed to be complete to within better than 0.1% in a time of 2 minutes by direct manometric observation. The rapidity and completeness of transfer of carbon dioxide from one part of a gas train to another in the absence of permanent gas impurities were utilized to determine with precision the volume of a counter tube relative to that of the constant-volume manometer. A gas sample at measured pressure inside the counter tube is completely transferred to the constant-volume manometer and the pressure inside the latter is measured. As an example of the reproducibility of this method, four independent measurements of the volume ratio manometer-tube furnished the following results: 0.4392, 0.4390, 0.4395, and 0.4395. This procedure is especially useful when the volume to be measured using gas laws is separated from the standard volume plus manometer by an intermediate volume of moderate or large magnitude. The above procedure in this case is preferable to the customary use of a gas such as air or nitrogen.

The volume of carbon dioxide recovered from a 200- to 300-mg. sample of C.P. barium carbonate is within 3% and on the average within 2% of that calculated for complete conversion. The loss is not significant for the determination of relative specific activity, because the amount of carbon dioxide is measured precisely using the constant-volume manometer.

Memory effects were observed to be of no significance inside the conversion trains and gas lines described above for the activity ranges used in these studies. Barium carbonate samples had a maximum total activity of 4000 disintegrations a minute. An inactive barium carbonate sample, run after a 5-minute nitrogen flush (about 100 ml. per minute), gave a normal background count. Using a 10-cm. carbon dioxide flush and a 20-minute pumping period, the counter tubes with silver plus colloidal graphite surface furnish a normal background after having been filled with the 4000 disintegration per minute sample. These results are based on over thirty such experiments performed during more than 6 months of filling and evacuation of several tubes. The absence of memory effects under these conditions makes it unnecessary to run background counts after each active filling and in general increases the number of samples that can be handled in a given time.

The cold finger volume and the over-all length of the Geiger-Müller counter tubes were made small in order to minimize effects due to incomplete mixing of the carbon disulfide vapor and carbon dioxide. After filling, the counter tube was detached from the line at the standard-taper joint and kept in an inverted vertical position for about 30 minutes, following a 0.5-minute immersion of the condensation finger in hot water. Under these conditions, counting rates were the same as those obtained after standing in the inverted position for several days. For this reason, mixing chambers for the counter tube filling were not provided.

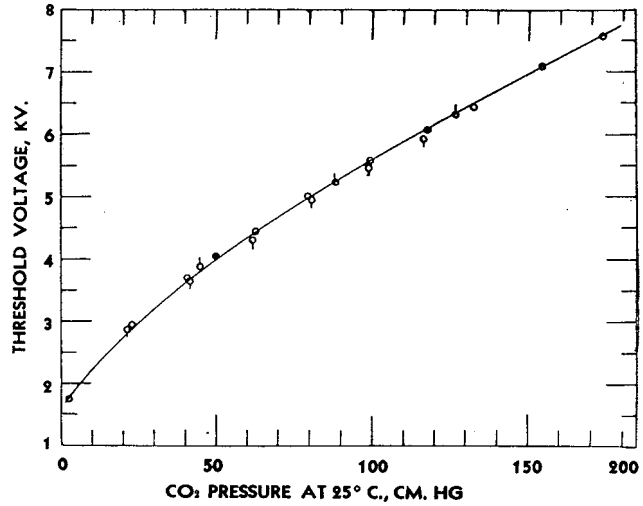

Figure 8. Threshold Voltage *vs.* Pressure of Carbon Dioxide

No systematic study was made of the effect of traces of impurities in the counting mixture, because the procedures described above, starting from precipitated and washed barium carbonate, should yield pure carbon dioxide with negligible traces of water vapor. It was observed in some early experiments that rapid pumping of the saturated nitrogen flushing gas through the dry ice traps, *E*, in Figure 1, resulted in tube fillings showing multiple pulses on the oscilloscope screen. In all subsequent runs, water vapor traces were minimized, as described above, by surrounding trap *F* in Figure 1 with a dry ice mixture before the converted gas was transferred to the manometer system. Accidental leakage of air into the counting gas mixture has a twofold adverse effect. Plateau lengths were shortened and slopes increased. The transfer of the carbon dioxide into the counter tube by condensation is rendered slow and incomplete when a permanent gas is present. Air leakage was minimized in the lines illustrated in Figure 1 by using precision-ground stopcocks with large grease surface area and stopcock bottoms integral with the line, so that they were always held in place by differential pressure. There were no rejected fillings in over 100 conversion and counting runs.

DISCUSSION

The results presented above and in Figures 3 and 5 have demonstrated the adequacy of this method for the quantitative determination of relative specific activity of carbon dioxide samples. Analyses made using different Geiger-Müller counter tubes can be brought to a consistent basis by correcting for the effective counting volumes and total volumes of the tubes being compared. Taking the extension of the effective volume axially

and radially to the physical limits of the cathode, Brown and Miller (*1*, *5*) showed that a variety of counters normalized for the cathode volume–total volume ratio fall on the same sensitivity curve. The procedure used by the author to obtain relative effective volumes in tubes of approximately similar diameter and construction has been to make a direct comparison of the counting rates of these tubes when filled simultaneously at the same pressure and temperature with active gas from the standard reservoir. This procedure eliminates end effect corrections that are at the present time difficult to handle in a theoretical manner.

Brown and Miller (*1*, *5*) pointed out that their data strongly suggest that the corrected counting rate is the absolute disintegration rate within the cylindrical volume defined by the cathode. The results presented in this paper lend additional weight to this hypothesis. In particular, these results include the demonstrated constancy of counting rate over a wide range of gas pressures and accompanying electric field strength in the neighborhood of the central wire. The observed development of the pulses along the plateau of several hundred volts, with no appearance of smaller spurious pulses able to activate the scaling circuit used, must also be considered to support this hypothesis. This conclusion should be considered to apply to the tube diameter used in the major part of these studies, about 15.5 mm., inasmuch as end effects too small to observe in the former may become significant in tubes of larger diameter.

Janney and Moyer (*3*) have compared the relative sensitivity of a Lindemann electrometer used by them for carbon dioxide samples with other methods. Taking as a basis a background and sample observation time of 1000 seconds and requiring a mean error of not over 10%, they calculate a minimum activity of 5.3×10^{-9} curie per gram of carbon in 100-cc. chambers at atmospheric pressure. The background count for a 15.5-mm. inside diameter Geiger-Müller tube used in the experiments reported in this investigation is close to 0.58 count per second. Using the equations derived by Janney and Moyer, a sample count of 0.398 count per second would yield a 10% standard deviation in 100 seconds when background and sample counting times are equal. Assuming that the 28.3-ml. volume is filled with the carbon dioxide sample at 2 atmospheres' pressure, this activity corresponds to 4×10^{-10} curie per gram. Operation with larger tubes would permit a several-fold lowering of the activity. Janney and Moyer cited data obtained by P. E. Yankwich for barium carbonate counting using a 5-cm. diameter mica window counter having a thickness of 2 mg. per sq. cm. In this case the limiting carbon specific activity for the conditions used above is 7.4×10^{-8} curie per gram of carbon. This comparison is significant when there is available a sample of carbon dioxide sufficient to fill the ionization chamber or counter tube at the conditions specified above. This has been the case in respiratory and many tissue combustion samples obtained in animal metabolism experiments.

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Electrometric Titration of Alcohols Using Lithium Aluminum Hydride

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THE possibility of using lithium aluminum hydride solution for the electrometric titration of several functional groups including hydroxyl, amino, carbonyl, and carboxyl in organic compounds was recently pointed out (*1*). In this paper the details involved in the development of the method and further experimental results in its application to hydroxyl compounds are presented.

DISCUSSION OF THEORY

The potentialities of lithium aluminum hydride as a reagent for quantitative determination of compounds containing active hydrogen or easily reducible groups have been widely recognized (*2–5*). Nearly all of the methods published have been based on modifications of the Zerewitinoff method, requiring relatively elaborate gasometric apparatus. The method proposed (hereafter referred to as the Higuchi-Lintner-Schleif method) differs essentially from those of previous workers in that it is a true volumetric method where a standardized solution is added from a buret to a stoichiometric end point. Such a procedure is, however, feasible only if a suitable means of end-point detection is available.

In the Higuchi-Lintner-Schleif method the stoichiometric point is located by a sudden change in the reduction potential of the system. In titration of a solution of lithium aluminum hydride with an alcohol, for example, the reduction potential of the solution up to the end point is very high, because hydrides are powerful reducing agents nearly in a class with free alkali metals. With introduction of a slight excess of the alcohol, however, the potential drops sharply, for now only lithium and aluminum alkoxides which are relatively weak reducing agents are present according to the equation

$$4ROH + LiAlH_4 \longrightarrow 4H_2 + LiOR + Al(OR)_3$$

This behavior is depicted in Figure 1 in the potentiometric

The details involved in the development of the electrometric titration of functional groups that react with lithium aluminum hydride are discussed. The method is based on the sharp change in the reduction potential of the system when the last trace of the hydride is removed by reaction. Silver or platinum wire is used as the indicator electrode and an isolated silver wire as the reference electrode. Tetrahydrofuran is used as the solvent. Experimental results obtained for thirteen different hydroxy compounds show fair agreement with theoretical values. The method also gives relatively good reproducibility. *p*-Aminoazobenzene is a possible chemical indicator which may be substituted for electrical end-point detection.

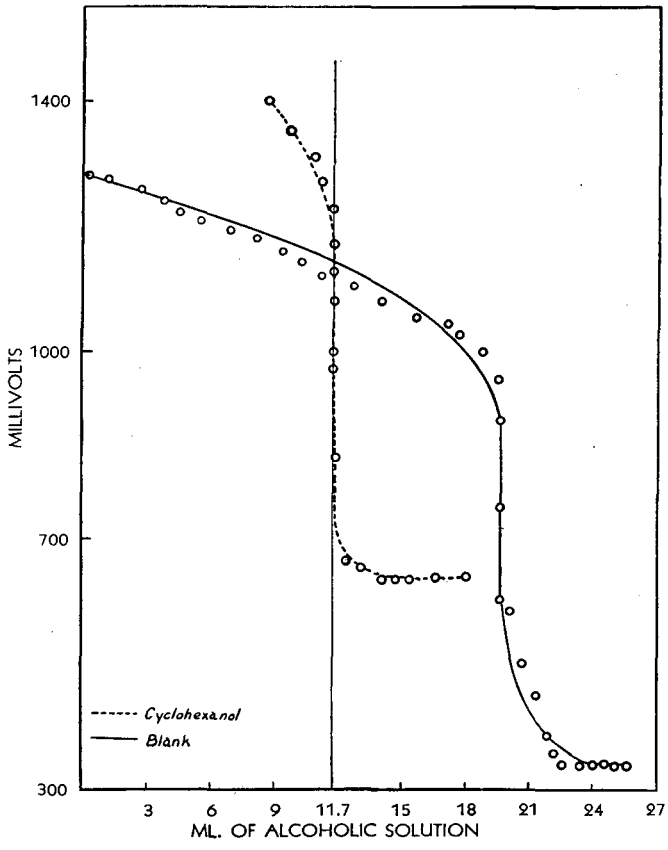

Figure 1. Potentiometric Titration Curve Obtained by Titrating Lithium Aluminum Hydride Solutions with Standard Alcohol Solution

titration curve (blank) obtained by titrating a hydride solution with 5% *n*-propyl alcohol solution in benzene. The voltage change corresponding to the end point is large compared to that encountered in most other types of potentiometric titrations. Absolute potential values are not too significant, because the electrode reaction at the indicator electrode is in all probability not reversible. The second curve shown was obtained under identical conditions, except that a weighed amount of cyclohexanol was added to the hydride before titration, the difference between the two titrations corresponding stoichiometrically to the amount of cyclohexanol added.

DEVELOPMENT OF METHOD

In the development of the method, the problems which presented themselves were (1) selection of a solvent medium suitable for electrometric titration, yet inert toward lithium aluminum hydride; (2) choice of a suitable pair of electrodes; and (3) development of a proper operational procedure for titration.

Selection of Solvent. Several solvents were considered for study. Strictly nonpolar hydrocarbons and ordinary ethers were ruled out because they were too nonconducting. Halogenated hydrocarbons, alcohols, esters, ketones, primary and secondary amines, and other similar functional types could not be employed because of their reactivity to the hydride. Pyridine, because of its excellent solvent properties and ready availability, was seriously considered; it proved unsuitable because of a slow interaction with the hydride. Tetrahydrofuran was finally chosen because of its relatively high polarity, which makes it a good solvent for many salts, and its inertness toward the hydride. Its principal drawback was its tendency to form peroxide with atmospheric oxygen. Although neither aliphatic nor saturated cyclic tertiary amines were studied, it is conceivable that some of these may be superior to tetrahydrofuran.

Electrode System. The choice of a suitable electrode system to measure the reduction potential of the titration mixture offered no special difficulty. Platinum and silver indicator electrodes were tried and found to be effective, the latter giving somewhat more stable results. The selection and design of the reference electrode were governed by the fact that it must be uninfluenced by the changing conditions in the titrating flask but still be in electrical contact with its content. This was accomplished by using an isolated silver electrode surrounded by an electrolyte of lithium bromide and iodine (tetrabutyl ammonium iodide was also added in some cases) in tetrahydrofuran. (The addition of iodine is probably superfluous. It was added with the thought that silver iodide may be formed.)

Titration Procedure. In the development of the operational procedure, the employment of standardized hydride solution for direct titration of samples was precluded for several reasons. Higher alcohols, ketones, aldehydes, esters, lactones, amines, etc., react too slowly to permit titration at a reasonable rate. All these compounds can be titrated by the indirect method. Moreover, the strength of hydride solution, because of slow reaction with atmospheric moisture and carbon dioxide, slowly changes on standing, necessitating frequent restandardization. Because the solvent used to dissolve the samples contains some moisture and peroxide, it is necessary to run a blank every day. It is very difficult, furthermore, to dispense the solution from a buret, inasmuch as all stopcock lubricants either are dissolved or react with the potent mixture. For these reasons, the reverse procedure of back-titrating an excess of the hydride with a standardized alcohol solution was adopted.

A solution of *n*-propyl alcohol in benzene was found to be generally satisfactory as the standard. Higher alcohols were generally too unreactive to permit direct titration. The use of methanol tended to lead to gel formation. Ethyl alcohol was fairly satisfactory, except for its high volatility. Branched alcohols were not studied, because branching usually results in lower reactivity. Benzene was chosen as the diluent for the

standard because it can be dried easily, does not form peroxides as ethers do, and is inert with respect to the hydride. It is, however, by no means an ideal solvent for this purpose, as its low polarity often results in precipitation of salts from the reaction mixture.

EXPERIMENTAL

Apparatus. Two different setups were used in studying the feasibility of the method. The first, shown schematically in Figure 2, was relatively crude and simple, as the titration was carried out in an open beaker. The reduction potential was followed by measuring with a Beckman Model H pH meter the voltage developed across a platinum indicator electrode and a reference electrode as shown in the diagram. Because the low resistance lead of the instrument (which normally connects to the calomel cell) was connected to the reference electrode, it was necessary to make the electrode resistance as low as possible to obtain stable readings. For this reason a fairly large opening was used on the electrode; this, however, resulted in slow cross diffusion of the electrode electrolyte and the beaker content. This apparatus, nevertheless, was employed for most part in the present study because of its simplicity.

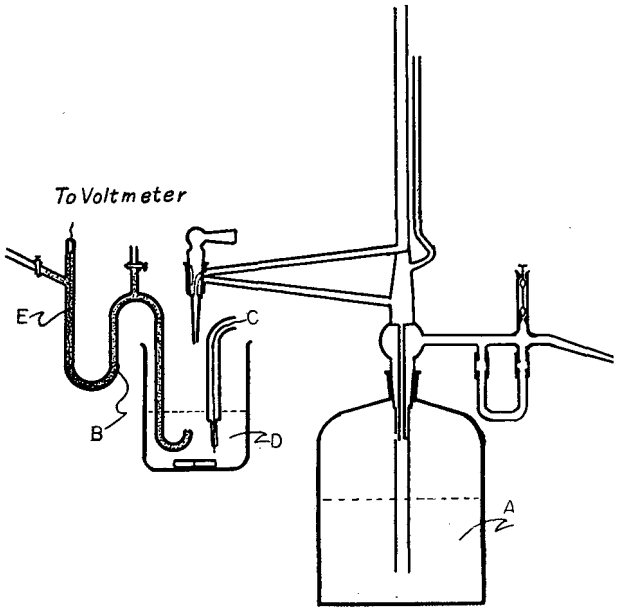

Figure 2. Schematic Drawing of Original Titrimetric Assembly

A. Alcohol-benzene mixture
B. Lithium bromide–iodine in tetrahydrofuran
C. Shielded wire to voltmeter
D. Platinum wire
E. Silver wire

The second setup, depicted in Figure 3, was somewhat more elaborate. An attempt was made in its design to reduce the moisture pickup noticed with the earlier apparatus. This was done by enclosing the reaction system, the only opening being a small hole to admit the tip of the automatic buret. In addition, the reference electrode was redesigned to cut down the exchange of solution between it and the titration mixture. A separate salt bridge chamber was introduced and the tip of the bridge was drawn down to a fine capillary. This change, which resulted in considerable decrease in the conductivity of the electrode, was made possible by connecting the reference electrode, to the high resistance lead (which is normally connected to the glass electrode in the usual pH setup) and the silver indicator electrode to the low resistance terminal of the voltmeter.

Reagents. Reagents and samples used were prepared in the following manner:

TETRAHYDROFURAN. Technical grade solvent as received from E. I. du Pont de Nemours & Company was purified by distilling twice over lithium aluminum hydride. This procedure was effective in removing water, residual peroxide, inhibitor, and all other impurities that may interfere with the titration. Waste solvent remaining in the titration flask was found to be recoverable in the same manner. Because purified tetrahydrofuran forms peroxide rapidly, it was usually purified as needed, no more than a few days' supply being distilled at any one time.

LITHIUM ALUMINUM HYDRIDE SOLUTIONS. A saturated solution of lithium aluminum hydride was prepared by refluxing an excess of the compound with tetrahydrofuran (purified). This was allowed to stand overnight and then centrifuged. The clear supernatant solution was poured off and stored in a bottle fitted with a tube of desiccant. The lower concentrations were prepared by dilution with purified tetrahydrofuran. On standing for several weeks the solutions usually turned cloudy, but were still usable.

STANDARD ALCOHOL IN BENZENE SOLUTION. *n*-Propyl and ethyl alcohol solutions were employed. In each case the alcohol was first distilled over sodium. The solutions were made up volumetrically, definite volumes of alcohols being added to volumetric flasks and made to the mark with dry benzene (distilled over sodium).

SAMPLES. *n*-Butyl, isobutyl, and *n*-amyl alcohols were prepared by drying analytical grade reagents over Drierite for 48 hours. They were then distilled after addition of metallic sodium and stored in glass-stoppered Erlenmeyer flasks fitted with a calcium chloride drying tube. Samples so prepared gave no color with anhydrous copper sulfate.

Eastman *p*-cresol was freshly distilled and recrystallized, the purified product melting between 34.5° and 36° C. Octadecyl alcohol (melting point 58.5° to 59° C.), cholesterin (Wilson brand, melting point 148° to 150° C.), and cetyl alcohol (melting point 49° to 49.5° C.) were used untreated except for drying at 50° C. in a hot air oven for 48 hours. Analytical grade phenol (melting point 40° to 41° C.) was used untreated except for drying by rubbing on a porous plate.

Procedure. The following procedure, with minor modifications, was employed in obtaining experimental results reported in this paper. In all cases only oven-dried glassware was used.

Exactly 50 ml. of purified tetrahydrofuran and 20 ml. of solution of lithium aluminum hydride were pipetted into the reaction vessel (see Figures 2 and 3). The weighed sample was added

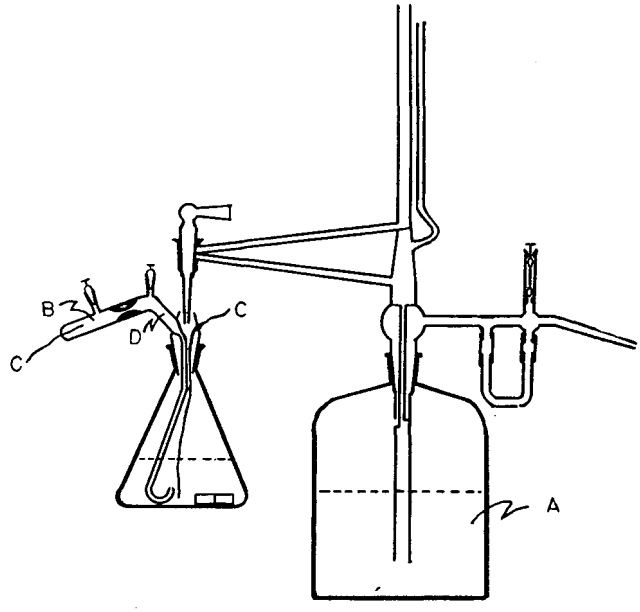

Figure 3. Schematic Drawing of Improved Titrimetric Assembly

A. Alcohol-benzene mixture
B. Lithium bromide–iodine in tetrahydrofuran
C. Silver wire to voltmeter
D. Lithium bromide in tetrahydrofuran

Table I. Analytical Results with Apparatus Shown in Figure 2

Alcohol	Sample	$LiAlH_4$ Soln.	Standard Alcohol Solution Consumed[a]		Alcohol Present		Difference	Error
			Blank	With sample	Theoretical	Found		
	Grams	*Ml.*	*Ml.*	*Ml.*	*Mole*	*Mole*	*Mole*	%
n-Butyl	0.8100	10	8.30	5.15	0.01093	0.01079	−0.0001	1.3
Isobutyl	2.6530	20	16.70	6.30	0.0358	0.0357	−0.0001	0.3
n-Propyl	2.2740	20	20.40	9.50	0.0378	0.0374	−0.0004	1.0
n-Amyl	2.5829	20	21.60	12.90	0.0293	0.0298	+0.0005	1.7
Octadecyl	2.4934	20	18.70	16.00	0.00907	0.00925	+0.0002	2.0
Phenol	2.5943	20	18.80	10.80	0.0275	0.0274	−0.0001	0.4
Cetyl	2.7342	20	18.70	15.40	0.0113	0.0111	−0.0002	1.8
p-Cresol	1.4927	20	18.80	14.80	0.0138	0.0137	−0.0001	0.7
Cholesterol	1.3692	20	16.80	15.75	0.00338	0.00360	+0.0002	6.5

[a] 20% ethyl alcohol in benzene solution (by volume) corresponding to 3.423 moles of alcohol per liter.

Table II. Analytical Results with Apparatus Shown in Figure 3

Sample	Sample	Standard Alcohol Solution Consumed[a]		Alcohol Present		Found/ Theoretical
		Blank	With sample	Theoretical	Found	
	Gram	*Ml.*	*Ml.*	*Mole*	*Mole*	
tert-Butyl alcohol	0.4981	20.33	9.13	0.006720	0.007496	1.116
	0.4860	20.33	9.34	0.006562	0.007356	(1.121)
Benzyl alcohol	0.5016	20.10	13.14	0.004638	0.004658	1.006
	0.7463	20.10	9.65	0.006902	0.006994	1.014
Thymol	0.2808	20.10	17.20	0.001869	0.001941	1.038
	0.3002	20.10	17.00	0.001998	0.002074	1.038
Menthol	0.4892	5.77	0.85	0.003131	0.003292	1.051
	0.4927	5.77	0.93	0.003153	0.003239	1.027
Octadecyl alcohol	0.5526	17.45	14.40	0.002043	0.002044	1.001
	0.2993	17.45	15.78	0.001105	0.001118	1.011
	0.4174	17.45	15.13	0.001543	0.001553	1.006

[a] 5% solution of *n*-propyl alcohol in benzene corresponding to 0.666 mole of alcohol per liter.

and the mixture allowed to react for 15 to 30 minutes under agitation. The reaction mixture was then titrated potentiometrically with a standard alcohol-benzene mixture. The end point was indicated by a large change in the voltage on addition of a small amount of the hydride reagent. Within a few tenths of a milliliter of the end point, it was necessary to wait 10 to 20 seconds after each addition before taking a reading.

A blank run was made for each set of determinations, identical procedures being used except for the addition of the sample. The number of gram equivalents present in the sample was calculated according to the formula

$$\text{No. of gram equivalents} = \frac{(b - v)M}{1000}$$

where b = ml. of standard alcohol solution consumed by the blank, v = ml. of standard alcohol solution consumed by sample titration, and M = molarity of the standard alcohol solution used

RESULTS AND DISCUSSION

In Table I are listed some results obtained with the apparatus shown in Figure 2. The agreements between the theoretical and the experimental columns are as good as can be expected with such an open system. Because moisture pickup occurred both in blank and in sample titrations, the values probably reflect a certain amount of automatic compensation for this source of error. These runs were made during winter months when relatively dry atmospheric conditions prevailed. As shown in Table I, the absolute errors were of the order of a few tenths of a millimole.

Improvement in the accuracy of the method with the revised setup (Figure 3) is evident in Table II, where analytical data for a phenol and several alcohols are presented. Smaller samples and less concentrated standard alcohol solution (5% *n*-propyl alcohol) were used in obtaining these results. In every case the analytical results were higher than would be expected theoretically. This was probably due to residual moisture in the samples. For a compound with an equivalent weight of 180, 0.05% of moisture would produce approximately 1% high result. Except in the case of *tert*-butyl alcohol, the difference between the theoretical and experimental was usually less than 0.1 millimole.

These analyses were made during the summer months, when relative humidity and temperature were both in the nineties.

Results of a reproducibility study are shown in Table III. Six samples of cyclohexanol were titrated with the improved apparatus. The mean error for the series is approximately 1 part in 1000, comparable to those found with usual good volumetric methods.

SOURCES OF ERROR

Water is the principal source of error for the method. A trace of moisture can cause a disproportionate error in the analytical result because of the low molecular weight of water. Inadequate drying of samples, wet glassware, and absorption of atmospheric moisture lead to spurious results. Where it is impossible to remove last traces of water, it may be necessary to determine the moisture concentration by Karl Fischer titration.

APPLICATION OF METHOD

The method can be employed to advantage in determining concentrations of functional groups for both analytical and characterization work. In this report its application to only hydroxyl-containing compounds has been covered. The method is equally applicable to all types of compounds reacting quantitatively with the hydride. As at present developed, it cannot distinguish, however, between functional groups containing active hydrogens and those possessing readily reducible groups. Because of slow interaction of the hydride with certain ester linkages, however, these may be differentiated by regulating the reaction time. Principal advantages of the method for studies of this nature are its relative simplicity and rapidity.

The applicability of the method in obtaining a useful chemical constant in the analysis of essential oils is under investigation. The extent of interaction of the hydride with the oils should be a measure of their hydroxyl and carbonyl content.

Table III. Reproducibility Study Using Cyclohexanol

Sample No.	Sample	Standard Alcohol Solution Consumed		Alcohol Present		Deviation	Error
		Blank	With sample	Theoretical	Actual		
	Grams	*Ml.*	*Ml.*	*Mole*	*Mole*	*Mole*	%
62	0.9675	38.65	24.20	0.00966	0.00967	+0.00001	0.1
13	0.9916	38.65	23.84	0.00990	0.00991	+0.00001	0.1
26	1.0321	38.65	23.30	0.01029	0.01028	−0.00001	0.1
10	1.0490	38.65	23.00	0.01047	0.01047	0.00000	0.0
64	0.9578	38.65	23.35	0.00956	0.00957	+0.00001	0.1
22	0.9982	38.65	23.75	0.00997	0.00997	0.00000	0.0

FUTURE DEVELOPMENTS

The design of the "improved" apparatus is still relatively crude as compared to the elaborate setups employed in Karl Fischer titration in keeping out extraneous moisture. It is hoped that interference from this source can be further minimized.

An investigation is now in progress, studying the feasibility of substituting a chemical indicator in place of the electrode assembly. Several compounds, in particular *p*-aminoazobenzene, have been found to change color sharply at the equivalence point. No data are available at the moment on the comparative sensitivity of the electrical and chemical indicator systems. The latter would be of special value in analysis of microsamples.

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Evaporation of Solvents and Thinners

Thin Film Evaporation vs. Evaporation of Bulk Liquids and Instruments for Their Measurement

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Producers and consumers of solvents and thinners have not agreed upon a standard method for measuring the evaporation rates of these liquids. Investigators have devised a variety of test methods and equipment for this purpose which, however, are largely based upon the evaporation of bulk liquids in disregard of practical use which most frequently involves evaporation of thin films from relatively large surface areas. The authors have reviewed this situation, have devised new equipment (which is being made generally available), and here present details of this equipment and of its use for a variety of applications. Their work shows that atmospheric humidity, the nature of surfaces from which liquids are permitted to evaporate, and the chemical constitution of solvents and solutes are significant factors which often assume greater importance in thin-film evaporation than in the evaporation of bulk liquids. It is hoped that this work and publication will assist in the much needed standardization of evaporation rate measurements and in the reporting of such data.

THE effect of the rates of evaporation of solvents and thinners upon the film properties of coating compositions is of recognized importance and ranks with solvent strength and other physical properties as important criteria in the selection of a solvent or thinner for specific application. Despite the need of some convenient and reliable method for measuring the evaporation rates of solvents and thinners which could be used by all laboratories and despite the publication of many proposed methods of accomplishing this, neither the solvent-producing nor consuming industries have widely accepted any one method. It is also significant that the American Society for Testing Materials has not approved any of the previously described methods as a standard A.S.T.M. procedure.

The literature on evaporation rate methods shows that the four principal types of instruments which have been used are bulk evaporation instruments employing metal cups or watch glasses and sample volumes ranging from about 7 drops to 25 ml.

The simplest of these is the Hart evaporation balance (*4*), which is a simple beam balance with a specially designed rider to facilitate reading directly in per cent, and a support for holding a watch glass from which the sample (0.2 gram or about 7 drops) evaporates.

The evaporometer designed by Wetlaufer and Gregor (*9*) departs considerably from the preceding type of instrument in that evaporation takes place from a closed graduated centrifuge tube. Preconditioned air is blown through the horizontally positioned tubes at a constant rate, and readings are made by adjusting the tubes to a vertical position. This instrument is the only one reported that gives results in volume per cent regardless of the composition of the sample.

A third type of bulk evaporation instrument, which is used in at least three modifications, utilizes shallow metal pans and sample volumes from 2 to 25 ml. Air circulation is provided by forced draft in the tunnel type of instruments designed by Wilson and Worster (*10*) and Follwell (*3*), by rotating the samples on a turntable on the Evap-O-Rotor (*7*), or by blowing intermittent blasts of air over the samples arranged in a circle, as is done in the method of Bent and Wik (*1*) of this laboratory. This latter method is believed to be an improvement over the other multiple-sample bulk-evaporation instruments, because the vapors from each sample are forced away from the test area, rendering contamination of other samples less likely. In this method a filter paper disk is placed in each cup to facilitate observation of the end point and to maintain a constant evaporation surface similar to the procedure proposed by Rubek and Dahl (*8*).

One other bulk liquid evaporation test method is mentioned very briefly in a comprehensive article on lacquer solvents by Doolittle (*2*) and is worth noting because the evaporation curves for a large number of materials are reported and these data have received wide circulation in the form of wall charts and by inclusion in at least two reference books on industrial solvents. This procedure employs samples of about 2 grams; to eliminate as much as possible the errors caused by erratic movements of air, the evaporation is carried out in a draftproof cabinet.

The lack of standardization in the methods of determining rates of evaporation is further illustrated by the frequent absence of specified temperature and humidity conditions for conducting the test. Often, however, the effect of these variables is nullified to some extent, providing the variations are not too great, by the inclusion of a reference standard such as *n*-butyl acetate with each test series.

Although the multiple-sample bulk-evaporation methods (primarily that of Bent and Wik) have been found useful in this laboratory for studying evaporation of solvents in sufficient volume to permit of their analysis at various stages during evaporation and to enable simultaneous testing of a considerable number of samples, they have been found less attractive in other respects, particularly in the imposed need of frequent and tedious removal of samples for weighing with attendant loss of precision and the excessive time for tests of even medium boiling point materials.

Few, if any, of these methods provide ratios of evaporation surface areas to volume of evaporating liquid which approach those that occur in the practical use of coatings.

Although few published data respecting other methods are available, except in trade literature, some laboratories have made extensive use of a modified Jolly balance for evaporation studies. However, in view of the general use of corrodible metallic springs and pans, relatively large bulk samples, and the frequent lack of temperature and/or humidity controls as well as inadequate control of air circulation facilities, the use of Jolly balances in these cases has not eliminated all the important shortcomings of other methods and on the other hand has introduced new difficulties.

It appeared to the authors that the majority of coating material formulators are most interested in the evaporation of solvents and thinners as thin films from relatively large surface areas and at ordinary temperatures and humidities, because such conditions would most closely simulate the conditions involved in the average use of coating compositions and dry cleaners. It was further considered that while standardizing the temperature and humidity for normal operation some provision could be made advantageously to permit controlled variation of temperature and humidity for research purposes or more closely to simulate special conditions of industrial use.

Thus by use of a Jolly balance in which sensitive quartz-fiber springs were substituted for corrodible metal springs and filter paper cones for nonporous metal pans, and by use of various other modifications and refinements, a much improved instrument was developed. This Shell Evaporometer (available from Precision Scientific Co., Chicago, Ill., manufacturing under license from Shell) and details of its use are reported in the present paper.

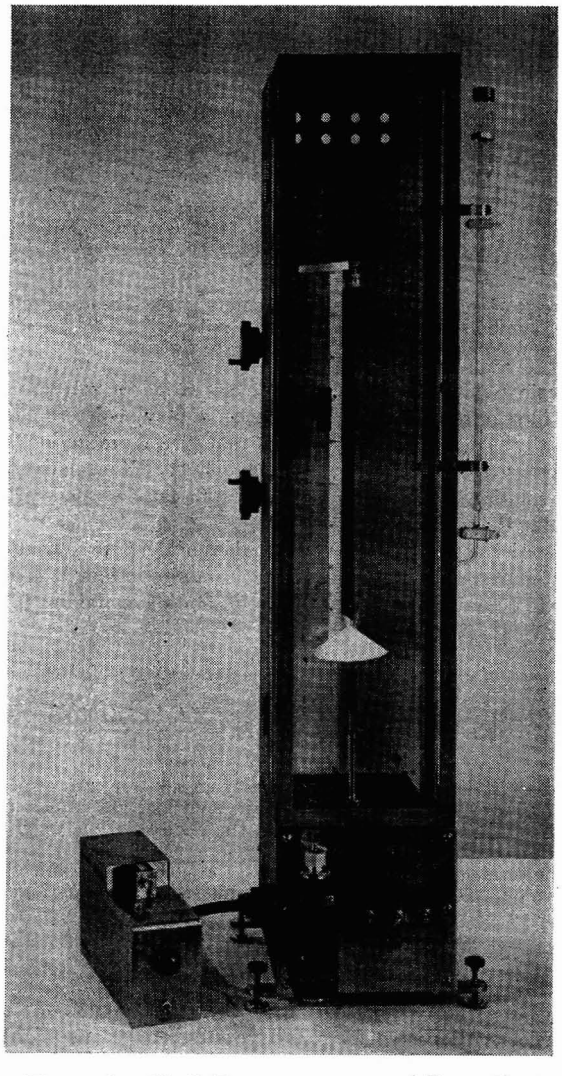

Figure 1. Shell Evaporometer and Repeating Interval Timer

DESCRIPTION OF INSTRUMENT AND METHOD

Scope. This method is intended for the determination of the evaporation rate of all volatile materials used in the coating materials and allied fields. The method is applicable to all liquids of low viscosity, including solutions of film-forming materials (resin solutions) from which an indication of solvent release characteristics of various solvents may be obtained. The method is limited only by the viscosity of the solution, which should not exceed about 50 cp.—i.e., should not be high enough to prevent the dispensing of an accurate sample volume from the buret. Special procedures for handling resin solutions of the proper viscosity and samples of very low volatility are also outlined.

Method Summary. An accurately measured volume of sample (0.7 ml.) is dispensed at a uniform rate during a period of 15 seconds onto a filter paper cone, suspended on a calibrated quartz spring, that is rotated at the rate of 4 r.p.m. Air at 77° F. and 50% relative humidity is passed over the cone at 21 liters per minute, and readings are made of the elongation of the quartz spring at convenient intervals as the sample evaporates and the cone returns to its original or no-load position. From these readings, knowing the zero point, volume of sample, density (grams per ml. at 25° C.) of the sample, and the spring constant (grams per cm. elongation) the weight per cent evaporated at each reading can be plotted as a function of time.

Apparatus. The Evaporometer, as illustrated in Figure 1, consists of a Jolly balance type of instrument enclosed in a cabinet through which downdraft air circulation at 21 liters per minute is maintained by means of a vacuum line, and a rotameter to measure the flow of air accurately. The quartz-fiber spring is supported through a swivel connection to a supporting arm, which can be raised or lowered from outside the case to compensate for cones of different weights and samples of a wide range of specific gravities. The filter paper cone is supported below a horizontal sighting disk on a wire frame which has a hook on the upper end for fastening to the quartz spring and a triangular soft iron armature on the other end that fits into a shallow triangular opening in the Bakelite cover of a rotating electromagnet protruding from the base of the case. The mirror and millimeter scale, which can be raised and lowered from outside the case to facilitate accurate setting of a zero point, are in a position directly behind the spring and cone assembly, so that when in perfect alignment the sighting disk and its image can be superimposed on each other with the left-hand edge of the disk slightly overlapping the scale. The microburet, 1-ml. capacity, has an offset tip that projects into the cabinet through a sliding window device, so that it can be swung directly over the cone to dispense the sample and then pushed back against the scale so as not to interfere with the freely hanging cone during the evaporation of the sample.

Apparatus Preparation. The Evaporometer cones are constructed from 11-cm. disks of No. 4 Whatman filter paper by removing a 75° segment, gluing the upturned edges with a water-soluble glue, and then trimming off the excess paper about 2 mm. above and parallel to the surface of the cone. To avoid errors due to change in moisture content of the filter paper, the cones should be conditioned overnight under the specified conditions of the test.

Quartz-fiber springs, suitable for use, may have elongations between 11 and 15 cm. per gram load, or spring constants from 0.091 to 0.066. A typical spring of this type is approximately 17.5 mm. in diameter composed of 38 spirals of quartz about 0.4 mm. in diameter and has a free hanging length of approximately 8.3 cm. Calibration of the spring is accomplished by the use of a small metal pan suspended on the spring and loading it with analytical balance weights in increments of 0.1 gram until a total load of 2.5 grams is obtained. The load *vs.* elongation curve is then plotted and the spring constant (total load–total elongation) calculated.

Operating Procedure. VOLATILE SOLVENTS. For the purpose of standardization, it is recommended that the evaporation tests be conducted in a room conditioned to 50% relative humidity at a temperature of 77° F. or that auxiliary equipment be provided to produce these conditions in the Evaporometer cabinet.

The instrument, for proper operation, must be level and must have the necessary adjustments made, so that with the cone and

spring in position, the armature of the cone support is centered directly above the shallow opening in the electromagnet. The source of vacuum should be connected in series with a dry ice–acetone cooled cold trap to prevent the drawing of solvents into the vacuum system.

With these adjustments made, the total elongation which will be caused by the 0.7-ml. sample is calculated by means of the equation:

$$\text{Spring elongation} = \frac{(d_1)(0.7)}{C}$$

where d_1 = density of the sample, grams per ml. at 77° F., and C = spring constant, grams per cm. elongation

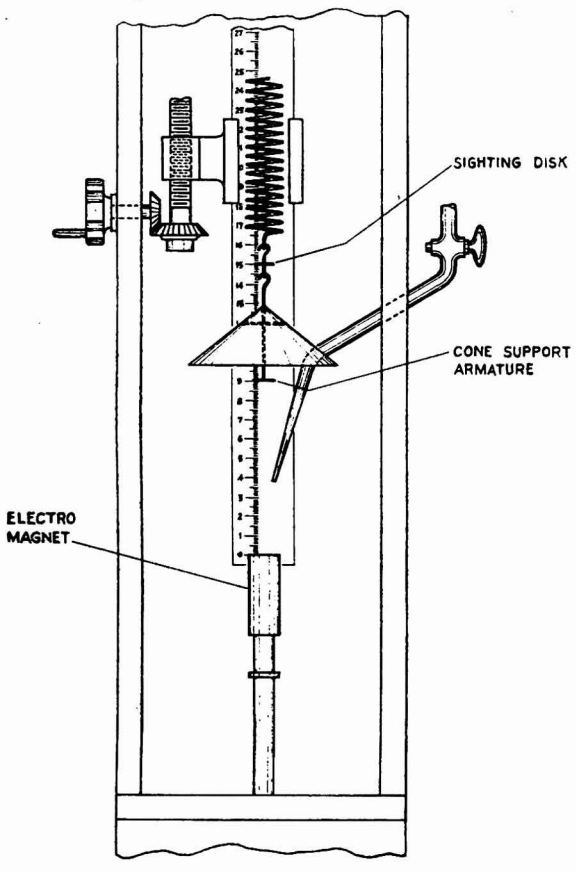

Figure 2. Spring and Cone Assembly
Showing first step in setting no-load point

A fresh filter paper cone is then suspended on the spring and a correction for sample volatility (dependent on the volatility of the sample and varying from about +3 mm. to −20 mm.) is made by raising or lowering the zero point of the scale the correct distance from a point level with the top of the electromagnet (Figure 2). (A minus correction is made only with fast evaporating samples to compensate for the amount of sample evaporated before the cone is released, thus preventing excessive spring vibration; while a positive correction, which increases the spring tension when the armature is in contact with the electromagnet, is made only with slowly evaporating materials to ensure release of the cone when the magnet is turned off.) The cone is then adjusted so that the scale reading corresponding to the total elongation due to the sample coincides with the position of the armature of the cone support. Then in order to use the sighting disk during the test, the scale is raised so that this scale reading coincides with the sighting disk position. The liquid level of the buret is then accurately set to zero, the magnet turned on, the triangular armature of the cone support engaged with the magnet, and the buret tip brought into position over the center of the cone. The test is started by turning on the motor and dispensing the sample (0.7 ml.) onto the cone at a uniform rate while the cone makes one revolution. The start of the evaporation period is indicated by

Table I. Evaporation Rate Data Sheet

Date 3-24-48

No. 463-181 Sample. Ethyl acetate (85% ester)
Spring No. 11 Spring constant (gram/cm. elongation). 0.06835.
Cone material. Whatman No. 4 Density. 0.8855 Sample volume. 0.7 ml.
Factor. 11.03 or $\frac{\text{spring constant} \times 100}{\text{density} \times \text{sample volume}}$
Zero scale reading. 9.07 cm. Wt. % evaporated = $R \times$ factor
Conditions. 50% R.H. at 77° F. Operator.....

Time, Seconds	Scale Reading = R	Wt. %, Sample Evaporated
0	0	0
40	3.675	40.5
50	4.65	51.4
60	5.45	60.0
70	6.225	68.6
80	7.025	77.4
90	7.675	84.6
100	8.1	89.5
110	8.3	91.5
120	8.45	93.4
130	8.525	93.9
150	8.6	95.0
190	8.65	95.6
230	8.775	96.7
290	8.825	97.2
340	8.875	97.8
420	8.925	98.3
580	8.975	98.9
650	9.025	99.5

the contact of the first drop of sample with the cone, and the timer is started at that instant. The buret tip is then quickly swung back against the scale, the motor and magnet are turned off, and readings are made at periodic intervals.

The frequency of reading depends on the volatility of the sample and the desired detail of the data. However, to obtain a detailed curve, the time interval selected should give a reading for every 4- or 5-mm. rise of the cone or about every 5% of the sample evaporated.

A suggested data sheet, with typical test results, is shown in Table I. The weight per cent of the sample evaporated at each reading is calculated by the equation:

$$\text{Sample evaporated, weight \%} = \frac{(R)(C)(100)}{(d_1)(0.7)}$$

where R = scale reading in centimeters at each reading and the other symbols are as noted above.

A new cone is used to run a duplicate test.

Resin Solutions. The rate of evaporation of solvents from thin films of resins deposited on the cones may be determined essentially as described above, except that special precautions must be observed to ensure accurate sample delivery of the relatively viscous solution and an additional calculation must be made prior to starting the test.

In order to make the evaporation data of the pure solvent comparable to that of the same solvent from a resin film, it is necessary to determine the volume of resin solution containing 0.7 ml. of solvent.

The resin solution sample volume is calculated as follows:

$$\text{Resin solution sample, ml.} = \frac{(d_2)(0.7)(100)}{(d_3)(100 - S)}$$

where d_2 = density of the solvent in resin solution, grams per ml. at 77° F., d_3 = density of the resin solution, grams per ml. at 77° F., and S = amount of solids in the resin solution, weight per cent.

The total spring elongation due to the volume of resin solution equivalent to 0.7 ml. of solvent is calculated by the equation:

$$\text{Spring elongation, cm.} = \frac{(d_2)(0.7)(100)}{(C)(100 - S)}$$

where C = spring constant, grams per cm. elongation

An initial zero point is then set as described above, using the spring elongation as calculated above and then, because of the solids in the solution, a final zero point must be determined. The following equation gives the spring elongation caused by the solvent in the sample and the final zero point to which the sighting

disk returns when the volatile component of the solution has completely evaporated:

$$\text{Spring elongation due to solvent, cm.} = \frac{(d_2)(0.7)}{C}$$

The results of tests are calculated as outlined in the previous section, using the same density and sample volume (0.7 ml.) as used for the pure solvents.

Very High Boiling Materials. The determination of the evaporation rate of materials such as spray base oils is carried out in much the same manner as described under the section dealing with volatile solvents, except that a positive volatility correction is necessary (the zero point set a distance above the magnet greater than the spring elongation caused by the sample), and it is not necessary to allow the cone assembly to remain suspended in the spring during the entire set, for in the interest of greater precision with such samples the readings are in general made by separate weighing.

The cone and support are weighed to the nearest 0.1 mg. before the test is started. Then after the evaporation has progressed for 20 to 30 minutes, or until the sample is completely absorbed into the cone, the spring may be removed from the balance assembly and replaced with a cord of about the same length as the elongated spring. The cone and support are removed periodically from the cabinet for weighings on an analytical balance and the test is complete when the original starting weight or a constant weight is attained. The amount of sample evaporated from the sample cone is calculated as follows:

$$\text{Sample evaporated, weight \%} = 100 - \left[\frac{(W - W_0) \times (100)}{(d_1)(0.7)}\right]$$

where W = weight in grams of cone and support at each weighing, W_0 = weight in grams of dry cone and support, and d_1 is as before

Reporting Results. The results of evaporation tests may be reported in one of two forms, depending on the type and number of samples tested.

1. The results may be expressed graphically when the data for a small number of samples are being reported or when the evaporation rate of a solvent is compared with and without a resin film present.
2. When a large number of samples are under consideration, it is recommended that the results be reported in tabular form (the time in minutes for each 10% of the sample evaporated, plus the 95% time).

Precision. The results of a large number of tests carried out at 77° F. and 50% relative humidity, on materials embracing the complete range of practical volatility, show that at corresponding times the results of two or more tests on the same material do not deviate from the mean by more than 3.0%.

Example of Typical Calculations. The calculation procedure may be summarized by the following data for a representative material and by the data sheet shown in Table I.

The sample, commercial ethyl acetate (85% ester), has a density of 0.8855 and the quartz spring used has an elongation of 14.62 cm. per gram load of a spring constant of 0.0684 gram per cm. elongation. The 0.7-ml. sample causes a spring elongation of 9.07 cm. as recorded at the top of the data sheet (Figure 2). A volatility correction of 0.6 cm. was used for this sample and this point on the scale was set level with the top of the electromagnet. The cone assembly was then adjusted so that the armature of the cone support was level with the 9.07-cm. point on the scale and then the scale was raised so that this point coincided with the level of the sighting disk. The test was started and reading made as recorded on the data sheet.

To facilitate rapid calculation of results, a factor is used to collect the various numerical constants of the experiment into one number. Substitution of the proper constants in the equation shown at the top of the data sheet gives:

$$\text{Factor} = \frac{(0.0684) \times (100)}{(0.8855) \times (0.7)} = 11.03$$

Thus, when the test is completed, or during the tests on slow-evaporating materials, the results can be calculated by one slide rule operation.

Repeating Interval Timer. The repeating interval timer illustrated with the Evaporometer in Figure 1 was designed in this laboratory specifically for use with the Evaporometer when all the available timers proved inadequate for this purpose (primarily because of the lack of any type of signaling device or mechanism for recording the total running time). (At the present time, manufacturing rights to the Shell repeating interval timer have not been licensed to a manufacturer. However, if sufficient demand arises for this type of timer, such arrangements will be made.)

The timer consists of a small synchronous motor which, through the proper gearing, operates a second counter and a mechanism for providing two audible signals of distinctly different tone. The timer may be set to signal at 10- or 20-second intervals with a 3-second warning signal preceding the on-time signal. Thus, it is possible to make rapid and accurate readings during an evaporation test without looking at the timer, and with the aid of the warning signal anticipate the reading and have sufficient time to locate the position of the indicator accurately on the scale. This timer can also be operated without the audible signals and may be used for a variety of purposes in the laboratory.

EXPERIMENTAL RESULTS

Selection of Cone Material. The particular design of the Evaporometer, the construction of an adequate film evaporation surface, and the desirability of obtaining greater precision than is realized from other evaporation rate methods demand that a material meet definite specifications to qualify for use as a suitable evaporation rate cone. The material of construction must be relatively rigid, so that it will retain a smooth symmetrical cone shape when supported only at the apex by a light-weight skeletal support; must be easily cut and formed into a cone, must be light in weight so that sensitive springs can be used without excessive elongation; must be uniform in texture, and must have the ability to absorb liquids completely and evenly, so that a constant evaporation surface is maintained during the entire test.

No. 4 Whatman filter paper (11-cm. disks) used throughout this investigation has performed very satisfactorily as a cone material and meets these requirements to a considerably greater extent than any other material tested, including No. 5 Whatman paper, with which was noted a slight tendency for slowly evaporating samples to migrate to the lower edge of the cone.

The use of light-weight glass cloth (Fiberglas) as a cone material has been investigated, but because of poor mechanical stability in fabrication and use, as well as a tendency toward uneven distribution of sample, it is considered unsatisfactory for use at the present time in routine tests.

In addition to filter paper and glass cloth, a variety of light-weight metallic screens, cloths, and foils (roughened and/or perforated) have been investigated as cone materials. All proved unsatisfactory.

Comparison with Other Methods. The evaluation procedure followed throughout the development stages of the Shell Evaporometer was to compare the evaporation curves with those obtained from the bulk evaporation method (*1*) previously used in this laboratory. These data from this bulk test method are in good agreement with published evaporation data from various sources. These data are also consistent with the relationship found by de Heen (*5*), that the quantity of a liquid evaporated in a given time is proportional to the product of its vapor pressure and molecular weight. It was further shown by Hofmann (*6*) that the rate of evaporation of a liquid at 25° C. relative to that of *n*-butyl acetate is about $^1/_{11}$ of the product (vapor pressure, millimeters of mercury) (molecular weight).

The thermal and molecular properties that control the vaporization of a liquid in any type of evaporation test have not been

separately investigated, inasmuch as we are primarily concerned with the measurement of relative rates of evaporation and not with an absolute determination where these properties would of necessity have to be considered.

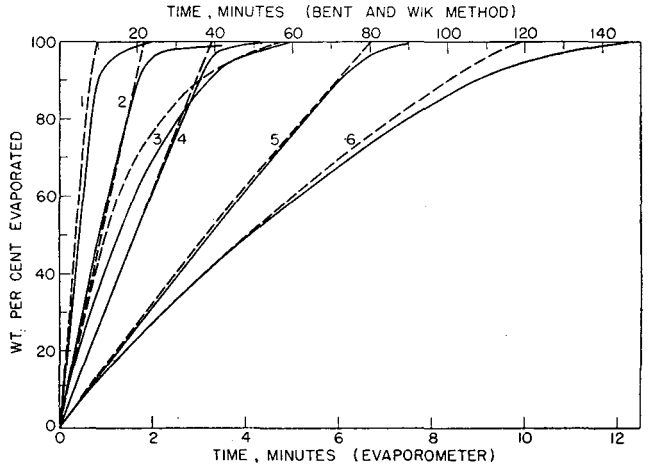

Figure 3. Comparison of Evaporation Rate Methods

Solid lines, Shell Evaporometer method
Broken lines, Bent and Wik bulk method
1. Low solvency lacquer diluent
2. Medium solvency lacquer diluent
3. Medium solvency lacquer diluent (western type)
4. Toluene
5. *n*-Butyl acetate
6. Xylene

In general, results from the Evaporometer show no great deviation from data obtained from other methods with the exception of volatile, highly polar, water-miscible compounds such as low boiling alcohols, which because of these inherent properties tend to evaporate more slowly than from the cups used with bulk evaporation methods. A graphical comparison of results from these two methods is shown in Figures 3 and 4. The curves obtained from the Evaporometer tests exhibit considerably more curvature, especially after about the 90% evaporation point, and in some cases the evaporation apparently was not complete. Undoubtedly, these same phenomena occur to a more limited extent with the bulk evaporation method than with the Evaporometer, but because of the greater surface area per unit volume of sample (215 sq. cm. *vs.* 4 sq. cm. per ml.) with attendant greater condensation of atmospheric moisture, the effect is intensified and more easily detected than with the bulk methods where, owing to the visual end point observed and the difficulty of making several weighings over a short time interval, the trend of the curve cannot be so accurately followed.

The large ratio of surface area to volume of the evaporating solvent used with the Evaporometer assumes added significance, from the standpoint of practical solvent applications, when compared with a comparable relationship calculated for a typical furniture lacquer, which at 8.4 pounds per gallon and 17% solids content is capable of covering 802 square feet per gallon at a wet film thickness of 2 mils. Calculation shows that such a lacquer has an effective evaporation surface of 210 sq. cm. per ml. of contained solvent.

Discussion of Results. The plotted data presented in Figures 5 and 6 show the evaporation curves for several lacquer solvents and a number of thinners and dry cleaning solvents, while Table II presents the same data in tabular form. The latter style of presentation is preferred, especially when a large number of samples are being considered, because of its ease of preparation and compactness and because of a clarity not obtainable when data for several samples having about the same evaporation time are plotted on the same coordinates. Preliminary over-all comparison can be quickly made from the tables and if graphical presentation is desired portions of the data can be plotted. This style of reporting also has a distinct advantage over the common method of expressing evaporation rates as the ratio of the evaporation time of a standard, such as *n*-butyl acetate or toluene, to that of the unknown material. This value, although adequate for some solvent applications and relatively pure materials, does not give a complete picture of the evaporation characteristics of materials having wide distillation ranges. This applies especially to lacquer solvent mixtures and mixed hydrocarbon thinners which are formulated to impart specific properties to the coating material. Here small differences in evaporation behavior (including degrees of induced moisture condensation) are important, yet often remain undetected with bulk evaporation test methods. With the Evaporometer, where a large number of readings can be accurately and easily made, small differences in evaporation characteristics are readily detected.

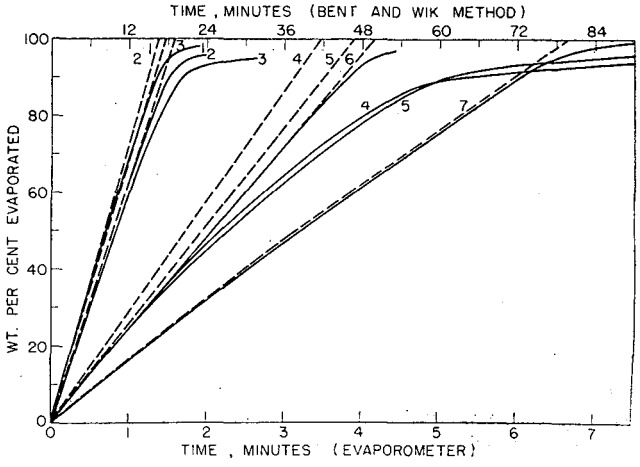

Figure 4. Comparison of Evaporation Rate Methods

Solid lines, Shell Evaporometer method
Broken lines, Bent and Wik bulk method
1. Benzene
2. Methyl ethyl ketone
3. Ethyl acetate
4. Ethyl alcohol (absolute)
5. Isopropyl alcohol
6. Methyl isobutyl ketone
7. *n*-Butyl acetate

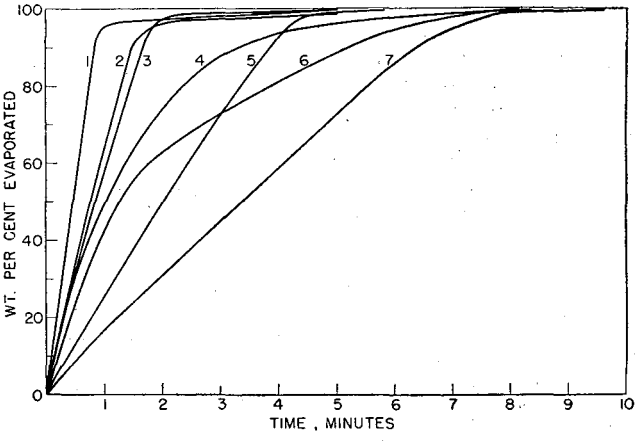

Figure 5. Evaporation Rate Data for Lacquer Solvents and Thinners

Temperature 77° F.
Relative humidity 50%
1. Low solvency lacquer diluent
2. Methyl ethyl ketone
3. Medium solvency lacquer diluent
4. Lacquer solvent mixture (see Table II)
5. Methyl isobutyl ketone
6. Methyl ethyl ketone xylene (50–50 mixture)
7. *n*-Butyl acetate

Table II. Tabulated Evaporation Rate Data for Curves Shown in Figures 5 and 6

Evaporated	Toluene	V.M. and P. Naphtha	Xylene	High Solvency Lacquer Diluent	Gum Spirits of Turpentine	Cleaning Solvent	High Solvency Naphtha	Paint Base Spirits
Weight %	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*
10	0.3	0.3	0.7	0.9	1.67	1.3	1.8	2.0
20	0.55	0.6	1.7	2.1	3.33	2.3	4.7	5.0
30	0.9	0.97	2.7	3.7	5.0	3.7	7.8	8.75
40	1.2	1.38	3.7	5.3	6.7	8.3	11.1	12.75
50	1.5	1.9	4.7	7.0	8.33	11.0	14.8	17.0
60	1.9	2.58	5.7	9.0	10.2	14.2	18.7	22.0
70	2.3	3.42	6.7	11.4	12.0	17.8	22.9	27.8
80	2.65	4.5	7.7	14.2	14.5	21.7	27.6	34.7
90	3.0	5.9	8.7	18.2	18.0	26.6	33.3	44.0
95	3.3	7.0	9.4	21.4	23.5	30.1	37.8	50.8
100	4.2[a]	9.83	11.1	26.6	45.0[b]	36.6	45.4	60.4

Evaporated	Low Solvency Lacquer Diluent	Methyl Ethyl Ketone	Medium Solvency Lacquer Diluent	Lacquer Solvent Mixture[c]	Methyl Isobutyl Ketone	50% MEK–50% Xylene Mixture	*n*-Butyl Acetate
	Min.	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*	*Min.*
10	0.08	0.12	0.17	0.15	0.37	0.22	0.58
20	0.18	0.28	0.32	0.32	0.79	0.43	1.25
30	0.27	0.45	0.48	0.50	1.2	0.65	1.96
40	0.35	0.6	0.67	0.72	1.6	0.93	2.66
50	0.45	0.77	0.85	1.0	2.03	1.28	3.38
60	0.55	0.95	1.00	1.37	2.45	1.78	4.12
70	0.65	1.13	1.25	1.83	2.92	2.73	4.82
80	0.75	1.3	1.43	2.43	3.36	3.86	5.55
90	0.85	1.5	1.68	3.36	3.86	5.2	6.37
95	0.98	1.81	2.00	4.43	4.15	6.1	7.02
100	5.8[d]	5.0[e]	5.8[d]	8.32[d]	5.8[f]	9.58[f]	8.1[c]

[a] 99.25% evaporated.
[b] 95.5% evaporated.
[c] Methyl isobutyl ketone 30%, Methyl ethyl ketone 10, Isopropyl alcohol 11, Methyl isobutyl carbinol 9%, Lacquer diluent A 30, Toluene 10
[d] 99.7% evaporated.
[e] 98.6% evaporated
[f] 99.6% evaporated

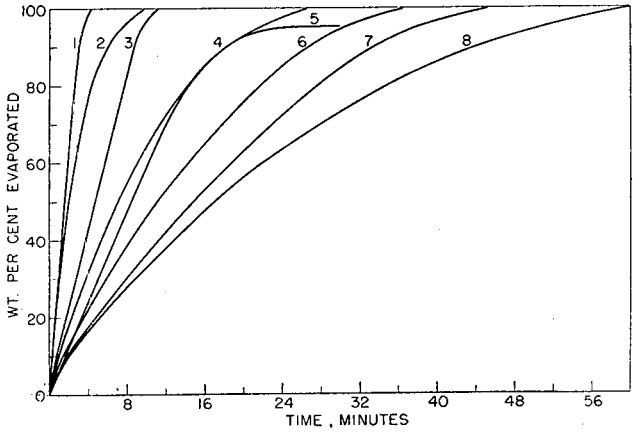

Figure 6. Evaporation Rate Data for Special Boiling Point Products and Gum Spirits of Turpentine

Temperature 77° F.
Relative humidity 50%

1. **Toluene**
2. **V.M. and P. naphtha**
3. **Xylene**
4. **High solvency lacquer diluent**
5. **Gum spirits of turpentine**
6. **Cleaning solvent**
7. **High solvency naphtha**
8. **Paint base spirits**

In addition to determining rates of evaporation of thinners, the Evaporometer may be used, as described above, for determining the relative solvent-release properties of film-forming materials by measuring the rate of release of solvents from thin films of such materials deposited on the standard filter paper cones. Comparison of these data with the evaporation curve of the pure solvent gives an indication of how the materials may perform when applied in a lacquer or other type of film. Representative data of this type are shown in Figure 7.

Investigation of Cause of Curve Deflection. The cause of the curve deflection noted in the plotted data for samples having evaporation times of less than 10 minutes was investigated. To study the possible effect of the paper (cellulose) on the shape of the curves, a series of four experiments was carried out using samples of distilled water and several representative types of compounds. The filter paper and glass cloth cones used in these tests were carefully conditioned to constant weight under the test conditions, and weighed before and after the test. Each filter paper cone was used only once. The tests were performed under the following conditions:

Approximately 1.5% Relative Humidity at 77° F. Using Filter Paper Cones. These atmospheric conditions were attained in the evaporation zone by metering air at the proper rate through an efficient drying train (large calcium chloride tubes and dry ice–acetone cold traps) attached to the air inlet port of the instrument. Special precautions were observed to maintain a slight positive pressure in the cabinet and the relative humidity at the cone position was determined by the use of an Alnor dew-point meter Model 7000 L.

Using Pretreated Filter Paper Cones at 77° F. and 50% Relative Humidity. Cone pretreatment was accomplished by thoroughly saturating the sample cone with the respective sample with which it was to be used and then allowing it to dry to constant weight under the test conditions.

Using Glass Cloth Cones at 77° F. and 50% Relative Humidity. This group of tests was carried out to determine the evaporation behavior of solvents when the conditions conducive to association of sample and cone material are minimized. The glass cloth cones were identical in size and shape to those constructed from 11-cm. disks of filter paper. Two glass cloth cones were used, and ample time was allowed between tests for the cone to return to its original weight through loss of moisture accumulated from a previous use.

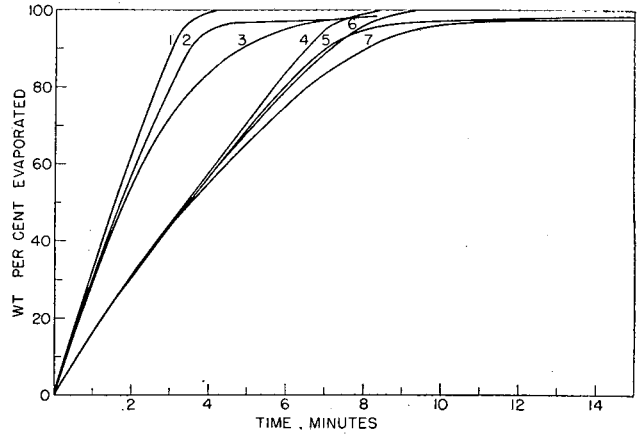

Figure 7. Comparison of Evaporation Curves of Solvents with Evaporation Curves of Solvents from Films of Resins

Temperature 77° F.
Relative humidity 50%

1. **Toluene**
2. **10% solution of Teglac Z-152 in toluene**
3. **10% solution of paraffin wax in toluene**
4. ***n*-Butyl acetate**
5. **20% solution of ester gum C in *n*-butyl acetate**
6. **Xylene–*n*-butyl acetate 50–50 mixture**
7. **20% solution of ester gum C in xylene–*n*-butyl acetate 50–50 mixture**

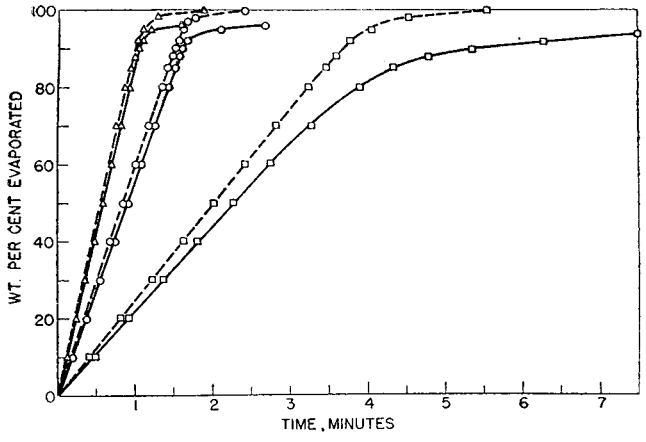

Figure 8. Effect of Humidity on Evaporation Rate of a Lacquer Diluent, Methyl Ethyl Ketone, and Ethyl Alcohol

Cone material, Whatman No. 4 filter paper
—— 50% relative humidity, 77° F.
- - - 1.5% relative humidity, 77° F.
△ Low solvency lacquer diluent
○ Methyl ethyl ketone
□ Ethyl alcohol (absolute)

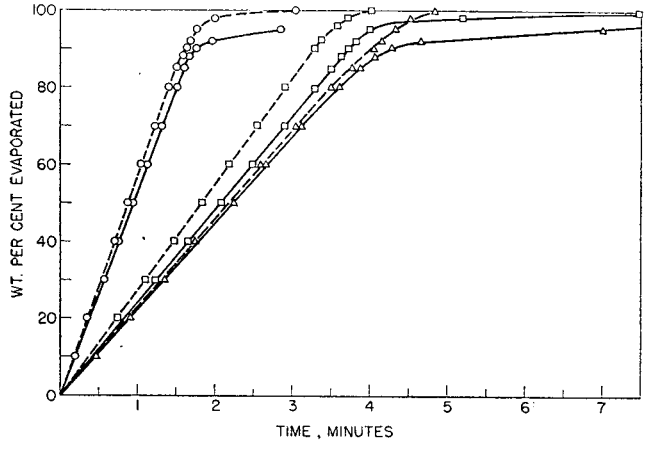

Figure 9. Effect of Humidity on Evaporation Rate of Ethyl Acetate, Methyl Isobutyl Ketone, and Isopropyl Alcohol

Cone material, Whatman No. 4 filter paper
—— 50% relative humidity, 77° F.
- - - 1.5% relative humidity, 77° F.
○ Ethyl acetate (85 to 88% ester)
□ Methyl isobutyl ketone
△ Isopropyl alcohol

USING UNTREATED FILTER PAPER CONES AT 77° F. AND 50% RELATIVE HUMIDITY. For purposes of comparison with the results from the above tests, each solvent was tested under these standard operating conditions and special precautions were observed to obtain even sample distribution and reproduce the same operating techniques.

RESULTS OF TESTS ON CURVE DEFLECTION. The deflection in the curves above approximately the 90% evaporation point was found to be primarily due to the condensation of water on the cone from the surrounding atmosphere due to the cooling effect of the rapidly evaporating sample as shown in Figures 8 and 9. This phenomenon is of practical significance, because it occasions the "moisture blush" of lacquers yet escapes detection and measurements by bulk evaporation test methods.

Although distilled water was found to have about the same rate of evaporation rate as mineral spirits, the water evaporation curve leveled out at approximately the 98% point and the test was not completed in a reasonable length of time. In contrast, mineral spirits readily evaporates to completion in a smooth curve. This illustrates that water is retained more tenaciously by the paper than hydrocarbons, and when accumulation of moisture occurs on the cone during the evaporation of a volatile material, rapid deflection of the curve is to be expected after most of the sample has vaporized.

When the tests were carried out in a dry atmosphere, the curve deflection was not completely eliminated, but in every case was delayed by amounts of about 4 to 8%, and a small decrease was noted in the over-all evaporation time. The relatively small amount of residual curve deflection noted is apparently due to the absorbent porous nature of the filter paper, which in this application simulates an applied film of a coating material; in fact, the deflection in this case is very similar to that shown by typical curves from measurements of weight loss *vs.* time during the drying of lacquer films.

The tendency for solvents to be semipermanently retained by the filter paper may be counteracted to at least a limited extent by cone pretreatment, as evidenced by a small gain in weight (0.2 to 1.0%) of the cones as a result of this treatment and a small displacement to the left of the normal evaporation curves. Maximum displacement varied from 2 to 8% with a mean of 5.5%, or

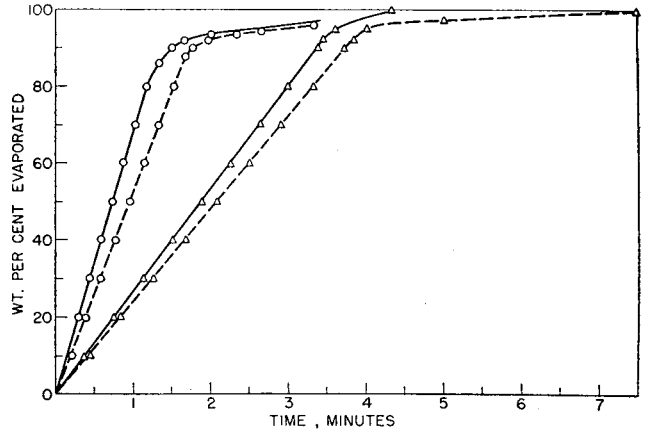

Figure 10. Effect of Cone Material on Rate of Evaporation of Solvents

50% relative humidity, 77° F.
—— Glass cloth cones
- - - Whatman No. 4 filter paper cones
○ Ethyl acetate (85 to 88% ester)
△ Methyl isobutyl ketone

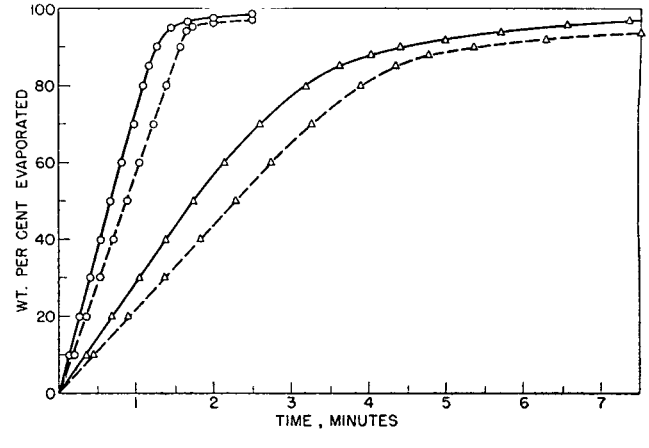

Figure 11. Effect of Cone Material on Rate of Evaporation of Solvents

50% relative humidity, 77° F.
—— Glass cloth cones
- - - Whatman No 4 filter paper cones
○ Benzene
△ Ethyl alcohol (absolute)

close to the limit of experimental error of the method. The overall evaporation times of the samples were not appreciably shortened nor was the amount of curve deflection due to moisture accumulation much different from that noted in tests carried out with untreated cones.

The results from tests carried out with glass cloth (Fiberglas) cones show that solvents less volatile than methyl isobutyl ketone cannot be tested on this material, owing to the loss of droplets of sample as a result of drainage to the lower edge of the cone. However, the plotted data, from tests of the more volatile samples (a portion of which is shown in Figures 10 and 11), closely approximated those from the method of Bent and Wik and in every case the shape of the evaporation curve was very similar to that obtained from tests on the same solvent using filter paper cones. This latter point is of particular significance in that it indicates that the chemical nature of the filter paper does not significantly effect the release of solvent. The apparent increase in rate of evaporation evidenced by the use of glass cloth may be logically attributed to its loose open texture, which does not mechanically retard the release of solvent to as great an extent as does the relatively dense close-textured filter paper.

POSSIBLE MODIFICATIONS AND IMPROVEMENTS

Since the Evaporometer was developed to the extent described above and a considerable amount of experimental data obtained, several problems relative to specific uses of solvents over a wide range of temperature and humidity conditions have arisen that cannot be studied with a bulk evaporation method but may be investigated with the Evaporometer after minor modification of the instrument and improvement of the design of some of the essential elements. These alterations, primarily to the instrument cabinet, include the installation of heating elements, proper thermal insulation, and modification of the air-inlet port to permit attachment to air-conditioning equipment.

The large number of tests conducted to date by various operators show that the free draining type of manually controlled buret does not introduce serious errors due to improper drainage or to uneven distribution of sample on the cone. In working with relatively viscous resin solutions this source of error may be significant, but it may be considerably reduced by the use of a modified mercury reservoir type of buret. Automatic operation of the buret, through connection to the magnet rotating motor, may also prove feasible.

ACKNOWLEDGMENT

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Analysis of Lactic Acid–Lactate Ester Systems

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A method is presented for determining the composition of reaction mixtures of lactic acid with methanol, both during the reaction and at equilibrium. This is achieved by combining a determination of the free carboxyl groups by titration and a calculation of the amount of hydrolysis of the polylactic acids based on a curve showing hydrolysis ratios as a function of temperature and time. These hydrolysis ratio curves were determined in a separate series of experiments on aqueous lactic acid.

THE ever-increasing importance of lactic acid and its derivatives as industrial chemicals has created a need for data on lactic acid–lactate systems. Fisher (*5*) has pointed to the versatility of the acid as a low-cost chemical intermediate because of its two reactive functional groups. To date exact work in this field has been made difficult by the lack of suitable analytical methods for reaction systems of lactic acid, lactic esters, alcohols, and water.

ANALYSIS OF THE PROBLEM

Although the constitution of lactic acid has been a controversial subject for many years, recent work (*1, 3, 4, 8*) indicates that the monomeric acid exists in equilibrium with polymeric condensation forms of polylactic acids. The extent of the polymerization or internal esterification depends on the concentration of the acid. Thus, in a mixture of lactic acid and an alkyl lactate, the monomeric form and polylactic acids are present in addition to the alkyl lactate, which in this work was methyl lactate.

In analyzing these systems, speed is as essential as accuracy in order to prevent a shift of equilibrium concentrations. The determination of free carboxyl groups by titration, followed by determination of free hydroxyl groups, was eliminated for want of a rapid, accurate method for determining hydroxyl groups. Also eliminated were gravimetric methods based on insoluble lactate salts, because the solubility of all these salts was too great for quantitative results. The Karl Fischer method was tried without success as a means of determining the amount of water present.

Physical methods were useless because of the large number

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of reactants and products to be resolved. However, these methods are of value in resolving binary mixtures and were used for lactic acid–water and methyl lactate–water systems.

A method that seemed promising was one in which the free carboxyl groups are titrated followed by the addition of a base which will saponify methyl lactate but not the polylactic acids. Many bases were tried under a wide range of conditions, but none gave satisfactory results, although it was discovered that methyl lactate saponifies more readily than the polylactic acids.

Solvent extraction using benzene, dichloroethane, and tetrachloroethane as solvents was attempted but was abandoned because of the failure of the system to form two phases with methanol present, unfavorable distribution coefficients, and slowness of the process, Dietz (*2*) successfully used dichloroethane in a simultaneous esterification-extraction process for dilute lactic acid solutions.

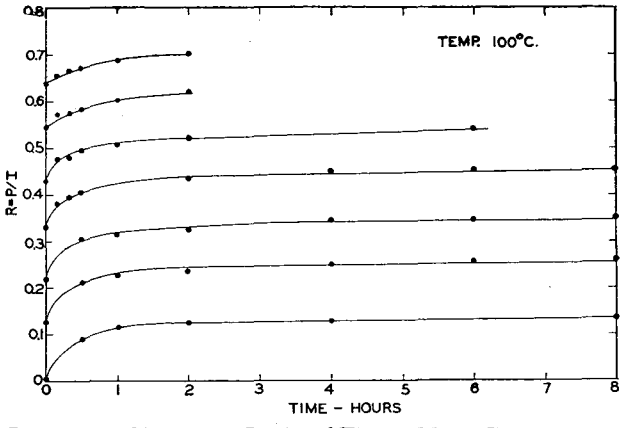

Figure 1. Change in Ratio of Titratable to Total Lactic Acid with Time

85% lactic acid used

In developing a distillation method it was difficult to prevent further esterification or hydrolysis during the process. The best method found for accomplishing this consisted of partially neutralizing the excess acid with aqueous base followed by a simple distillation. The use of aqueous base not only provided a buffer (sodium lactate) but also added water which permitted an azeotropic distillation of the methyl lactate at a lower boiling point. Because this azeotrope was only vaguely known (*2*, *6*, *7*, *9*), numerous fractionations were performed in an effort to locate it more exactly. The boiling point was found to be 99.1° C. at 752 mm. of mercury and the composition to be about 26.5% methyl lactate by weight. It is believed that the vapor-liquid equilibrium curve is flat over a wide range at the water end. Recovery from known mixtures of 5- to 10-ml. volume by the distillation method was 97.5% or more complete.

This is also the yield obtained when the same volume of methyl lactate, pure or mixed with water, is distilled. This method of analysis should prove satisfactory at equilibrium for large quantities and where speed is not essential.

The method found most suitable consisted of determining concentration ratios between monomeric and polymeric lactic acid in aqueous solution as a function of time and titratable acidity. This assumes that the polylactic acids that are present hydrolyze in a definite manner, regardless of the means by which the quantity of monomeric lactic acid is reduced.

A check between the yield of methyl lactate at equilibrium as determined by the proposed method and by distillation should indicate that this method may be applied to mixtures at any time, regardless of whether or not equilibrium has been attained. Accordingly, a series of experiments was performed on mixtures at equilibrium.

For the sake of simplicity, the results of the distillation of the reaction mixture reported in Run B below are used. To 4.5 grams of this mixture 10 ml. of 0.1 *N* sodium hydroxide solution were added to neutralize the free lactic acid partially and to provide water for the azeotropic distillation of the methyl lactate. This mixture was then distilled; saponification of the distillate indicated the presence of 37.6% methyl lactate in the equilibrium mixture as compared with 37.91% by the proposed titration method. For any experimental esterification at equilibrium a distillation gave at least 97.5% of the methyl lactate value determined by titration.

EXPERIMENTAL

Methyl lactate, furnished by National Dairy Research Laboratories, was analyzed by saponification with standard sodium hydroxide, by boiling point determination, and by refractive index and density measurement. The purity was 100.0%. Reagent grade 85% lactic acid was assayed by titration and saponification with standard base. Average of five assays was 72.55% titratable acidity and 85.67% total acidity (both reported as lactic acid). Absolute methanol which had a purity of 100.0%, as determined by boiling point and density measurements, was employed.

To study the hydrolysis of polylactic acid, approximately 50-ml. samples of 85% lactic acid were weighed out and chilled in an ice bath. To each sample standardized saturated sodium hydroxide solution was added from a calibrated buret while the sample was agitated vigorously in the ice bath. The amounts of sodium hydroxide added were calculated to divide the region of titratable acidity of the lactic acid into equal parts. For example, for the hydrolysis run at 100° C., the region of titratable lactic acid acidity involved in the esterification experiment was divided into seven approximately equal divisions, by adding to seven 50-ml. samples of the 85% lactic acid 6.52, 9.76, 13.10, 16.28, 19.60, 22.85, and 26.00 ml. of 18.00 *N* sodium hydroxide solution, respectively. After the sodium hydroxide had been added, the mixture was agitated for 1 minute and approximately 8-ml. samples were pipetted into ampoules. These ampoules were sealed and placed in a constant temperature bath.

Samples were run at temperatures of 25°, 40°, 60°, 80°, and

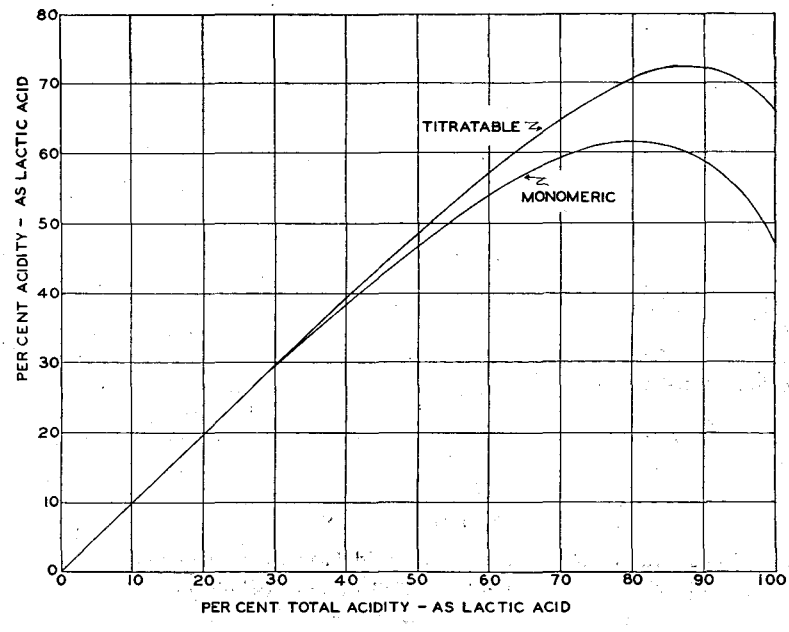

Figure 2. Relation between Titratable, Monomeric, and Total Acidity of Lactic Acid Solutions

Table I. Equilibrium Values of Titratable and Monomeric Lactic Acid in Aqueous Lactic Acid Solutions

% Total Acidity, as Lactic Acid	% Titratable Acidity, as Lactic Acid[a]	% Monomeric Acidity, as Lactic Acid (4)
10	10.0	10.0
30	29.5	29.5
50	48.67	46.67
60	57.0	53.87
70	64.67	59.0
80	70.67	61.45
85	72.33	61.0
90	72.33	58.67
95	70.5	54.67
100	66.0	47.0

[a] Average of literature values and author's investigations. Results of all investigations in rather close agreement.

100° C. At definite intervals of time an ampoule was removed, chilled, and broken open. A small aliquot was removed and weighed. This was then titrated with standard base, using phenolphthalein indicator, followed by the addition of more than sufficient base to neutralize the total acidity. After boiling 5 minutes, an excess of standard acid sufficient to render the solution colorless was added and the sample was back-titrated with standard base. From the data obtained, values of the ratio, R, between titratable acid at any time, P, and the original total acid, I—i.e., before addition of the 18.00 N base—were plotted against time (Figure 1).

The equilibrium values between lactic acid and its polymers are reported in the literature (*1*, *4*, *8*). In order to correlate the data from the several sources with the present work, 85% lactic acid was diluted with different amounts of distilled water and allowed to stand at room temperature until equilibrium was established between titratable and total acidity as determined by titration and saponification. Because in previous determinations of this equilibrium some variation existed among the values determined by the various workers, it was considered worth while to present a curve based on the average of all the determinations including this current work. The data determined in this work are given in Table I and Figure 2, which show monomeric lactic acid present in different strengths of solution as presented by Filachione and Fisher (*4*).

These data may be used in the following manner:

Run A. In following the course of the esterification of lactic acid and methanol, ampoules containing the reaction mixture were removed from a constant temperature bath at intervals, chilled, and opened. Aliquots of approximately 2 ml. were pipetted out, weighed, and titrated to the neutral red end point with standard base. Sufficient sodium hydroxide to provide an excess over that needed to neutralize the total acid present was added and the mixture was boiled for 5 minutes in a flask fitted with an air condenser. Phenolphthalein was added, followed by an excess of standard hydrochloric acid over that needed to neutralize the solution, and the mixture was then back-titrated with standard base. This analysis was also performed on a sample of the original mixture.

The change in the titratable acidity as the reaction proceeds is shown in Figure 3 for a typical reaction. The mole ratio of methanol to lactic acid for this reaction was 3.88. The temperature of reaction was 100° C. and no catalyst was present.

The mechanism by which the esterification takes place is assumed to consist of the following simultaneously occurring steps.

1. The methyl alcohol and monomeric lactic acid begin to combine to form methyl lactate.

$$CH_3CHOH.COOH + CH_3OH \longrightarrow CH_3.CHOH.COOCH_3 + H_2O \quad (1)$$

2. This shifts the equilibrium existing between monomeric and polymeric lactic acid by removing the monomer and diluting the reaction mixture with the water formed.

3. The polymeric lactic acid begins to hydrolyze to monomer, probably in several steps, in order to re-establish equilibrium between the monomeric and polymeric forms.

$$HO\left[\begin{array}{l} CH_3 \\ | \\ -CH-COO- \end{array}\right]_n H + (n-1)\,H_2O \rightleftharpoons n\,CH_3.CHOH.COOH \quad (2)$$

4. The monomeric lactic acid formed in the preceding steps proceeds with the esterification process as in step 1.

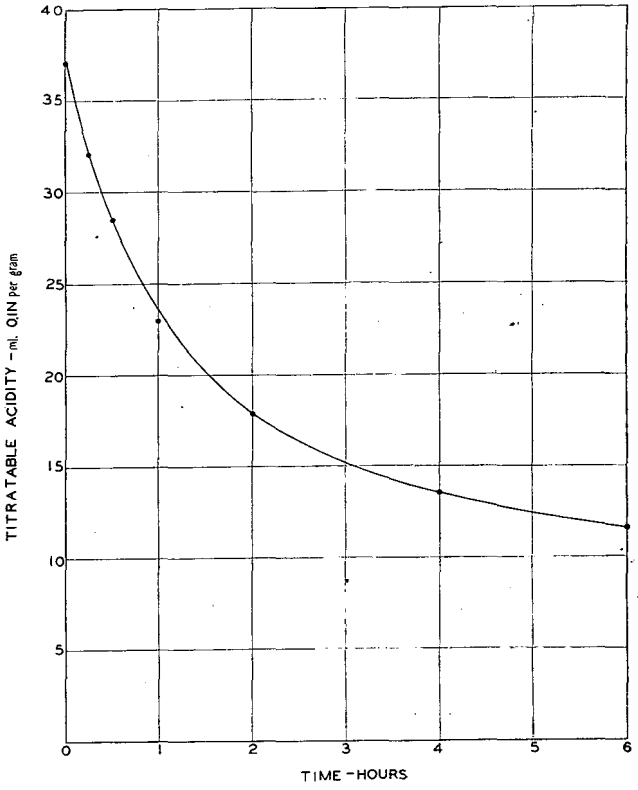

Figure 3. Rate of Change in Titratable Acidity for Typical Reaction between Methanol and 85% Lactic Acid at 100° C. (Run A)

If it were not for the hydrolysis of polymeric lactic acid (step 3), the decrease in titratable acidity obtained by subtracting the acidity at time θ from the initial acidity would represent the carboxyl groups that have been esterified. However, new carboxyl groups have been produced by this hydrolysis to replace some of those esterified. For each period of time, θ, that the reaction has proceeded a definite ratio exists between the titratable acidity at that time and the original total acidity. Using the hydrolysis curves at the temperature of the experiment (Figure 1), this ratio and time are located on a curve (or as an interpolated point between curves). The curve can then be followed back to zero time and the ratio of titratable to total acidity found at zero time. The ratio at zero time minus the ratio at time θ gives a value which is multiplied by the original total acidity of the reaction mixture to obtain the increase in titratable acidity due to the hydrolysis of polymeric lactic acid (step 3). Sample calculations illustrate the manner in which these calculations are made.

Sample Calculation. To find the concentration of methyl lactate at the end of 0.5 hour in Run A at 100° C., mole ratio of methanol to lactic acid 3.88, no catalyst.

Original titratable acidity = 37.00 ml. of 0.1 N base per gram of solution.

Total acidity = 43.66 ml. of 0.1 N base per gram of solution = 4.366 me. per gram of solution. On Figure 3 read titratable acidity at the end of 0.5 hour at 28.53 ml. of 0.1 N base per gram of solution = 2.853 me. per gram of solution. Disappearance of titratable acidity 37.00 − 28.53 = 8.47 ml. of 0.1 N per gram of solution = 0.847 me. per gram of solution.

Ratio of titratable acidity (0.5 hour) to original total acidity, $P/I = 28.53/43.66 = 0.653$.

Locating this ratio on the hydrolysis chart, Figure 1, at a time of 0.5 hour and following the curves back to zero time, a ratio of 0.621 is obtained at zero time.

Polylactic acids reverting to monomeric acid and forming methyl lactate $(0.653 - 0.621)(43.66) = 1.40$ ml. of 0.1 N base per gram of solution = 0.140 me. per gram of solution.

Total methyl lactate formed = 0.847 + 0.140 = 0.987 me. per gram of solution.

Run B. To obtain the equilibrium composition for the reaction, the equilibrium curve (Figure 2) for aqueous lactic acid and its polymers is used. It is convenient to assume for stoichiometric purposes that the lactic acid used consists only of monomeric lactic acid and water.

Thus, in the sample calculation given below the solution is considered to consist of 85.67% monomeric lactic acid and 14.33% water. This value for water is used for stoichiometric purposes and it saves involved calculations of the amount of water needed to hydrolyze the polymeric lactic acid. Such assumption causes no appreciable error because the amount of polymeric form at equilibrium is small. The initial total acidity minus the titratable acidity at equilibrium is considered to be equivalent to the methyl lactate formed. This is also the amount of water formed in the reaction (Equation 1). The total water at equilibrium is approximately the sum of the water introduced with the lactic acid plus that formed in the reaction.

In order to use Figure 2, the lactic acid concentration must be calculated as though no methanol and methyl lactate were present. Thus the percentage of total lactic acid in this hypothetical solution is the weight of lactic acid times 100 divided by the weights of lactic acid and water. This value is used as the abscissa on Figure 2 and the corresponding percentage of titratable acidity is read from the ordinate scale. The ratio of these values of percentage total acidity to titratable acidity is multiplied by the titratable acidity at equilibrium to obtain an equilibrium value of total lactic acid which is more nearly correct than the value originally assumed.

Now one of the original approximations can be corrected. The initial total acidity minus the total lactic acid just calculated is a more nearly correct value for the methyl lactate or water formed. Using this new value for water formed, the above calculations may be repeated if the change in the ratio of percentage total acidity to titratable acidity is sufficient to warrant another calculation. The methanol remaining in the equilibrium mixture is equal to the methanol in the original mixture minus the methyl lactate formed. This now gives values for all components in the equilibrium mixture.

Sample Calculation. To find equilibrium composition in Run A at 100° C., mole ratio of methanol to lactic acid 3.88, no catalyst.

Total acidity at the start = 43.66 ml. of 0.1 N base per gram of solution = 4.366 me. per gram solution.

Water at start of reaction $\frac{(4.366)\ (14.33/18)}{(85.67/90)} =$ 3.659 me. per gram of solution, where 85.67 is the per cent total lactic acid in the lactic acid used in the experiments. Molecular weights of lactic acid and water are 90 and 18, respectively.

Titratable acidity at equilibrium 7.09 ml. of 0.1 N base per gram of solution = 0.709 me.

Assuming first that no polymer is present, 0.709 represents the total milliequivalent lactic acid at equilibrium. Methyl lactate formed is 4.366 − 0.709 = 3.657 me. per gram of solution. This must also equal the water formed.

Total water at equilibrium = 3.659 + 3.657 = 7.316 me. per gram of solution.

Strength of acid solution in water at equilibrium

$$\frac{(0.709 \times 90)\ (100)}{(7.316 \times 18) + (0.709 \times 90)} = 32.60\%.$$

From Figure 2 the titratable acidity in equilibrium with this strength acid is 32.1%. Therefore some polymer exists at equilibrium. Total acidity at equilibrium 0.709 (32.6/32.1) = 0.720 me. per gram of solution.

Methyl lactate formed = 4.366 − 0.720 = 3.646 me. per gram of solution.

Water formed = 3.646 me. per gram of solution.

Total water at equilibrium = 3.659 + 3.646 = 7.305 me. per gram of solution.

The strength of lactic acid at equilibrium is now calculated to be 33%. Because 33/32.5 is not sufficiently different from 32.6/32.1, no further refinement will be made.

Methanol at the start (4.366) (3.88) = 16.92 me. per gram of solution.

Methanol used 3.646 me. per gram of solution.

Methanol at equilibrium 16.92 − 3.646 = 13.274 me. per gram of solution.

Equilibrium Composition

	Me./G. Solution	Weight %
Lactic acid	0.720	6.48
Methyl lactate	3.646	37.91
Methanol	13.274	42.47
Water	7.305	13.14
		100.00

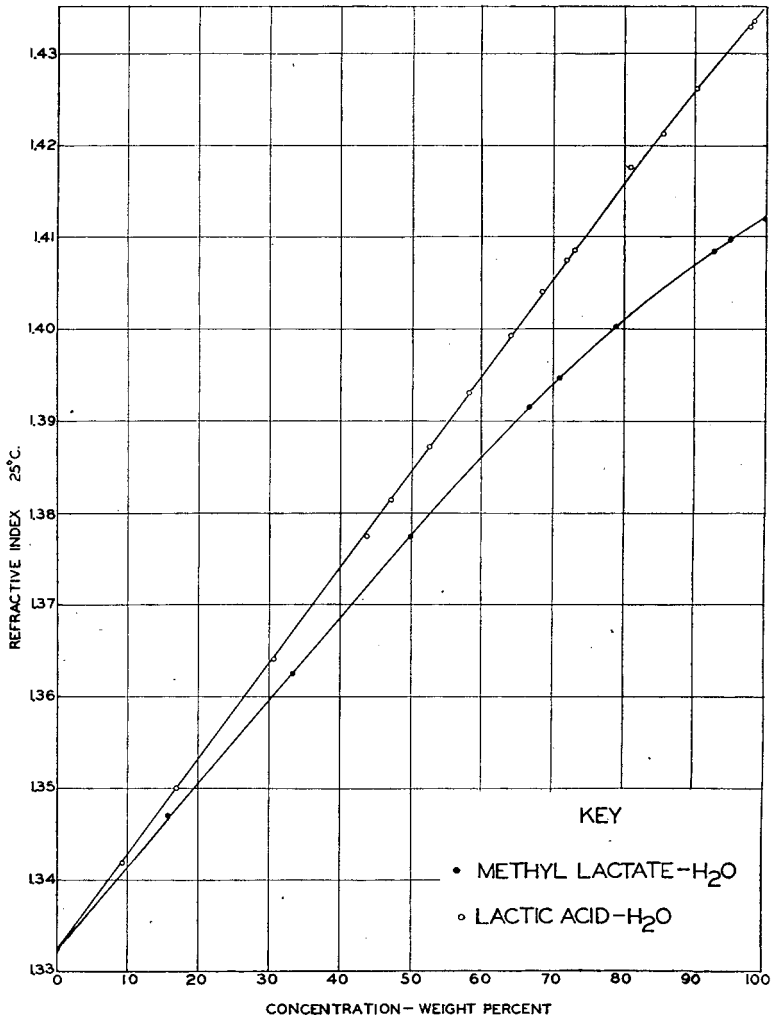

Figure 4. Refractive Indexes of Lactic Acid–Water and Methyl Lactate–Water Mixtures at 25° C.

Table II. Refractive Indexes of Methyl Lactate–Water and Lactic Acid–Water Mixtures

Methyl Lactate, Wt. %	Refractive Index at 25° C.
0.00	1.33260
15.75	1.34710
33.30	1.36258
50.00	1.37748
67.00	1.39156
71.00	1.39467
79.00	1.40043
92.75	1.40840
95.50	1.40981
100.00	1.41205
Lactic Acid	
0.00	1.33260
9.18	1.34182
16.95	1.35014
30.60	1.36416
43.76	1.37753
47.21	1.38153
52.56	1.38727
58.10	1.39324
64.07	1.39939
68.44	1.40401
72.00	1.40745
72.93	1.40863
76.34	1.41217
78.42	1.41417
81.00	1.41772
85.67	1.42132
90.35	1.42639
97.90	1.43293
98.27	1.43367

Refractive indexes of lactic acid–water mixtures and methyl lactate–water mixtures were obtained using a Bausch & Lomb precision refractometer. These data are presented in Table II and Figure 4. Although no difficulty was experienced in analyzing methyl lactate–water mixtures, the lactic acid–water system values were difficult to reproduce because of the presence of a series of converging parallel lines rather than sharp demarcation between light and dark areas.

DISCUSSION

The procedure given here is based on certain assumptions for which no proof is possible. In view of the fact that at equilibrium the results of this method can be checked by distillation, it seems logical to assume that the results are accurate at any stage of the reaction. The procedure was developed after a careful investigation of the factors influencing its accuracy. To establish that no saponification of polylactic acids occurs during titration, a comparison was made of results obtained by use of both aqueous and alcoholic base with those reported in the literature for various strengths of the acid in the range 0 to 85% lactic acid. In this range the experimental results substantially checked those of the literature.

Because methyl lactate hydrolyzes readily, it was necessary to determine how the titration would affect this ester. It was found that if the dilute base was added in a slow steady stream with excellent agitation no saponification of the ester occurred until all the free acid had been neutralized. Neutral red was chosen as indicator because its color change at pH 7 minimized the danger of hydrolysis. The technique of titration increased in importance as equilibrium in the esterification mixture was approached.

The determination of the breakdown of the polymeric acid is a more complex problem. It was decided to assume that the mechanism is that previously discussed. To evaluate this hydrolysis it was decided to use a substance that would remove the monomeric acid and at the same time add water. Lactic acid to which calcium lactate had been added was heated to study the possibility of a "salt effect." After determining that the salt effect did not influence the hydrolysis of the polylactic acids, the use of basic materials was studied. Solid bases proved too insoluble in the mixture and their distribution and heat output were too difficult to control. The use of alcoholic sodium hydroxide resulted in some esterification between the alcohol and the acid at high temperatures. Finally, saturated aqueous sodium hydroxide solutions were utilized with satisfactory results.

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Determination of Sulfur Trioxide in Chlorosulfonic Acid

Thermometric Methods

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BECAUSE the concentration of free sulfur trioxide in chlorosulfonic acid is of importance in some of the uses of this acid, it became necessary to develop a more precise method for its determination than that generally used, which involves a total acid value and a chloride value (*2, 3, 5, 6*). This method is not sufficiently precise because it is necessary to determine the sulfur trioxide indirectly, and the factors involved are such that an error of 0.1% each in the acid value and the chloride value causes an error of 1.0% sulfur trioxide.

Considerable heat is evolved when hydrogen chloride reacts with sulfur trioxide. According to Ogier (*4*), the heat of formation of chlorosulfonic acid from sulfur trioxide (solid) and hydrogen chloride (gaseous) is 14.4 kg.-cal. and its specific heat is 0.282 calorie per gram. The method finally developed, involving measurement of the temperature rise when gaseous hydrogen chloride is passed into chlorosulfonic acid containing sulfur trioxide, is not only sufficiently precise for the determination of low concentrations of sulfur trioxide, but gives more precise values than the old method for samples containing high concentrations of sulfur trioxide.

METHOD OF ANALYSIS

Apparatus. All parts of the apparatus which come into contact with the sample must be thoroughly dry. In Figure 1 are shown a cylinder or generator of dry hydrogen chloride; a gasometer for measuring the hydrogen chloride consisting of a

3-liter, round-bottomed flask, G, connected to a 2-liter Mariotte bottle, H, with kerosene as the retaining liquid; and a vessel for carrying out the reaction, which consists of an 8 × 1.5 inch test tube, I, equipped with a four-hole stopper containing a sintered-glass bubbling tube, E, a thermometer calibrated in 0.1°, A, a gas outlet equipped with indicating-grade Drierite, F_2, and a glass tube for introducing the sample, B. This tube is equipped with a rubber sleeve which fits over the tip of the buret or pipet used to introduce the sample. At all other times, the tube is closed off from the air by the screw clamp, J_1. The test tube is kept in a wide-mouthed bottle, C, about 10 inches high and 5 inches in diameter with a mouth 3 inches in diameter. This bottle is packed with glass wool to insulate the test tube. (The insulated bottle and test tube may conveniently be replaced by a small Dewar flask of such dimensions that the thermometer bulb is completely covered by the sample.)

Procedure for Samples Containing Less Than 3% Sulfur Trioxide. The apparatus assembly, reagents, and sample should be at room temperature. With the reaction vessel disconnected from the rest of the apparatus, dry hydrogen chloride gas is swept through the apparatus to displace the air, and a measured amount (about 2 liters) of gas is stored in the gasometer by adjusting the appropriate clamps and measuring the increase in the volume of liquid in the Mariotte bottle.

The test tube and stopper assembly, previously dried by heating and aeration with a stream of dry air, is placed in the bottle of glass wool, and the bubbler tube is attached to the rubber connection on the drying tube with clamp J_3 closed. Through the opening provided for the purpose, 100 ml. of the sample are introduced from a buret or pipet. Immediately after addition of the sample, the rubber tube, J_1, is clamped shut.

If a pipet is used to transfer the sample, precautions should be taken to prevent contamination by moisture during the transfer of the sample. To do this, the pipet is fitted with a two-hole stopper which fits the opening of the sample bottle. A drying tube containing Drierite is placed in the other hole. The pipet itself is protected with a tube containing Drierite. To control the flow of the sample, a small glass bead is placed in the short rubber tube connecting the pipet and drying tube. The whole assembly is placed in the sample bottle as soon as the stopper is removed and the pipet filled by suction. If the sample is delivered from a buret, it must be protected by drying tubes.

After the temperature of the solution in the test tube has become constant, it is noted as t_1. The hydrogen chloride gas is then swept through the sample after opening clamp J_3. The kerosene head is about 18 inches. Under these conditions the flow of hydrogen chloride is about 300 ml. per minute. The temperature begins to rise immediately, and after about 3 minutes reaches a maximum. The maximum temperature is noted and from this is subtracted the original temperature, t_1, to give the rise in temperature, Δt. The sulfur trioxide content is then calculated from a standard equation:

$$\% \, SO_3 \text{ (by weight)} = 0.291 \, \Delta t \qquad (1)$$

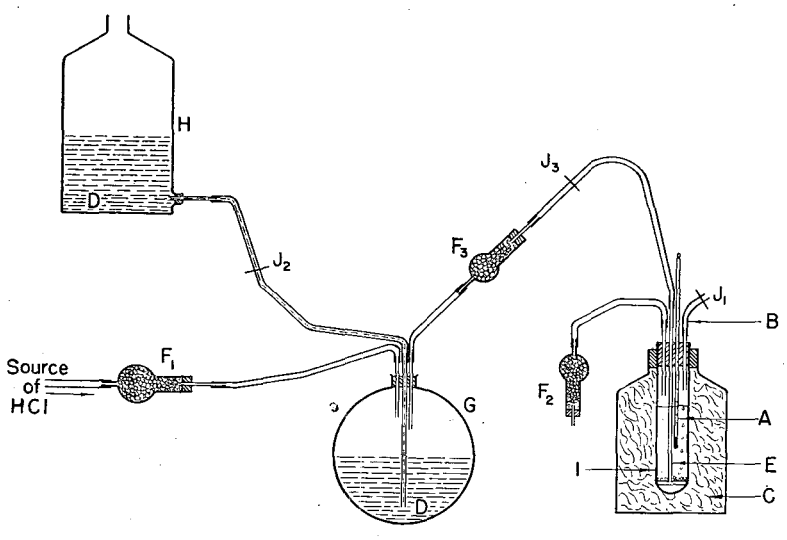

Figure 1. Apparatus Used

A.	Thermometer	F_1, F_2, F_3.	Drierite tubes
B.	$ClHSO_3$ inlet	*G.*	3-liter gasometer
C.	Bottle containing glass wool	*H.*	Mariotte bottle
D.	Kerosene	*I.*	8-inch test tube
E.	Bubbler	J_1, J_2, J_3.	Screw clamps

The parameter 0.291 is a constant for the particular weight of sample taken and apparatus used. It was derived by analyzing known mixtures of sulfur trioxide and chlorosulfonic acid. It has since been found for most vessels used that this constant will be applicable with an error of only a few per cent at the most, but for the highest accuracy any particular apparatus should be calibrated before use.

Procedure for Samples Containing More Than 3% Sulfur Trioxide. It is necessary to dilute samples containing more than about 3% sulfur trioxide with a stock solution of chlorosulfonic acid of known low sulfur trioxide content, because such samples require more hydrogen chloride than is used in this procedure. For the dilution it was found more convenient to measure the sample by weight than by volume because there is an appreciable variation of specific gravity with sulfur trioxide content. The diluent could be measured by volume.

The volume of diluent needed, 90.0 or 95.0 ml., is added to the test tube to be used for the analysis through the opening in the rubber stopper provided for that purpose. The opening is then clamped shut. A Lunge pipet, previously calibrated to deliver 5.0 or 10.0 ml., thoroughly dry, and with no lubricant on the stopcocks, is filled to the desired mark from the sample bottle by suction. The tip of the pipet is wiped with a dry cloth, the protective bottom part is put in place, and the pipet and contents are weighed to ±5 mg. (W_1). The pipet is capped with a drying tube to dry the entering air. Two drops of the sample are drained into the protective cap of the Lunge pipet to remove any acid which may have come into contact with air, and the protective bottom part is removed and stoppered immediately with a rubber stopper. The Lunge pipet is placed in the opening of the stopper for admitting the sample, the entire contents of the pipet are run into the test tube, the cap is replaced, and the Lunge pipet is weighed again (W_2).

$$W_1 - W_2 = W = \text{weight of sample taken}$$

The analysis is then made as described for samples containing less than 3% of sulfur trioxide.

M = % sulfur trioxide in the diluted mixture calculated from the temperature rise = $0.291 \, \Delta t$

P = % sulfur trioxide in the diluent as determined by averaging several values obtained from analyses of the diluent

Then for a tenfold dilution:

$$\% \text{ sulfur trioxide} = \frac{(156.6 + W)\,M - 156.6P}{W}$$

For a twenty-fold dilution:

$$\% \text{ sulfur trioxide} = \frac{(165.3 + W)\,M - 165.3P}{W}$$

The values 156.6 and 165.3 are the weights, respectively, of 90.0 and 95.0 ml. of diluent.

PREPARATION OF STANDARD CURVE

Because no other method was available for accurately determining low concentrations of sulfur trioxide in chlorosulfonic acid, it was necessary to establish the equation relating temperature rise and sulfur trioxide concentration by diluting a known concentrated solution of the sulfur trioxide in chlorosulfonic acid with a chlorosulfonic acid for which the temperature rise had been previously determined. The concentrated solution had to be analyzed by the only available method (*2, 3, 5, 6*), which has poor precision. However, by averaging the values from seven determinations of total acidity and seven determinations of chloride, the relative error in the sulfur trioxide determination was reduced to the same order of magnitude as would apply to

A method proposed for determining sulfur trioxide in chlorosulfonic acid involves measuring the temperature rise obtained by reaction with hydrogen chloride. The method has a precision of ±0.024% sulfur trioxide, expressed as the standard deviation of a single value from the mean, and is considerably more precise and more rapid than the usual method involving the determination of total acidity and chlorides. Sulfuric acid, at least up to 5%, does not interfere. There is no evidence of any systematic error. There is some evidence for the existence of the equilibrium $ClSO_3H \rightleftharpoons HCl + SO_3$ in chlorosulfonic acid at and below room temperature.

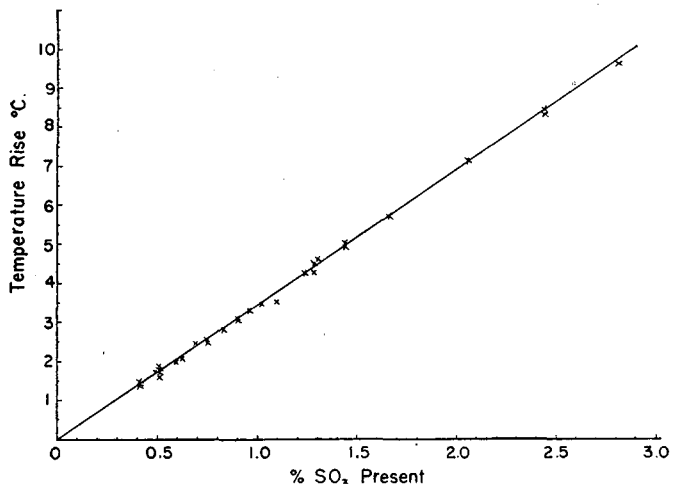

Figure 2. Calibration Curve

a single value obtained by the proposed method at a sulfur trioxide level of about 2%. The average value obtained by the titration method for the sulfur trioxide content of the concentrated solution was 31.2 ± 0.3% (absolute standard error of the mean) or approximately ±1% of the total sulfur trioxide content. Various volumetric mixtures of this solution and the chlorosulfonic acid of known temperature rise were analyzed by the thermometric method. A plot was made of the temperature rise and the per cent sulfur trioxide added. The best straight line was drawn through these points. The equation for this line was

$$\% SO_3 \text{ added as concentrate} = 0.291\Delta t - 0.41$$

If it is assumed that there is no heat of solution of hydrogen chloride in chlorosulfonic acid, then the 0.41 must be the concentration of sulfur trioxide in the stock solution of chlorosulfonic acid used as diluent (which gave a temperature rise of 1.43° C.). A plot of these data is shown in Figure 2. No information has been found concerning the heat of solution of hydrogen chloride in chlorosulfonic acid, but samples of chlorosulfonic acid have been analyzed which gave a temperature rise corresponding to only a few hundredths of a per cent of sulfur trioxide, so that for practical purposes the heat of solution may be considered to be negligible.

EFFECT OF SULFURIC ACID

Because sulfuric acid would be formed in chlorosulfonic acid if it had been exposed to moisture, a few additions of 99.9% sulfuric acid were made to chlorosulfonic acid, and the sulfur trioxide was determined. From the results given in Table I it is evident that sulfuric acid, at least up to 5% by volume, has no effect on the values found.

PRECISION AND ACCURACY

Titration Method. The individual values for total acidity and hydrochloric acid obtained in the analysis of the stock solution of sulfur trioxide in chlorosulfonic acid are given in Table II. By using the formulas given by Scott (*5*), the sulfur trioxide value of 31.2% may be found as follows:

$$HCl \text{ as } \% SO_3 = 21.13 \times 1.0978 = 23.20$$

$$\% \text{ total } SO_3 = 101.83 - 23.20 = 78.63$$

$$\% \text{ combined water} = 100.00 - (78.63 + 21.13) = 0.24$$

$$\% H_2SO_4 = 0.24 \times 5.44 = 1.30$$

$$\% \text{ chlorosulfonic acid} = 21.13 \times 3.1956 = 67.52$$

$$\% \text{ uncombined } SO_3 = 100.00 - (67.52 - 1.30) = 31.18$$

By an application of the usual statistical methods, the uncertainty (as the standard deviation of a single value from the mean) in the sulfur trioxide value may be calculated as follows from the standard deviation of the components shown below which enter into the final calculation for sulfur trioxide:

$$HCl \text{ as } \% SO_3. \quad 1.0978 \times \pm 0.078 = \pm 0.086$$

Table I. Effect of Sulfuric Acid

Chlorosulfonic Acid	Sulfuric Acid Added	Sulfur Trioxide	
		Present	Found
Ml.	*Ml.*	*Gram*	*Gram*
100	0	...	0.73
98	2	0.72	0.72
97	3	0.71	0.75
95	5	0.69	0.69

Table II. Analysis of Standard Solution of Sulfur Trioxide in Chlorosulfonic Acid

Total Acidity as % SO_3	Chlorides as % HCl
101.80	21.22
101.90	21.20
101.90	21.13
101.76	21.03
101.84	21.16
101.79	21.02
101.84	21.14
Av. 101.83	21.13
Standard deviation ±0.054	±0.078

Standard deviation = $\sqrt{\frac{\Sigma d^2 a}{n-1}}$, where da = deviation of each single value from average, and n = number of single values.

$$\% \text{ total } SO_3. \quad \pm\sqrt{\overline{0.054^2} + \overline{0.086^2}} = \pm 0.102$$

$$\% \text{ combined water. } \pm\sqrt{\overline{0.102^2} + \overline{0.078^2}} = \pm 0.128$$

$$\% H_2SO_4. \quad 5.44 \times \pm 0.128 = \pm 0.70$$

$$\% \text{ chlorosulfonic acid. } 3.1956 \times 0.078 = \pm 0.25$$

$$\% \text{ uncombined } SO_3. \quad \pm\sqrt{\overline{0.70^2} + \overline{0.25^2}} = \pm 0.74$$

Thus the standard deviation of a single value from the mean would be ±0.74% sulfur trioxide. Inasmuch as the average was determined from seven independent values, the standard error of the mean is

$$\frac{\pm 0.74}{\sqrt{7}} = \pm 0.28\% \text{ sulfur trioxide}$$

Thermometric Method. An indication of the precision of the thermometric method is given by the distribution of the points in Figure 2. The standard deviation of a single value of per cent sulfur trioxide present from that read from the graph, calculated from 31 determinations on 25 samples containing from 0.4 to 2.8% sulfur trioxide, is ±0.024% (absolute) of sulfur trioxide, or about ±1% of the total sulfur trioxide content at the 2% level. The deviations varied from −0.06 to +0.05%. If it is necessary to dilute the sample, the precision of the method will be decreased accordingly, but up to about a twenty-fold dilution it has been found to be at least as good as the method involving the chloride and acid values. If greater precision is required, the results of several determinations can be averaged. A comparison of the values obtained on samples of high sulfur trioxide content is given in Table III. The two methods agree as well as can be expected.

Accuracy. Except for the possible small error which could be caused by some heat of solution of hydrogen chloride in chlorosulfonic acid, there is no reason to believe that the method involves any systematic errors.

Table III. Comparison of Values Obtained by Thermometric and Titration Methods

Sample No.	% Sulfur Trioxide Found: Thermometric method	Titration method[a]
I	28.0, 28.0, 28.7 Av. 28.2	28.5
II	19.9, 20.5, 20.6, 20.5 Av. 20.4	20.6
III	35.8, 35.3, 35.0 Av. 35.4	34.8
IV	21.4, 21.8, 21.8 Av. 21.7	21.8

[a] Calculated from average of two total acidity values and two chloride values on each sample.

EVIDENCE OF EQUILIBRIUM IN CHLOROSULFONIC ACID

In order to determine whether or not hydrogen chloride has any heat of solution in chlorosulfonic acid, an attempt was made to prepare pure chlorosulfonic acid by saturating it with hydrogen chloride to react with any sulfur trioxide which may have been present, and then blowing out the excess hydrogen chloride with a stream of dry air.

In carrying out these experiments, 100 ml. of chlorosulfonic acid were subjected to the conditions of the sulfur trioxide determination. The temperature rise, Δt, was noted. Air, dried in succession with a number of desiccants and finally with phosphorus pentoxide, was then passed through the bubbler. The exit gases were bubbled through standard alkali for definite periods of time and the excess alkali was titrated with standard acid. Curves were obtained by plotting consumption of alkali against time. In each experiment similar curves were obtained, a large amount of acid, probably the hydrogen chloride in the system, being expelled immediately, after which the curve sloped off gradually. Even after several hours of aeration, the curves did not reach zero alkali consumption, although they approached this value. Samples of the exit gases, when dissolved in distilled water, gave positive tests for both chloride and sulfate.

After air had been passed through for several hours, hydrogen chloride was passed in again from the gasometer as in the regular determinations. The values obtained are given in Table IV. Experiment 4 was carried out by blowing air cooled to about −15° to −20° C. through chlorosulfonic acid kept at about this temperature.

As can be seen from Table IV, contrary to expectations, a greater Δt was obtained in each case after blowing air through than before. These results can be explained by assuming that the following equilibrium exists in chlorosulfonic acid:

$$SO_3HCl \rightleftharpoons SO_3 + HCl \qquad (2)$$

Table IV. Effect of Aeration

Experiment	Δt, Before Aeration	Δt, After Aeration
1	1.79	2.17
2	1.70	2.17
3	2.12	3.25
4	1.55	1.62

The hydrogen chloride, being the most volatile of these substances, is preferentially removed, and thus the sulfur trioxide concentration is built up to a point after which little more gas is lost. The reason the curves of alkali consumption against time did not reach zero alkali consumption is that chlorosulfonic acid has an appreciable vapor pressure (8.65 mm. at 20° C. and 12.23 mm. at 30° C., *1*). It is known that chlorosulfonic acid dissociates to some extent at a high temperature (*7*, *8*), but there seems to be some disagreement over the products. Williamson (*8*) stated that the acid decomposed to some extent into hydrogen chloride and sulfur trioxide at the boiling point, while at a high temperature (216°) Williams (*7*) gave as the product of the dissociation sulfur trioxide, sulfur dioxide, water, and chlorine. These latter products are obviously unlikely at room temperature.

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Determination of Chloride in Water

Improved Colorimetric and Titrimetric Methods

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This paper describes improved colorimetric and titrimetric methods for determination of chloride ion in water. In both methods, dilute mercuric nitrate solution is added to acidified water in the presence of diphenylcarbazone indicator. At the mercury-chloride equivalence point, a blue-violet, mercury-diphenylcarbazone complex forms, which is proportional in intensity to the excess of mercury ion present. The colorimetric test is restricted to clear uncolored waters without significant heavy metal contamination. The titrimetric procedure is independent of practically all common interference.

A SIMPLE, reliable method for quantitative determination of chloride ion in water has been sought for many years. The need for such a test is particularly acute in the Navy, where practically all fresh water needs must be supplied by evaporation of sea water, at the risk of chloride contamination by leakage or carryover, and where many tests must be conducted by personnel without laboratory experience. Ideally, a chloride test for naval use should involve a minimum of manipulations and provide a sharp, well defined end-point signal. It should be equally applicable to the vanishingly low chloride concentrations of sea water distillate and to the relatively high concentrations of chloride in contaminated boiler water. The traditional silver nitrate–potassium chromate titration procedure (Mohr) now in general use is unsatisfactory, because of its subtile end-point color change and its insensitivity to low concentrations of chloride. Only the mercuric nitrate–diphenylcarbazide and mercuric nitrate–diphenylcarbazone methods described by Dubsky and Trtilek (*1*, *2*) showed promise of meeting these exacting requirements. The latter proved to be superior from the standpoint of stability of indicator and discernibility of end point. Accordingly, this investigation was confined to development of improved mercuric nitrate–diphenylcarbazone methods.

Table I. Sensitivity and Reproducibility of Mercury-Diphenylcarbazone Complex

Hg^{++} Concentration, Me./Ml. × 10^5	% Transmission, 520 Mu Coleman Spectrophotometer					
	Run 1	Run 2	Run 3	Run 4	Run 5	Av.
16.9	6.7	7.2	6.9	6.2	7.0	6.8
11.7	9.9	12.3	9.3	9.9	10.0	10.3
6.4	22.9	23.8	22.0	20.0	23.9	22.5
1.3	63.8	63.0	63.0	70.0	67.0	65.2

DEVELOPMENT OF COLORIMETRIC METHOD

Diphenylcarbazone is an orange crystal which dissolves in ethyl alcohol to form a clear red solution. This solution reacts with mercuric ion to form an intense blue-violet complex. The complex has a single absorption maximum at 520 millimicrons and is color-stable for periods up to 30 minutes. Table I shows the order of its reproducibility and sensitivity.

In acidic chloride solutions, the formation of weakly ionized mercuric chloride prevents development of the mercury-diphenylcarbazone complex until the mercury-chloride equivalence point is reached. It was assumed that chloride ion might be determined by adding acid, mercuric ion, and diphenylcarbazone to chloride solution and measuring the excess of mercuric ion in terms of color intensity. Tests confirmed the general soundness of this hypothesis. However, the rapid increase in color intensity with increase in the excess of mercuric ion made it difficult to

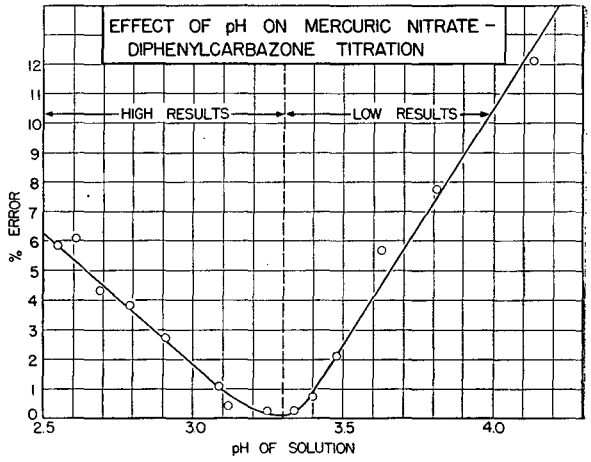

Figure 1

cover a wide range of chloride concentrations with a given increment of mercuric ion. This deficiency was overcome by using multiple increments of the mercuric nitrate reagent (1 ml., 2 ml., etc.), so that a single set of color standards sufficed for several orders of chloride concentrations. A slide comparator kit including nine color standards in permanent form was prepared for this laboratory by W. A. Taylor & Company, Baltimore, Md., and was used successfully in routine chloride analyses. This colorimetric method is applicable only to clear waters which contain neither actual nor potential color interference. Most heavy metal ions cause color interference. It differs from most colorimetric methods in that color intensity varies inversely with the concentration of the ion being measured.

DEVELOPMENT OF TITRIMETRIC METHOD

The mercuric nitrate–diphenylcarbazone chloride titration proposed by Dubsky and Trtilek (*1*, *2*) suffers from the deficiencies of creeping end point and significant variation of accuracy with variation in pH and concentration of diphenylcarbazone indicator. Both high pH and high concentration of indicator yield low chloride values. The problem of creeping end point was overcome by masking the premature blue with a tolerable background color. All background colors in the range from green to orange improved the sharpness of end point, but best results were obtained with the greenish yellow, acid color of bromophenol blue indicator. With this background color end points could be reproduced within 0.1 ml. of 0.025 *N* mercuric nitrate solution.

The optimum pH was determined by titrating acidified solu-

tions of potassium chloride with 0.025 N mercuric nitrate, using diphenylcarbazone indicator in the presence of bromophenol blue. Figure 1 shows that maximum accuracy was obtained in the pH range 3.0 to 3.5. Conveniently, bromophenol blue indicator covers the same pH range (3.0 to 3.6) and makes the first detectable change from its alkaline blue to acid yellow at approximately pH 3.6. It therefore can serve the dual purpose of masking premature color and adjusting pH. A relatively wide range of indicator concentrations proved to be tolerable at the optimum pH of 3.3. Best results were obtained with 5 to 10 drops each of 0.5% diphenylcarbazone and 0.05% bromophenol blue, both by weight in 95% ethyl alcohol. A mixed alcoholic indicator containing these concentrations of the chemicals yielded the same results. The stability and performance of this mixed indicator have not been affected by 4 months of storage in a clear bottle under normal laboratory light.

Roberts (*3*) used bromophenol blue in the determination of chloride with mercuric nitrate and diphenylcarbazide. He recommended that the samples first be alkalized to the blue color of bromophenol blue and then adjusted to the pH range 1.5 to 2.0 with a relatively large addition of acid. He made no mention of the beneficial effect of the yellow, acid color of bromophenol blue, but stated that this color did not interfere with the titration.

APPARATUS

Both the colorimetric and the titrimetric chloride tests can be conducted with the glassware normally available in an analytical laboratory. The colorimetric test can be applied more conveniently with a colorimeter or a spectrophotometer. It is expected that slide-comparator equipment will be marketed for simplified application of this test in the field.

REAGENTS

Potassium chloride stock solution, 1000 p.p.m. of chloride ion. Prepared by dissolving 2.103 grams of C.P. special potassium chloride in 500 ml. of reagent grade water and diluting to 1 liter.

Potassium chloride standard solutions, 2, 4, 6, and 8 p.p.m. of chloride ion. Prepared by accurate dilution of potassium chloride stock solution with reagent grade water.

Nitric acid, approximately 0.05 N. Prepared by diluting 3.2 ml. of C.P. nitric acid (specific gravity 1.42) to 1 liter with reagent grade water.

Sodium hydroxide solution, approximately 0.05 N. Prepared by dissolving 1 gram of C.P. sodium hydroxide in reagent grade water and diluting to 1 liter therewith.

Diphenylcarbazone indicator, 1.0% by weight. Prepared by dissolving 1 gram of C.P. crystalline diphenylcarbazone in 75 ml. of 95% pure ethyl alcohol and diluting to 100 ml. therewith. Store in a brown bottle for maximum stability. (Pure methanol can be used if 95% ethyl alcohol is not available.)

Diphenylcarbazone–bromophenol blue mixed indicator. Prepared by dissolving 0.5 gram of C.P. crystalline diphenylcarbazone and 0.05 gram of C.P., crystalline bromophenol blue in 75 ml. of 95% pure ethyl alcohol and diluting to 100 ml. therewith. It is stored in a brown bottle for maximum stability. (Application has been made for letters patent covering diphenylcarbazone-bromophenol blue mixed indicator.)

Mercuric nitrate solution, approximately 0.025 N. Prepared by dissolving 4.1710 grams of C.P. mercuric nitrate, $HgNO_3 \cdot {}^1/_2\ H_2O$, in reagent grade water and diluting to 1 liter therewith. It is accurately standardized against the potassium chloride stock solution by titration in the presence of diphenylcarbazone–bromophenol blue indicator at pH 3.2 to 3.4. The pH is adjusted with 0.05 N nitric acid. Standard mercuric nitrate solution can be prepared directly from mercuric oxide according to Roberts (*3*).

Mercuric nitrate solution, 0.0141 N, is prepared from the above standardized mercuric nitrate solution by accurate dilution with reagent grade water. Each milliliter of this solution is equivalent to 10 p.p.m. of chloride ion.

PROCEDURE

Colorimetric Determination of Chloride. Pour 50-ml. portions of the four standard potassium chloride solutions and the water to be tested into separate beakers or Erlenmeyer flasks. Add 5 drops of 1% diphenylcarbazone indicator to each and then add 0.025 N sodium hydroxide dropwise until the solutions become orange in color. This addition of sodium hydroxide can be omitted from alkaline waters which turn orange immediately on addition of the indicator. To each orange solution add 0.05 N nitric acid dropwise until the color changes to yellow and add 1-ml. excess. Finally add 1 ml. of 0.0141 N mercuric nitrate to each yellow solution and stir or shake to develop the blue-violet, mercury-diphenylcarbazone complex. If the water sample fails to develop the color complex with 1 ml. of mercuric nitrate solution, it contains more than 8 p.p.m. of chloride ion. In this case, continue to add 0.0141 N mercuric nitrate in 0.5-ml. increments, with shaking, until the first persistence of blue-violet color, and record the quantity of mercuric nitrate reagent required.

Transfer portions of the blue water sample and chloride standards to 5-ml. Nessler tubes and compare the color of the water with those of the standards by diametrical comparison, using a daylight lamp or a good source of north daylight. The former is preferable. When a color match has been obtained, determine the chloride content of the water by the following equation:

$$Cl^-, \text{p.p.m.} = C + 10V - 10$$

where C = p.p.m. of chloride in the matching standard, and V = ml. of mercuric nitrate consumed.

If the chloride content of the water exceeds 30 p.p.m., reduce it below that concentration by measured dilution of the sample with reagent grade water. Perform the determination on the dilute solution and calculate the chloride content by the following equation:

$$Cl^-, \text{p.p.m.} = \frac{50C + 500V - 500}{S}$$

where S = ml. of sample water in the 50-ml. portion.

Titrimetric Determination of Chloride. Pour into a porcelain casserole 100 ml. or less of sample water containing not more than 20 mg. of chloride ion, and dilute to a final volume of approximately 100 ml. Add 5 drops of diphenylcarbazone–bromophenol blue mixed indicator and stir the sample. If a blue-violet or red color develops, add 0.05 N nitric acid dropwise until the color changes to yellow and then add 1 ml. excess of the nitric acid. If a yellow or orange color forms immediately on the addition of the indicator, develop the blue-violet color by adding 0.025 N sodium hydroxide solution dropwise and then proceed with the acidification. To the yellow, acidified solution, add 0.025 N mercuric nitrate solution dropwise from a 10-ml. or 25-ml. buret (0.05-ml. or 0.1-ml. divisions) until a blue-violet color persists throughout the solution. Read the mercuric nitrate buret and calculate the chloride content by the following equations:

$$Cl^-, \text{mg.} = V \times 35.46\ N$$

Table II. Reliability of Mercuric Nitrate–Diphenylcarbazone Colorimetric Test

Chloride Present, P.P.M.	Chloride Found, P.P.M.				
	Skilled technician	Unskilled Technicians			Laboratory messenger
		A	B	C	
2	2	2	2	2	2
4	4	4	4	4	4
6	6	6	6	..	6
8	8	8	8	8	8
10	10	10	8	10	..
12	..	12	12	13	12
14	14	14	14	14	14
16	16	15	16	15	16
18	18	..	..	17	18

Table III. Reliability of Mercuric Nitrate–Diphenylcarbazone Titrimetric Test

Chloride Present, P.P.M.	Chloride Found, P.P.M.			
	Skilled technician	Unskilled technician	Laboratory messenger	Power-plant operator
0	0.3	0.4	0.5	0.6
2	1.95	2.13	2.66	2.31
4	3.99	3.73	4.35	4.44
6	5.95	5.91	6.22	6.84
8	7.90	7.90	8.61	8.44
10	9.87	9.85	10.31	10.90
20	19.71	19.00	20.42	19.09
40	40.14	39.34	41.56	39.8
60	60.03	58.6	60.67	59.4
80	80.38	78.32	80.07	79.7
100	99.46	98.48	103.01	99.27
200	199.62	196.44	201.04	196.5
5000	4988	4977	4981	4973

[a] Titration made directly with 0.25 N mercuric nitrate solution and 50-ml. buret.

$$Cl^-, \text{ p.p.m.} = \frac{V \times 35{,}460 N}{S}$$

$$Cl^-, \text{ e.p.m.} = \frac{V \times 1000 N}{S}$$

where V = milliliters of mercuric nitrate consumed, N = normality of mercuric nitrate, and S = milliliters of sample water.

If titration must be made on solutions which consistently exceed 1000 p.p.m. of chloride, it will be preferable to employ a higher concentration of mercuric nitrate.

EXPERIMENTAL DATA

The precision and accuracy of the colorimetric and titrimetric tests were evaluated by various laboratory personnel, using gravimetrically standardized solutions of C.P. potassium chloride in distilled water. The results are shown in Tables II and III.

On completion of these analyses of pure chloride solutions, additional titrimetric tests were made on solutions contaminated with positive and negative ions apt to be encountered in industrial waters. No effort was made to overcome effects of the ions by modification of the titration. When used individually, 1000 p.p.m. of nitrate, sulfate, phosphate, magnesium, calcium, and aluminum did not significantly affect the titration. The heavy metal ions, zinc, lead, ferrous, nickel, and chromium, affected solution colors, but 100 p.p.m. concentrations of these ions did not reduce accuracy. Cupric ion was tolerable in concentrations up to 50 p.p.m. On the other hand, chromate and ferric ions ruined the titration in concentrations as low as 10 p.p.m. These two ions must be removed or otherwise counteracted before determination of chloride by this method. In the absence of interference, the colorimetric test has an estimated accuracy of ±0.5 p.p.m. The titrimetric test has the same accuracy up to 200 p.p.m. When extended beyond that range by dilution of the sample, the estimated error in parts per million is $50/S$.

CONCLUSIONS

The improved analytical methods described in this paper are applicable to the determination of chloride ion in all types of waters. They require only standard laboratory equipment and can be effectively applied by personnel with very limited laboratory experience. When implemented with slide-comparator equipment, the colorimetric test is ideally suited to field testing. The titrimetric method is independent of practically all common interferences.

ACKNOWLEDGMENT

Acknowledgment is made to Genevieve Ziurys, who conducted most of the development tests concerned with the colorimetric method, and to Mary Q. Garner, who conducted the performance tests connected with the titrimetric method. The service of W. A. Taylor & Company in preparing a slide comparator for use with the colorimetric method, also is acknowledged.

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Water Content of Hydrocarbons

Modified Karl Fischer Method

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A modification of the Karl Fischer method applicable to the determination of water in hydrocarbons or petroleum fractions is described. The method involves extraction of the water from the hydrocarbon by dry ethylene glycol and subsequent titration of the glycol extract with Fischer reagent. Under normal conditions, over 90% of the water present is absorbed in one extraction. The method is elastic in that, when properly used, equally accurate determinations can be made on very dry or relatively very wet stocks.

NUMEROUS analytical methods have been developed for the determination of water in hydrocarbons. These methods may be roughly classified into those that employ physical means for measurement and those that use chemical means. Some physical methods are: the A.S.T.M. distillation procedure (*4*), the cloud effect (*10, 11, 18, 23*), and the electrical conductivity method (*5, 9*). A few of the methods that employ chemical means are: titration of acid resulting from the action of water on acetyl chloride (*15, 20, 25*), measurement of the volume of gas liberated by the action of water on calcium carbide (*19, 26*), methyl magnesium iodide (*14, 24*), or metallic sodium (*8*), and the Karl Fischer method.

With the exception of the A.S.T.M. distillation procedure, the Karl Fischer method is by far the most widely used because of its greater accuracy in the determination of water content over the range 0.0005 to 0.5%. There are, however, certain difficulties encountered in the conventional use of this method on petroleum fractions.

The Fischer reagent is not miscible with hydrocarbons. This property in conjunction with the relatively low solubility of water in hydrocarbons produces an indefinite titration end point.

The visual end point is difficult to detect in colored petroleum fractions.

Because of the low solubility of water in hydrocarbons, the actual quantities of water are very small if samples of convenient size are taken. Some method of concentration of the water from a large volume of sample into a relatively small volume of extract for analysis is required for accurate determinations.

The conventional method cannot be employed on stocks of high vapor pressure, such as butane, propane, isopentane, etc.

Certain compounds, notably ketones, aldehydes, and mercaptans (thiols), interfere with the determination by combining directly with the Fischer reagent.

In view of the above-mentioned difficulties various modifications of the Fischer method have been proposed: elimination of the two-phase condition in the titration by addition of a solvent to the hydrocarbon phase—e.g., chloroform, pyridine, methanol, or certain mixtures of these compounds (*1, 13, 22*), and elimination

of visual end point difficulties by electrometric titration (*2*, *3*, *16*, *27*, *28*).

These modifications do not, however, provide for concentration of the water from a large volume of hydrocarbon into an extract suitable for titration, nor do they permit the use of the Fischer reagent in the determination of water in volatile stocks. Thus, when it became necessary, in the course of some laboratory investigations, to determine the water content of propane and butane more accurately than was possible by the change in color of cobaltous bromide (*12*), the need of a method of extracting the water from these materials by a suitable solvent was indicated. Ethylene glycol was found to be ideal for this purpose. It is relatively insoluble in hydrocarbons, it is inert to Fischer reagent but completely miscible in it, and in a dry state it has a high affinity for water.

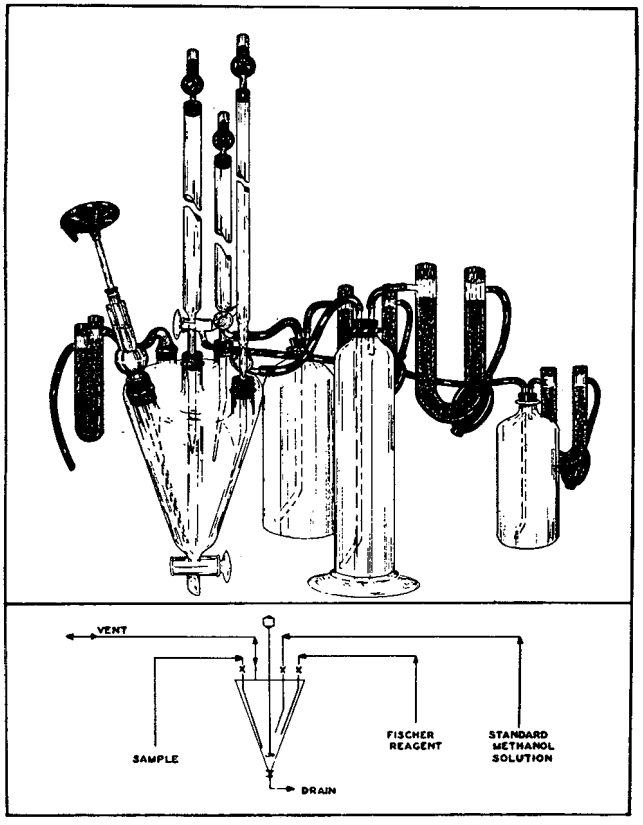

Figure 1. Titration Equipment

The proposed modification of the Karl Fischer method may be briefly summarized as follows: The dissolved or suspended water in the hydrocarbon is extracted by shaking with a known quantity of dry ethylene glycol, and aliquot portions of the glycol solution are titrated with standard Fischer reagent. The data reported by Gester (*7*), in his work on hexane, were obtained in the authors' laboratory by the method described in detail in the sections that follow.

REAGENTS

The Karl Fischer reagent is prepared according to the method given by Smith, Bryant, and Mitchell (*21*), or it may be purchased commercially. This reagent deteriorates on standing and must be standardized daily, or, if not used that frequently, before use. Standardization is made against a methanol-water solution by the method described by Karl Fischer (*6*).

The water equivalent of the Fischer reagent as received in the laboratory is usually about 0.004 gram per ml., but because of the unstable nature of the reagent this value decreases with time (*17*). The methanol-water solution used to standardize the Fischer reagent is prepared with about 0.002 gram of water per ml.

Commercial ethylene glycol used in the extraction is rendered practically anhydrous by fractional distillation. The crude product is charged to an all-glass still fitted with a packed distillation column, reflux condenser, and overhead take-off line. The glycol is refluxed for 30 minutes, and a 10% overhead cut is removed. This is discarded, and the distillation is continued until a cut equal to 80% of the still charge is obtained. This procedure reduces the water content of the glycol to approximately 0.0002 gram per ml.

APPARATUS

The apparatus is shown in Figure 1. The titration vessel is cone-shaped with the apex at the bottom, and it is equipped with a drain cock. The base of the inverted cone is fitted with five openings for the following equipment: (1) Fischer reagent buret, (2) sample buret, (3) standard methanol solution buret, (4) vent, and (5) spiral glass stirrer connected through a mercury seal to an air motor.

All reagent bottles, burets, and the vent are protected from atmospheric moisture by Drierite tubes.

The sample containers are usually quart bottles, each fitted with a down tube reaching to the lowest point in the bottom of the bottle and a vent tube connected to a Drierite tube. Larger bottles, approximately 1 gallon, are used for very dry stocks. Metal bombs of 1 to 3 liters' capacity, and similarly equipped, are used for volatile stocks such as propane, butane, etc.

Two other pieces of equipment which are used but are not shown in Figure 1 are: a shaded electric light in conjunction with a white background behind the titration vessel and a mechanical shaker of the type of Precision Scientific Company, Catalog No. 5855. The shaker is used to agitate the sample and glycol.

DETERMINATION OF WATER CONTENT IN HYDROCARBONS

A measured amount of the dried ethylene glycol, usually 200 ml., is charged to the 1-quart sample container. The bottle and the glycol are shaken to remove the adsorbed moisture from the inside of the container. Twenty-milliliter portions of the glycol are titrated in the titration vessel with the Fischer reagent to establish a blank on the glycol. The amount of glycol remaining in the sample container after completion of these blank titrations may be determined either by weight difference or by subtracting the total volume used for the blanks from the volume charged. The sample container is weighed before and after transferring the sample to it. The sample and glycol are then shaken for 15 minutes in a mechanical shaker of the type mentioned above.

The glycol-water extract settles out when allowed to stand for a few minutes after shaking. The sample buret (Figure 1) and sample container are then connected by dry tubing. The walls of the tubing are brought to the same condition of moisture content as the extract by purging with a portion of the extract. The sample for analysis is then taken into the sample buret. Ten- to 20-ml. samples are titrated in the titration vessel to a constant Fischer reagent value. The water content of the petroleum sample may be calculated as follows:

$$\text{Weight \% water in sample} = \frac{(B - A) \times C \times V \times 100}{v \times W}$$

where

B = ml. of Fischer reagent used in titration of v ml. of ethylene glycol after extraction
A = ml. of Fischer reagent used in titration of v ml. of ethylene glycol before extraction
C = water equivalent of Fischer reagent in grams of water per ml. of reagent
V = total volume of ethylene glycol shaken with sample
W = weight of sample in grams
v = volume of sample of glycol used in each titration

If greater accuracy is required, or if the water content of the material is very low, the sample size should be increased to as much as 1 gallon. The glycol-hydrocarbon ratio should not be less than 10 ml. per 100 grams for the average sample. However, it may be necessary to increase this ratio for stocks with entrained or suspended water. Likewise for very dry stocks, the accuracy of the determination may be increased by decreasing the ratio sufficiently to widen the differential between the blank and final titrations. Under such conditions longer shaking periods will be necessary to ensure complete absorption of the water by the glycol.

Table I. Relative Solubility

Hydrocarbon	Vol. % Solubility of Hydrocarbon in Ethylene Glycol at 75° F.
Benzene	7
Toluene	4
Xylenes (mixed)	2
n-Hexane	1.3
Iso-octane	1
n-Decane	0
Cyclohexane	1
1-Pentene	2
Petroleum paint thinner	0.5
Petroleum paint thinner + 15% benzene	1.5
Mixed hexanes + 30% benzene	4

	Boiling Range, ° F.	Approximate Composition % paraffins	% naphthenes	% aromatics
Petroleum paint thinner	300–400	13	70	17
Mixed hexanes	140–160	77	19	4

When liquefied petroleum gases are sampled, steel sample bombs are substituted for the glass containers, and the samples are taken without venting. To ensure complete extraction of the water from these stocks, the shaking period is increased to about 25 minutes. When the glycol is removed from the bomb after shaking, it usually is necessary to allow the glycol to weather in the glycol (sample) buret—that is, to allow entrained and dissolved hydrocarbons to distill out of the solution. With the exception of these three differences, the method of analysis is the same as the procedure followed with higher boiling stocks.

The solubility of glycol in hydrocarbons is very low; conversely, the solubility of nonaromatic hydrocarbons in glycol is also low. Benzene and toluene are, however, appreciably soluble in glycol, so that in determining the water content of these compounds by the glycol extraction method, it is necessary to correct for the increase in volume of the glycol which results from contact with the hydrocarbons. The approximate relative solubilities of various hydrocarbons are shown in Table I.

Table II. Efficiency of Ethylene Glycol As Water Absorbent

Hydrocarbon	Benzene	Decane	Petroleum Paint Thinner
Weight of dry sample, grams	688	1862	2348
Weight of water added, gram	0.2646	0.5224	0.2364
Glycol-hydrocarbon ratio, ml./100 grams	18	7.5	8.8
Shaking time, min.	15	15	15
Weight of water recovered, gram	0.256	0.490	0.224
% of water found as shown by Fischer reagent titration of glycol	96.6	93.8	94.7

Table III. Effect of Repeated Contacts with Ethylene Glycol on Water Content of Benzene Saturated at 70° F.

First extraction	
Glycol-hydrocarbon ratio, ml./100 grams	16.5
Shaking time, min.	20
% water by first absorption	0.062
Second extraction	
Glycol-hydrocarbon ratio, ml./100 grams	9.0
Shaking time, min.	20
% water by second absorption	0.00054
Third extraction	
Glycol-hydrocarbon ratio, ml./100 grams	4.0
Shaking time, min.	15
% water by third absorption	0.00008

Table IV. Efficiency of Ethylene Glycol as Water Absorbent

	Benzene, C.P.			Petroleum Paint Thinner			
	Saturated at 75° F.	Saturated at 70° F.	Supersaturated at 75° F.	Saturated at 75° F.	Partially saturated at 75° F.	Supersaturated at 75° F.	
First extraction							
Glycol-hydrocarbon ratio, ml./100 grams	16.3	15	14.7	10.5	5.3	10.5	11.2
Shaking time, min.	15	10	12	15	15	15	15
% water by first extraction	0.0644	0.06	0.074	0.021	0.0049	0.0525	0.0680
Second extraction							
Glycol-hydrocarbon ratio, ml./100 grams	...	14.8	11.3	9.0	6.2	16.5	15.4
Shaking time, min.	...	10	12	15	15	15	15
% water by second extraction	...	0.002	0.004	0.0022	0.00014	0.0041	0.0033
Total % water	...	0.062	0.078	0.023	0.0050	0.0566	0.0713
% of total water shown by first extraction	...	97	95	92	98	93	95.5

PRECAUTIONS

Both the Fischer reagent and the dried ethylene glycol are hygroscopic and therefore must be prevented from coming into contact with moist air. The air used in pressuring the various solution reservoirs for charging the burets must be dried by passing through drying tubes. The titration vessel as well as all the vents from the burets must also be protected in the same way.

It is essential to keep the tubing connecting the sample container holding the glycol-water extract as short as consistent with good operation and to purge it with the extract before a sample is taken into the sample buret.

In the field, it is necessary to use extreme care to obtain truly representative samples and avoid contamination. Lines should be thoroughly purged, and there should be no appreciable temperature drop in the line from the source to the bomb. This is important, because the solubility of water in hydrocarbons decreases rapidly with decreasing temperature.

Petroleum fractions containing interfering compounds such as hydrogen sulfide, mercaptans, ketones, etc., cannot at present be analyzed for water by this method. Although the ethylene glycol does extract the water, these compounds are likewise absorbed to some extent and consequently introduce errors in the determinations.

EXPERIMENTAL

Tables II, III, and IV show the extraction efficiency of ethylene glycol when used with various hydrocarbons.

The procedure followed in obtaining the data given in Table II was as follows: The hydrocarbons were dried by agitation with dry glycol, weighed quantities of water were added, and the samples were well shaken. Finally, the water contents were determined by the modified method. The extraction efficiencies of the three samples were 96.6, 93.8, and 94.7%, respectively.

In order to determine the effect of repeated extractions on the same sample, benzene saturated with water was subjected to three successive extractions with dry glycol. If we consider the sum of the three extractions as being the total water content of the benzene, then 99% of the water was absorbed in the first extraction. These results are given in Table III.

On the same basis, Table IV shows the efficiency of extracting water from benzene and petroleum paint thinner with water contents varying from 0.005 to 0.08%. In this series, the extraction efficiency for a single treatment with glycol ranged from 92 to 98%. The number of determinations was, however, insufficient to establish a relation between the extraction efficiency and the glycol-hydrocarbon ratio or the water content of the stock.

From the foregoing data, it may be concluded that, employing only one extraction, this method can be used to determine the water content of hydrocarbons with an accuracy of at least 92%.

OTHER APPLICATIONS OF METHOD

The data given in Tables II, III, and IV are for hydrocarbons which are clear and have low vapor pressures—i.e., are stable liquids at room temperature. However, the method has also been

used for several years in the authors' laboratory with very satisfactory results in the following special applications:

Determination of water in stocks of high vapor pressure such as propane and the butanes.

Determination of water in colored stocks such as lubricating oils, transformer oils, etc., in which the color bodies are not soluble in the glycol.

Studies of the water solubility–temperature relationship for hydrocarbons over the temperature range 60° to 180° F. There seems no reason to doubt that the upper temperature may not be further increased.

SUMMARY

A modified Karl Fischer method for determining the water content of hydrocarbons and petroleum fractions involves extraction of the water from the hydrocarbon by dry ethylene glycol and subsequent titration of the glycol with Fischer reagent. With one extraction, over 90% of the water present in the hydrocarbon is absorbed by the glycol.

Increased accuracy with stocks of low water content may be obtained by concentration of the water from a large volume of hydrocarbon in a small volume of extract. The difficulty of titration in a two-phase liquid is eliminated. The method is applicable to high vapor pressure stocks such as liquefied petroleum gases. Colored stocks, such as lubricating oils, transformer oils, etc., in which the color bodies are not soluble in glycol, may be analyzed for water without difficulty. This method may be used to determine the solubility of water in hydrocarbons and petroleum fractions at temperatures up to about 350° F.

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Rapid Routine Calculation of Multicomponent Mixtures with Punched Card Machines

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To facilitate rapid routine determination of ten-component samples, multicomponent analysis was performed on an infrared spectrometer. The formidable task of calculating hundreds of samples was handled by punched card machines. Using standard accounting office equipment, solutions were obtained (after conventional inversion of the matrix of absorption coefficients) in a mean time of 3 minutes per sample. Limits to the accuracy of the method are discussed.

THE laborious calculation of the composition of multicomponent mixtures may be handled by automatic computing equipment with speed and economy. Such automatic equipment is frequently available in accounting installations in the form of I.B.M. punched card machines. In the method described below, advantage is taken of the speed of these machines in performing routine calculations.

A multicomponent mixture may be completely analyzed by measuring sufficient independent, additive properties, if these properties of the individual components are known. A set of simultaneous equations may be formed from the latter and may be solved for the concentrations of the components. The case where these properties are infrared absorbances has been treated by Brattain, Rassmussen, and Cravath (*2*), Fry, Nusbaum, and Randall (*6*), and others. There is some loss in accuracy by assuming linear relationship between concentration and absorbence when practical slit widths are employed. When greater accuracy is not required, rapid routine multicomponent analysis may be set up as follows:

1. Obtain the coefficients of the linear equations, $a_{11}x_1 + a_{12}x_2 + \ldots a_{1n}x_n = k_1$, where each coefficient a_{ij} is the slope of the absorbence *vs.* concentration curve at wave length λ_i. K_i is the total measured absorbance at λ_i.
2. Invert the matrix of coefficients, using either a desk calculator (*3*, *9*) or an analog computer (*1*).
3. Solve each set of inverse equations by an arithmetical substitution into the inverse matrix.

In conjunction with a process development study, a large number of multicomponent samples were submitted for infrared analysis. Preliminary survey showed that only ten compounds were likely to appear in the reaction products. Although few samples contained all ten, every sample was treated as a ten-component mixture, in order to eliminate the handling of each sample as an individual problem. The over-all procedure used for each sample was as follows:

1. One milliliter of sample was diluted to volume with carbon disulfide in a 10-ml. volumetric flask.
2. Using the turret pin mechanism of a Beckman IR-2 spectrometer and a predetermined slit program, absorbences were measured at ten selected wave lengths. Samples were measured in a 0.1-mm. cell.
3. After correcting absorbences for false energy (*2*), the usual

cell-plus-solvent blank was subtracted from each reading. The sample absorbences were recorded on specially devised sheets.

4. Data for 25 samples were accumulated into a "set" and sent to the tabulating department.

5. The calculation and the preparation of the final report were handled by punched card machines as described below. The final report (plus check sheets) was returned to the research laboratory.

USE OF PUNCHED CARD MACHINES

General principles of punched card computation have been discussed by Eckert (*4*, *5*) and King (*8*). The following International Business Machines Corporation equipment was available for the computations:

1. Keypunch, verifier, and card-counting sorter.
2. Reproducing punch No. 519.

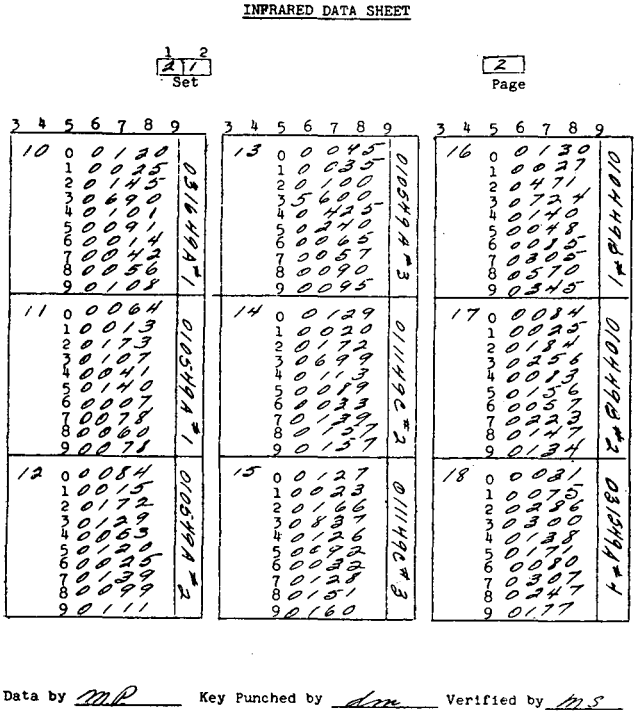

Figure 1. Form Used to Transmit Absorbence Data to Tabulating Department

Fourth line in upper left-hand box would be keypunched 211030690. 2110 is sample number, 3 is a code for wave length, and 0690 represents an absorbance of 0.690

3. Accounting machine No. 405 (standard equipment, plus two digit selectors, card cycle total transfer and group indication elimination).

These machines, which represent a basic accounting group, were used for the calculation. It was recognized that the use of a calculating punch and a collator would expedite the operation, but these machines were not available.

A general description of the method is given below. Detailed description of the machine methods and wiring diagrams are available on request from the author. "Pointer 461" (*7*) may also be consulted.

The sums of small groups of products can best be obtained on an addition-type machine by a process known as "digiting." Although this process seems long and involved, the rapid operation of punched card machines more than compensates for the apparent clumsiness of the method. This process is carried out in three steps, each performed automatically.

1. Each multiplicand in the group is entered into three counters controlled by the multiplier digits as follows: The multiplier digits are factored successively into sums of ± 1, $+3$, and $+5$. The presence or absence of each factor impulses three counters labeled "1," "3," and "5" to add, subtract, or skip the corresponding multiplicand.

Example. $347 \times 6 + 289 \times 7 = 4105$

Counter "1"	Counter "3"	Counter "5"	
347		347	$6 = 1 + 5$
−289	289	289	$7 = -1 + 3 + 5$

2. The three counters are totaled.

"1"	"3"	"5"
58	589	636

3. The corresponding totals are added, respectively, 1, 3, and 5 times, then added together.

Example.

$58 \times 1 =$	58
$289 \times 3 =$	867
$636 \times 5 =$	3180
Total	4105

4. When the multiplier consists of more than one digit, this process must be performed for each digit. The corresponding sums of products are multiplied by 10, 100, 1000, etc., and then added together.

In practice, the operation is performed by the tabulating department using a simple routine. Absorbence data are punched into cards, which are merged with a permanent set of cards containing the inverse matrix coefficients. The merged cards are passed through the reproducer, yielding a new set containing both the absorbence and the matrix element on the same card which is processed as above. The final step, multiplication by 1, 3, and 5, is combined with the preparation of the final report as follows: Previously prepared "compound name cards" as well as cards to control the proper repetitive transfer of totals are merged with cards summarizing the results of step 2 above.

2901	COMPOUND	1		1	COMPOUND	2			20	38
2901	COMPOUND	3		3	COMPOUND	4			20	38
2901	COMPOUND	5			COMPOUND	6	100	1	20	38
2901	COMPOUND	7		1	COMPOUND	8			20	38
2901	COMPOUND	9			COMPOUND	10		1	20	38
2902	COMPOUND	1	24	1	COMPOUND	2		5	20	38
2902	COMPOUND	3	14	7	COMPOUND	4	4	4	20	38
2902	COMPOUND	5	4	0	COMPOUND	6	37	7	20	38
2902	COMPOUND	7	1	1	COMPOUND	8	5	5	20	38
2903	COMPOUND	9	1	9	COMPOUND	10	*	5	20	38
2903	COMPOUND	1	23	3	COMPOUND	2		9	20	38
2903	COMPOUND	3	17	1	COMPOUND	4	2	0	20	38
2903	COMPOUND	5	3	3	COMPOUND	6	40	4	20	38
2903	COMPOUND	7		7	COMPOUND	8	4	7	20	38
2903	COMPOUND	9	1	5	COMPOUND	10	*	6	20	38
2904	COMPOUND	1	11	1	COMPOUND	2		3	20	38
2904	COMPOUND	3	12	4	COMPOUND	4	1	6	20	38
2904	COMPOUND	5	1	6	COMPOUND	6	57	3	20	38
2904	COMPOUND	7		2	COMPOUND	8	2	4	20	38
2904	COMPOUND	9		8	COMPOUND	10	*	2	20	38

Figure 2. Form Printed by I.B.M. Machine as Final Calculations Are Being Made

Sample number is at extreme left, followed by two double columns listing compounds and their corresponding volume per cent. (Blank column represents decimal point, since machines do not print decimal points.) Final two columns are checks which indicate correct machine operation. "Sample 2901" is a check substitution of part of original data into inverse matrix

Samples of the submitted data sheet and the final report are shown in Figures 1 and 2.

SOURCES AND CONTROL OF ERROR

In a complex multicomponent analysis and calculation, sources of error may be both numerous and cumulative. Therefore, it is essential to recognize every source of error. In the analysis discussed above, errors may be classified as those of measurement, calculation, and theory. Sources of measurement errors include dilution and spectrometry. When instrument temperature was maintained constant to 0.5° C., no significant wavelength shifts were observed. The instrument maker's claim of less than 0.5% transmittance error was well substantiated.

In the computation, human error may be involved in the keypunching of the data on cards. Use of the verifier should greatly reduce the probability of undetected error. Once the data are properly punched, machine errors may be minimized by incorporating numerous automatic safeguards. The pessimistic assumption is made that the machines will make all possible errors. The operation incorporates check methods which are printed on the final report. Thus, the machines will signal an error or fail to print the proper check values in the event of a misplaced or missing card, incorrect operation, machine part failure, etc. A final proof consists of the substitution of a column of the calibration matrix for the absorbence data. The results appear as 100.0%, 0, 0, ...0. There is a small systematic error of about 0.1%, which is the cumulative effect of dropping rather than rounding off the last significant figure in successive steps.

By far the largest error is that introduced by the neglect of curvature in the absorbence-concentration curve. Although it is possible to perform second-order corrections (*2*) using the I.B.M. machines, the increased machine time outweighs the increased accuracy for most process study programs. The effect of curvature was minimized by measuring all samples in dilute solution. The nominal concentration thus averaged 1 to 3% for any one component. When the compounds that evidenced the greatest curvature were high in concentration, accuracy decreased as evidenced by a departure from 100% total concentration.

CONCLUSIONS

Use of automatic computing equipment reduced calculation time to 3 minutes from a minimum of 15 minutes by desk calculator or 11 minutes by analog computer. The 3 minutes represents combined operator and machine time per sample when calculated in groups of 25 samples. The machines require operator attention less than half of the time. The cost of materials consists primarily of 10 cents' worth of cards per sample computed.

In a 6-month period, 750 ten-component analyses and computations were performed without an undue strain on the spectroscopy group. The rapid accumulation of an array of analytical figures greatly facilitated the work of the process study group.

ACKNOWLEDGMENT

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Rapid Photometric Determination of Iron in High Temperature Alloys

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A rapid method for the photometric determination of iron in high temperature alloys is based on the reaction of the ferrous ion with 1,10-phenanthroline. The sample is dissolved in aqua regia and a few drops of hydrofluoric acid, and diluted to 500 ml. A 10-ml. aliquot sample is reduced with hydroxylamine hydrochloride and the orange colored complex is formed by the addition of 1,10-phenanthroline. The reproducibility is good and the average error is ±0.02% of the amount present.

THE chief sources for the work reported in this paper are Fortune and Mellon's complete report on the spectrophotometric method for the determination of iron with 1,10-phenanthroline (*2*), and the writer's work on the determination of iron in aluminum alloys (*4*).

A number of papers (*1, 3, 5, 7*) have reported on the use of 1,10-phenanthroline for the determination of iron in a variety of samples. A summary of the work done with 1,10-phenanthroline up to 1944 was made by Smith and Richter (*6*).

The purpose of the work described in this paper was the development of a rapid and accurate method for the determination of iron in high temperature alloys based upon the orange colored complex formed by ferrous iron and 1,10-phenanthroline.

EXPERIMENTAL WORK

The preliminary work covering the following problems is fully described by Fortune and Mellon (*2*) and the writer (*4*).

A suitable reductant for iron. A 1% solution of hydroxylamine hydrochloride was reported as the most effective reductant.

A wave length that would produce maximum absorption 4900 A. was found the most suitable.

Conformity to Beer's law. Beer's law was followed by the color system and was proved by the straight line obtained when readings of the observed transmittancies at 4900 A. for concentrations up to 5.00% iron were plotted.

The new problems that arose in adapting the methods to high temperature alloys were: a suitable solvent for the material, sample size and aliquot portion, and interference from other elements present.

Table I. Determination of Iron in Alloys

Sample No.	Alloy No.	Other Methods[a], %	Photometric Method, %
1	RAE 1032 (X-40)	1.04	1.10
2	RAE 1032 (X-40)	1.09	1.07
3	RAE 1032 (X-40)	1.03	1.04
4	RAE 1032 (X-40)	1.03	1.03
5	RAE 1032 (X-40)	1.39	1.30
6	AMS 5668 (Inconel)	7.47	7.48
7	RAE 1032 (X-40)	0.92	0.98
8	Vitallium	1.60	1.60
9	Vitallium	1.48	1.48
10	Inconel X	6.54	6.52

Each value is an average of ten determinations.

[a] Gravimetric and permanganate methods.

A survey of the present methods revealed that aqua regia plus a few drops of hydrofluoric acid is generally used to dissolve high temperature alloys. This was suitable because there was no interference with the reaction of ferrous iron and 1,10-phenanthroline.

In order to obtain the intensity of the orange color produced which would be in the middle of the electrophotometer scale, a system of dilutions and aliquot portions was devised. A 0.500-gram sample was found suitable, and is described below.

The first attempts to determine iron using 1,10-phenanthroline involved complete separation of iron from the other elements present. This was done because it appeared that the heavy concentration of cobalt, chromium, nickel, molybdenum, and tungsten might cause interference. The results obtained were favorable. The next step was to determine iron without separation from the other constituents. The results were also satisfactory, indicating that it was unnecessary to remove the other elements present.

Very few ions seriously interfere with the production of the quantitative color reaction. Fortune and Mellon studied fifty-five possible interfering ions (*2*). Bismuth and silver interfere because of the precipitate formed with 1,10-phenanthroline, which also precipitates cadmium, mercury, and zinc. However, none of these elements is present in appreciable amounts in high temperature alloys.

All photometric measurements were made with the Coleman Universal spectrophotometer Model 11; the optical cell thickness is 13 mm. For routine work the Fisher AC Model electrophotometer is used. The filter is 490 mμ, the optical cell thickness is 23 mm.

Reagent Required. Hydroxylamine Hydrochloride, 10%. Dissolve 10 grams of C.P. hydroxylamine hydrochloride crystals in 100 ml. of distilled water. (Store in refrigerator. Do not use if solution has a brown color.)

Sodium Acetate. Dissolve 20 grams of C.P. sodium acetate crystals in 100 ml. of distilled water.

1,10-Phenanthroline, 0.25%. Dissolve 0.500 gram of C.P. 1,10-phenanthroline monohydrate crystals in 150 ml. of boiling distilled water. Cool, transfer to a 200-ml. volumetric flask, and dilute to the mark. (Store in refrigerator. Do not use if the solution has a brown color, as this indicates decomposition.)

Standard Iron Solution. Dissolve 1.000 gram of pure iron wire in 5 ml. of concentrated hydrochloric acid. Transfer to a 1000-ml. volumetric flask. Dilute to mark with distilled water (1 ml. = 0.1% iron or 0.001 gram of iron).

Method. Dissolve a 0.5000-gram sample in aqua regia (30 ml. of hydrochloric acid and 10 ml. of nitric acid) and a few drops of hydrofluoric acid, using a 250-ml. beaker. Filter into a 500-ml. volumetric flask, using Whatman No. 41 paper. Wash five times with hot distilled water, cool, and dilute to the mark with distilled water. Pipet 10 ml. of solution into a 100-ml. volumetric flask if the sample contains up to 2.00% iron; or 5 ml. of solution if the sample contains over 2.00% iron. Add 1 ml. of hydroxylamine hydrochloride and mix. Add 10 ml. of sodium acetate and mix. Add about 50 ml. of distilled water and then 10 ml. of 1,10-phenanthroline. Dilute to the mark with distilled water and let stand for at least 15 minutes. Using the Coleman spectrophotometer, set wave-length dial at 490 and measure the color density of the solution. If a Fisher electrophotometer is used, a 490 mμ filter is required. Use distilled water as a reference solution.

A shortage of standard samples made it necessary to develop a method by which a pure iron solution could be used. This was possible because of the absence of interfering elements. A 1.000-gram sample of pure iron wire was dissolved in 50 ml. of hydrochloric acid, then transferred to a 1000-ml. volumetric flask, and diluted to the mark with distilled water.

All results obtained in this investigation are calculated on the basis of using a pure iron solution as a standard. Results are shown in Table I.

DISCUSSION

A method of analyzing high temperature alloys for iron content has been developed and found highly successful when used on various types of high temperature alloys.

The formation of the complex when ferrous iron reacts with 1,10-phenanthroline is represented by the radical $(C_{12}H_8N_2)_3Fe$. This is an orange colored compound whose intensity varies with the concentration of iron present.

The ferrous phenanthroline complex will not develop at a pH below 2, and the reduction of iron with hydroxylamine is slow at a pH above 3. The pH at which the determination is made is 2.8; thus a final adjustment of pH is unnecessary.

Another important advantage of this method is the elimination of tedious separations which are usually required in other methods for the determination of iron. These separations are a source of error where speed is required in the analysis.

The sources of errors of the proposed method are the instrument, and transfer and dilution of samples. With all the possible sources of error, the average error was ±0.02% of the amount present.

SUMMARY

An orange colored solution is formed when 1,10-phenanthroline reacts with ferrous iron. The color intensity varies with the iron concentration. The iron is reduced from ferric to ferrous by hydroxylamine hydrochloride.

None of the elements present in high temperature alloys interferes with the reaction of iron and 1,10-phenanthroline.

A shortage of standard samples resulted in making use of pure iron solution as a standard.

The proposed method takes less time to complete than the standard volumetric and gravimetric method for the determination of iron in high temperature alloys.

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Procedures in High Precision Ebulliometry

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An ebulliometer, designed for stable operation with highly sensitive differential thermometers over a wide range of operating temperatures, is described. This instrument enables the routine used of thermometer-solvent couples of up to twelve times the conventional sensitivity. The application to solutes from 300 to 13,400 number average molecular weight is illustrated with 2% precision throughout this range.

THE measurement of molecular weight of materials in the range from 1000 to 10,000 has been a difficult problem for the physical or analytical chemist. Osmotic pressure measurements are almost impossible, because of membrane permeability, and ebullioscopic methods to date have not been sufficiently sensitive and stable to the small quantities in question. Recourse has been taken to the measurement of noncolligative properties, particularly viscosity, with attendant difficulties in calibration and interpretation of results. The measurements described here represent a tenfold extension of the range and sensitivity of the Menzies-Wright (*5*) type ebullioscopic method, thus encompassing the region of difficulty. They are made possible by the coupling of solvents boiling in an elevated range (above 130° C.) with the conventional water thermometer, or, alternatively, by using lower boiling thermometric liquids with conventional solvents.

The limit of ebulliometric measurement to date—roughly 1000 with the benzene-water couple—is simply an experimental limitation expressing the inability to measure boiling point elevations at solute concentrations compatible with the assumptions in the derivation of the relation of boiling point elevation to solute molecular weight. The most obvious approach to measurement of smaller temperature differences is increasing the sensitivity of the differential thermometer. This is easily possible, because the sensitivity of a given thermometer is proportional to the slope of the vapor pressure–temperature curve of the thermometer liquid at the operating temperature. By raising the operating temperature—i.e., by using higher boiling solvents—this slope may be very greatly increased. The same sensitivity increase may also be gained by coupling a lower boiling thermometer liquid with conventional solvents.

The use of such thermometers and operating conditions necessitates the construction of a highly stable ebulliometer capable of stably maintaining the small temperature differences involved, and of operating at any desired temperature. An upper operation temperature limit of 118° C. was found by Kitson, Oemler, and Mitchell (*3*) using a vacuum insulated ebulliometer. Kitson and Mitchell (*2*) and Barr and Anhorn (*1*) have constructed nonaqueous differential thermometers and report their use close to their normal boiling point. A thermometer preparation apparatus similar to that described by Kitson and Mitchell (*2*) has been employed here.

The ebulliometer constructed for this study has been successfully operated with a water thermometer up to 170° C. It employs an outer vapor jacket, maintained at a slightly lower temperature, rather than vacuum insulation. This eliminates the excessive heat losses throughout the reflux column. The super-heating attendant on the large vapor throughout required to satisfy these heat losses is believed to be the cause of previous operational limits. The stability of the present apparatus is adequate throughout its operational range.

PREPARATION OF SOLVENTS

The extreme sensitivity of the thermometers as employed require solvents of high purity.

Satisfactory solvents have been prepared by fractionation through a glass-packed 5-foot (150-cm.) column at high reflux ratio, followed by passage through a chromatographic adsorption column containing silica gel and/or activated alumina. This product is then distilled in a simple all-glass, nonjointed system to remove any nonvolatiles entrained in the original still head. Isomeric hydrocarbons have proved the most difficult to purify, as is to be expected. Water contamination in low boiling solvents is to be guarded against.

CONSTRUCTION OF EBULLIOMETER

The apparatus developed for these measurements is shown in Figure 1.

The apparatus consists of an inner chamber containing the solution under study and a concentric water chamber containing pure solvent. Each chamber is provided with a resistance heater at the lower extremity and a condenser at the top. The inner surface of the lower portion of each chamber is coated with powdered glass, sintered into position. The thermometer and

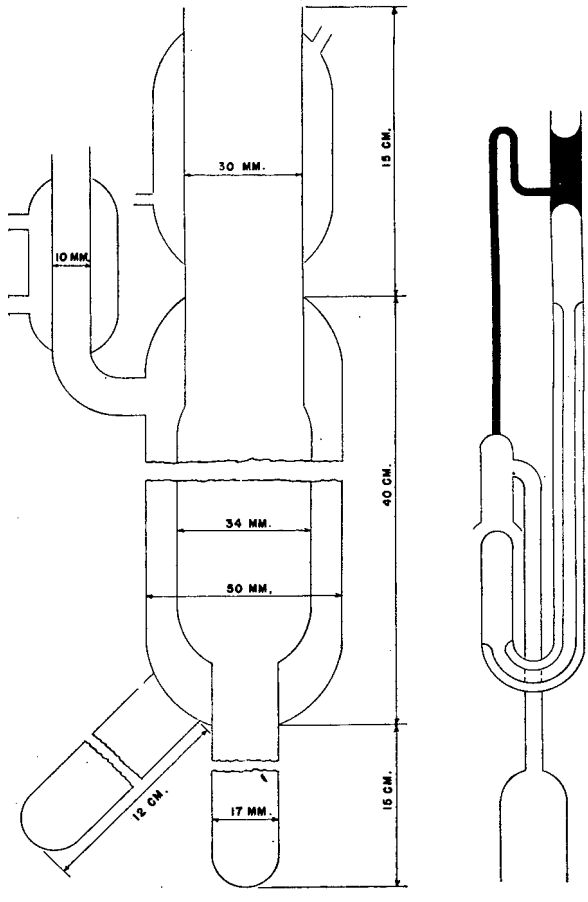

Figure 1. Apparatus

pump are a separate unit, which is clamped into position, and is removed during rinsing and cleaning operations.

The heating legs of the apparatus are wound individually. Each is covered with a thin asbestos strip and approximately 5 feet of No. 20 Nichrome wire are wound over this. The coil is wound to concentrate its heat near the sintered surfaces at the lower end, and is then covered with several layers of asbestos insulating tape. The winding to the inner jacket is connected to a Variac which is connected to a 20-volt autotransformer. The winding to the outer jacket is connected directly to a Variac which is connected to the 110 volt supply lines. The inner winding is operated at about 17 volts, the outer at about 35. The ratio of input energies is about 1 to 4, so only 20% of the heat input is applied to the inner column. The condenser jackets are fed directly from the mains and no thermostating has been found necessary. With extremely high boiling solvents (above 150° C.), the condensers may be cooled with an air stream.

The powdered glass surfaces are made by sintering fragments of about 20 to 60 mesh to the inner surfaces. Excessive heating is to be avoided during this operation. The sintered region extends about 3 inches (7.5 cm.) from the tip of each heating leg. The proper use and care of these surfaces are important for continued satisfactory operation.

The Cottrell vapor lift pump, attached to the thermometer as shown in Figure 1, is positioned to draw from the upper portion of the boiling liquid. The upper opening of the pump is about 1 mm. above the thermometer bulb. A small lip is raised in one quarter of this opening to prevent liquid seal formation between pump opening and thermometer bulb. A temperature difference of about 6° C. between the inner and outer jackets serves to give adequate condensate return to the upper bulb. Thin glass spirals may be attached to the upper bulb and to the part of the lower bulb not observed in the cathetometer. These prolong the contact time of the condensate and pumped solvent, respectively, thus facilitating the attainment of steady state conditions

OPERATION OF EBULLIOMETER

The apparatus is rinsed with pure solvent and drained. It is then clamped in position and the heaters are turned on to drive residual solvent from the sintered glass onto the reflux walls. The measured quantity of solvent (usually 30 ml.) is pipetted slowly into the still warm inner chamber and about 15 ml. of solvent are added to the outer chamber. This procedure makes "holdup volumes" on the walls of the apparatus negligible, so that the pipetted weight of solvent is very close to the actual effective weight of solvent. If this procedure is followed carefully, the new solvent has been added to a surface containing tiny crevices full of vapor, and small bubbles are formed in intimate contact with the liquid phase. If boiling stops owing to power failure during a run, the apparatus cannot be merely turned on again, for these crevices are useless when once filled with liquid. The entire cleaning procedure must be followed before resumption of work.

The pressure in the outer chamber is reduced to approximately 80 mm. less than atmospheric and the condenser water is turned on. The heater to the outer jacket is adjusted to maintain the reflux level just inside its condenser. The inner chamber heater is then adjusted to maintain the inner reflux level at its condenser, with the outer jacket operating as described. At proper operating conditions, 20% or less of the total heat input is directed to the inner chamber and is sufficient to maintain these conditions.

The thermometer-pump unit is then inserted and placed to draw liquid from near the top of the boiling liquid. With solutions which foam excessively it may be necessary to reposition the pump after maximum foaming is reached.

The positions of the thermometer menisci are then measured on a cathetometer reading to 0.1 mm. The original or solvent elevation requires about 45 minutes, starting with cold apparatus and solvents boiling around 130° C. Subsequent elevations due to solute additions reach equilibrium within 30 minutes.

Once the solvent elevation has been established, small weighed portions of solute are added, and the elevation due to each increment is noted. Several solute additions are made to test any deviation from the linear rise of boiling point with solute concentration, and to eliminate any anomalies caused by addition of the first solute—principally foaming or change in pumping rate with changing surface tension.

The actual operating temperature of the ebulliometer may be directly determined with a thermometer or thermocouple, as it is slightly dependent on barometric pressure.

The barometric pressure variations observed to date have not necessitated recalculation of the thermometer sensitivity. The thermometer stability to 0.1 mm. is taken as a criterion of constant conditions, including operating temperature and superheating. The use of the internal standard further eliminates the effect of such small variables.

The apparatus has been used with liquids boiling as high as 170° C. with uniform success. New designs of ebulliometers in which the inner chamber is completely vapor-jacketed are being tested.

The apparatus as described is as stable as needed for determinations of molecular weight up to 15,000. It has repeatedly held elevations constant to 0.1 mm. for periods up to 24 hours. This, using a water thermometer at 132°, corresponds to a maximum temperature variation of 0.00011° C.

EBULLIOMETRIC LIMITATIONS

The relation of boiling point elevation of a solution to the molecular weight of the solute may be simply expressed as

$$\text{Molecular weight } (MW) = 1000 \frac{K_b}{\Delta T} \times \frac{\text{weight of solute}}{\text{weight of solvent}} \quad (1)$$

where K_b = ebullioscopic constant of the solvent, degree per mole per 1000 grams; ΔT = elevation of the boiling point, ° C.; and weight of solvent = weight of solvent actually containing solute—i.e., not including vapor phase and column holdup.

The measurement of ΔT is accomplished by use of a liquid-filled differential thermometer (*4*). The relation of the temperature difference between the upper and lower bulbs to the rise of the liquid pressure head may be expressed as

$$h = (dp/dt)_{T.L.} \frac{\rho_{Hg}}{\rho_{T.L.}} \times \Delta T = S \times \Delta T \quad (2)$$

where h = observed rise of the meniscus; $(dp/dt)_{T.L.}$ = slope of the vapor pressure-temperature curve of the thermometric liquid at the boiling temperature of the solvent, T_b; ρ_{Hg} = density of mercury at 0°, $\rho_{T.L.}$ = density of the thermometric liquid at T_b; and S = sensitivity of the thermometer, mm. per ° C.

Thus Equation 1 becomes

$$MW = 1000 \times K_b \times \frac{S}{\Delta h} \times \frac{\text{weight of solute}}{\text{weight of solvent}}$$

No theoretical limitation has been placed on the molecular weight to which this relation applies. The restrictions are that the solute have a negligible vapor pressure and that no solute-solute or solute-solvent interaction occur. The exact upper concentration limit is, of course, dependent on the particular solvent and solute in question. No data are ordinarily taken in this laboratory at solute concentrations greater than 5 weight %. With one exception, no dependence of observed molecular weight on solute concentration has been noted, completely eliminating the process of extrapolating data to zero concentration. The exception, polyethylene in chlorobenzene, was such a "poor" solution that a 2% solution set to a gel at room temperature.

SENSITIVITY OF DIFFERENTIAL THERMOMETERS

As indicated in the previous section, the higher molecular weight ranges may be approached by employing differential thermometers of high sensitivity. Table I is a summary of the calculated sensitivities of various thermometers at various temperatures. The ebullioscopic constants of the solvents boiling at these temperatures are listed, as they must be considered in evaluating the range in which a thermometer-solvent couple may be applied.

The sensitivities of the water thermometer are calculated from the "degree by degree" vapor pressure data readily available. The nonaqueous dp/dt values are taken from a tangent drawn to a plot of available data of orthobaric pressure-temperature. In

actual use of nonaqueous thermometers, more precise evaluation of the sensitivity is made by use of an "internal standard" (*6*). This eliminates the bothersome determination of effective volume of solvent. The effect of the orthobaric density of the vapor is negligible with thermometers operating at pressures less than 15 atmospheres.

Table I. Calculated Sensitivities of Thermometers

Thermometric Liquid	Operating Temperature, ° C.	Sensitivity, Mm./° C.	Operating Pressure, Atm.	Probable Solvent	K_b/Mole/1000 Grams
Water	56	64	0.15	Acetone	1.71
Water	80	199	0.5	Benzene	2.53
Water	110	513	1.4	Toluene	3.29
Water	132	925	2.8	Chlorobenzene	4.15
Water	156	1630	5.4	Bromobenzene	6.26
Ethyl ether	56	942	2.0	Acetone	1.71
Ethyl ether	80	1640	3.9	Methyl ethyl ketone	2.28
Ethyl ether	101	3000	18	Dioxane	2.75
Ethyl chloride	80	2260	7	Benzene or methyl ethyl ketone	
Methyl ether	80	8360	22		

The methyl ether thermometer has not yet been used successfully, although found to withstand the pressure involved.

The validity of these sensitivity calculations has been tested by examination of known materials and found to be excellent. Data presented in Table II demonstrate that a standard of molecular weight 670 may be determined to 1.5% accuracy by a water thermometer in chlorobenzene or an ethyl ether thermometer in acetone. These accuracy values include all assumptions as to thermometer sensitivity, solvent ebullioscopic constant, and validity of the theoretical derivation of the relation of the boiling point elevation to molecular weight.

EXPERIMENTAL RESULTS

The molecular weight values here designated as "incremental molecular weights" are the actual values calculated for the individual additions of solute. The "cumulative molecular weight" values, containing the total solute added, are listed for comparison only, as they are merely averages of the individual experiments and strongly minimize any dependence of observed values on solute concentration. Obviously, no extrapolations are involved in the interpretation of the incremental molecular weights.

DISCUSSION OF RESULTS

The calibration and testing in high ranges are limited by the supply of compounds of high purity and high molecular weight. Standards ranging from 330 to 910 have been used with uniform success. No standard of known high purity has been available in the range above 1000.

Example III was chosen to illustrate the errors that arise on calculation of data without regard to changes in the surface tension characteristics on addition of the first portion of solute. This effect is confined to the first addition, as evidenced by the constancy of the other three values. On the basis of the cumulative molecular weight values, ordinary practice would indicate an extrapolation to a value about 1350, whereas the true molecular weight is near 1050. This change on addition of first solute is not to be confused with deviations from linearity due to interactions of the solute. In the latter case the values would vary continuously throughout the range of investigation.

The third example illustrates the application of high sensitivity methods to compounds of low molecular weight. Here the small sample size requires greater care in weighing and addition to solvent to prevent any loss.

Polyethylene glycol solutions, as illustrated by Example IV, foamed on first solute additions and were run with a small addition of solute in the original elevation.

The fifth example, involving use of an internal standard and an ethyl ether thermometer, illustrates the range attainable with ordinary solvent and nonaqueous thermometric liquids. The osmotic molecular weight was approximately 30,000 after attempts to correct for membrane permeability. The intrinsic viscosity of this material is 0.527 in cyclohexanone at 20.0° C.

A further study of osmotic pressure–ebullioscopic correlations is contemplated. A membrane impermeable to the lower polymer fractions has not yet been found. Ebullioscopic measurements using high boiling solvents have been made in the range up to 35,000 with a precision of 5%. No osmotic data are yet available on these materials.

Table II. Experimental Results

Wt. of Sample, Mg.	Observed Elevation, Mm.	Increment, Mm.	Incremental Molecular Weight	Cumulative Molecular Weight
Example I. Calibration with di-*n*-octadecyl phthalate, formula weight 670. Prepared by R. H. Peterson of this laboratory. 25 ml. of chlorobenzene. Water thermometer				
Solvent	12.0	...	...	...
78.2	28.0	16.0	675	675
81.0	44.4	16.4	680	678
90.5	62.8	18.4	668	674
Total solute concentration at end of run, less than 0.85 weight %				
Example II. Calibration with di-*n*-octadecyl phthalate. 30 ml. of acetone. Ethyl ether thermometer				
Solvent	3.3	...	...	
74	9.8	6.5	783	
57	15.6	5.8	665	
102	26.0	10.4	665	
108	36.8	10.9	672	
Total solute concentration at end of run, less than 1.2 weight %				
Example III. Low molecular weight polyester. 30 ml. of chlorobenzene Water thermometer				
Solvent	23.9	...	...	...
80.8	31.1	7.2	1280	1280
83.9	39.9	8.8	1070	1190
118.5	53.7	13.8	1040	1090
98.9	64.1	10.4	1050	1070
Solution foamed on addition of first solute Total solute concentration at end of run, less than 2 weight %				
Example IV. Mixed penta- and heptadecyl imidazoline. 30 ml. of chlorobenzene. Water thermometer				
Solvent	29.4	...	...	...
78.6	58.9	29.5	306	306
55.8	80.1	21.2	303	305
52.0	99.8	19.7	304	304
Total solute concentration at end of run, less than 0.6 weight %				
Example V. Polyethylene glycol. 30 ml. of chlorobenzene. Water thermometer				
Solvent + 194	19.1	...	...	
371	31.0	11.9	3600	
381	43.2	12.2	3620	
388	55.3	12.1	3680	
Total solute concentration at end of run, less than 4 weight %				
Example VI. Vinylite VYHH, vinyl chloride-acetate copolymer. 30 ml. of methyl ethyl ketone. Ethyl ether thermometer				
Solvent	31.4	...	...	
206	32.9	To establish foaming		
Di-*n*-octadecyl phthalate internal standard, molecular weight 670				
117	53.0	20.1	...	
766	59.8	6.8	13,200	
808	67.0	7.2	13,400	
Total solute concentration at end of run, less than 7 weight % Stability: Elevation changed less than 0.2 mm. over 12 hours.				

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Colorimetric Codetermination of Cobalt and Nickel

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A simple, quantitative, and time-saving method is described for the separation and codetermination of small amounts of nickel and cobalt ions, using 3-nitrososalicylic acid as the organic reagent. The method depends upon the formation of a brown colored complex with cobalt which is soluble in petroleum ether, and the formation of a red complex with nickel which is soluble in water. Both colored complexes obey Beer's law. The method is accurate to ±2% for both the nickel and cobalt ions. Ferrous and cupric ions interfere, but means are discussed for their removal.

BECAUSE nickel and cobalt are frequently found together, methods for their separation and determination are of particular interest. Many methods have been investigated in which either nickel or cobalt is determined in the presence of the other ion.

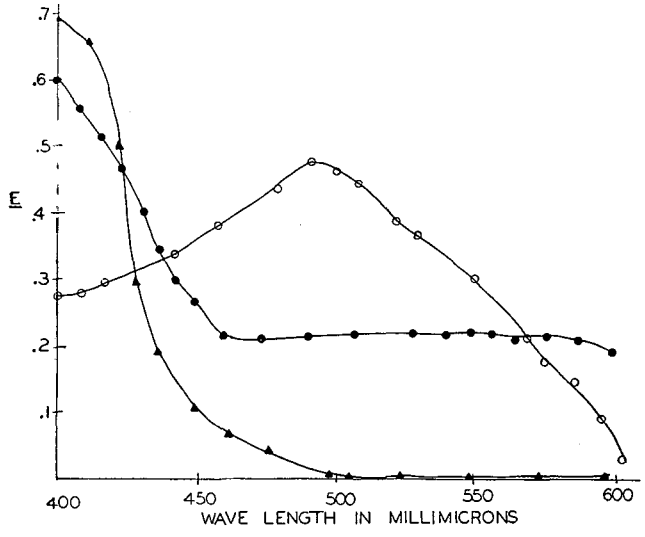

Figure 1. Absorption Spectra

○ **Nickel complex. Nickel concentration 100 micrograms**
● **Cobalt complex. Cobalt concentration 50 micrograms**
▲ **3-Nitrososalicylic acid reagent**

Several colorimetric methods have been developed for the determination of cobalt or nickel in the presence of the other ion. 1-Nitroso-2-naphthol, ammonium thiocyanate, and nitroso R salt are the common reagents used for the colorimetric determination of cobalt. 2-Nitroso-1-naphthol has also been studied as an analytical reagent for cobalt (*9*). Among the many ions that interfere with the 1-nitroso-2-naphthol and 2-nitroso-1-naphthol methods are nickel, copper, manganese, and chromium (*8, 9*). The interference caused by large amounts of nickel in the ammonium thiocyanate method for cobalt can be removed by extracting the blue cobalt thiocyanate complex with amyl alcohol (*5, 6*). The nitroso R method is very sensitive for the determination of cobalt, even in the presence of small amounts of nickel (*3, 5*).

The principal method for the colorimetric determination of nickel in the presence of cobalt is the extraction of nickel dimethylglyoxime with chloroform; however, large amounts of cobalt will lower its accuracy (*5*).

Cronheim mentioned that *o*-nitrosophenol formed a red complex with nickel, which was soluble in water, and a brown complex, which was soluble in petroleum ether. He also noted that the cobalt complex obeyed Beer's law (*2*). Overholser and Yoe observed that *o*-nitrosoresorcinol reacted with cobalt, forming a colored, water-soluble complex, which also obeyed Beer's law. A method was developed for the determination of cobalt in the presence of nickel, but it is time-consuming and is practical only within certain concentrations of cobalt and nickel. Ferric and cupric ions also interfere (*4*).

Because *o*-nitrosophenol reacts not only with cobalt and nickel but also with copper, ferrous, ferric, zinc, mercuric, and palladium ions, a more specific reagent was desired. Because 3-nitrososalicylic acid contains a deactivating and a possible steric hindering —COOH group, it was thought that this compound might react with fewer metallic ions than *o*-nitrosophenol and therefore be more specific and useful. Preliminary work on the determination of nickel with this reagent was performed by VanderVoort and co-workers (*7*).

A detailed study showed that an accurate codetermination of nickel and cobalt could be easily performed with 3-nitrososalicylic acid.

EXPERIMENTAL

Both the absorption curves of the nickel and cobalt complexes and the pH curves for the formation of the complexes had to be ascertained before any procedure could be devised.

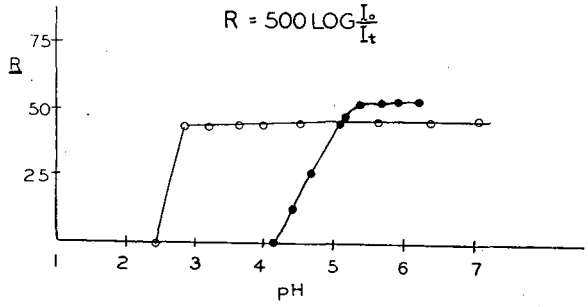

Figure 2. Complex Formation *vs.* pH

● **Nickel complex. Nickel concentration 20 micrograms**
○ **Cobalt complex. Cobalt concentration 20 micrograms**

The absorption curves were prepared using a Beckman spectrophotometer with 1-cm. cells (Figure 1). Because the maximum absorption of the nickel complex occurred in the vicinity of 500 mμ, a green filter was selected. Although the maximum absorption of the cobalt complex occurred at a wave length of 400 mμ, 520 mμ was chosen for the determination of cobalt because the reagent itself does not absorb at this latter wave length. Therefore, a green filter is also used for the determination of cobalt.

The pH range for the formation of nickel and cobalt complexes was determined by taking a known concentration of nickel and cobalt and causing these to react with 3-nitrososalicylic acid until a maximum colorimetric reading was obtained with the colorimeter, using a green filter. The pH curves for the formation of both the nickel and cobalt complexes are given in Figure 2.

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Table I. Codetermination of Nickel and Cobalt

Nickel Added, γ	Cobalt Added, γ	Nickel Obtained, γ	Cobalt Obtained, γ	Error, % Nickel	Error, % Cobalt
50	20	50.0	20.4	0	+2
50	50	51.3	50.4	+2.6	+0.8
50	450	50.9	460.0	+1.8	+2.2
10	20	10.0	20.5	0	+2.5
50	20	51.5	20.5	+3.0	+2.5
100	20	100.0	20.0	0	0
500	20	505.0	20.4	+1.0	+2.0
1000	20	1009.0	20.0	+1.0	0
20	1000	23.0	977.0	+15	−2.3

Table II. Interferences

Cobalt Added, γ	Nickel Added, γ	Copper Added, γ	Cobalt Found, γ	Nickel Found, γ	Copper Found, γ
50	50	50	50	47.6	50
50	50	50	48	50	50
50	50	50	50	49	52
50	50	50	47.5	51	50
100	100	100	97.5	109	96.4

Straight lines resulted when colorimetric readings were obtained with concentrations of cobalt and nickel ions varying from 0 to 200 micrograms, indicating that Beer's law is obeyed over the above concentration range.

PREPARATION OF 3-NITROSOSALICYLIC ACID

The reagent is prepared by the Baudisch reaction (*1*, *5*). The reaction mixture is prepared in 1000-ml. portions. Benzoic acid is added to boiling distilled water, the solution is allowed to cool to room temperature, and the excess benzoic acid is removed by filtration. To the filtered solution, 2 grams of copper sulfate and 8 grams of hydroxylamine hydrochloride are added, followed by 10 ml. of 30% hydrogen peroxide. On the addition of hydrogen peroxide, the blue solution turns to a deep red color. After thorough shaking, the solution is allowed to stand 24 to 60 hours in the refrigerator or 5 minutes at room temperature. The reagent is extracted from this solution by transferring 100-ml. portions of the reaction solution to a separatory funnel, acidifying with 200 ml. of 2 *N* hydrochloric acid, and extracting for 1 minute with 60 ml. of petroleum ether. The water layer is drawn off and is extracted again with 60 ml. of petroleum ether. The green petroleum ether fractions are combined and washed three times with distilled water.

The reagent is now extracted from the combined green petroleum ether fractions for concentration purposes by shaking with 200 ml. of a filtered saturated calcium hydroxide solution. This step is repeated. If the reagent is not being prepared for immediate use, it should be kept in the form of the calcium salt under refrigeration. Under these conditions, the reagent is stable for several months.

To prepare the reagent for use, 400 ml. of the calcium salt solution are transferred to a separatory funnel and acidified with 10 ml. of hydrochloric acid, and the reagent is extracted by shaking with two consecutive 100-ml. portions of petroleum ether. The combined green petroleum ether fractions contain 3-nitrososalicylic acid ready for use.

APPARATUS

A Klett-Summerson photoelectric colorimeter with a K.S. filter No. 54 (transmittance maximum at 525 mμ) is used.

ANALYTICAL PROCEDURE

Extraction and Determination of Cobalt. The pH of the solution containing both the nickel and cobalt ions is adjusted to 5.6 to 6.0 with a dropwise addition of sodium acetate–acetic acid buffer and the solution is poured into a 150-ml. separatory funnel. Five milliliters of the concentrated 3-nitrososalicylic acid petroleum ether solution are added to the solution in the separatory funnel. The solution is shaken for 1 minute and the petroleum ether layer containing the cobalt 3-nitrososalicylic acid complex is transferred to a 25-ml. volumetric flask. The water layer is added to a second separatory funnel, 5 ml. of the reagent are again added to the water solution, and the solution is shaken. This is repeated until the color of the cobalt complex is no longer formed in the petroleum ether layer. For a range of 0 to 200 micrograms of cobalt, 5 to 10 ml. of the reagent are sufficient. The brown colored petroleum ether fractions are added to the 25-ml. volumetric flask and the flask is filled to the mark with petroleum ether. The color intensity of the solution is determined with a Klett-Summerson photoelectric colorimeter equipped with a green filter. No blank need be determined for the cobalt determination, as the 3-nitrososalicylic acid does not absorb at a wave length of 525 mμ.

Determination of Nickel. The pH of the original solution now containing the nickel ions is checked and, if changed, is readjusted to pH 5.6 to 6.0. The solution and 5 ml. of the reagent are added to a separatory funnel and shaken for 1 minute. When the petroleum ether layer retains a greenish color, this indicates an excess of 3-nitrososalicylic acid and all the nickel has been complexed. The red aqueous nickel complex solution is poured into a 25-ml. volumetric flask, which is filled to the mark with distilled water. The color intensity of the solution is determined with a Klett-Summerson photoelectric colorimeter equipped with a green filter. A blank for the reagents is obtained by carrying through the steps of the nickel determination using distilled water. Reference is made to the calibration curves for converting the colorimetric readings directly to nickel and cobalt concentration.

RESULTS

Results are given in Table I for the codetermination of nickel and cobalt by the above procedure. Table I shows that nickel and cobalt can both be determined in solutions where the nickel-cobalt ion ratio or the cobalt-nickel ratio is 50 to 1.

INTERFERING IONS

Many ions were tested with 3-nitrososalicylic acid at concentrations varying from 0 to 100 micrograms through the pH range 0 to 7, to determine which ions would interfere with the above procedure. Only the ferrous and cupric ions caused interference in a concentration range of 0 to 200 micrograms. Silver, calcium, permanganate, potassium, sodium, dichromate, aluminum, cadmium, chloride, ammonium, sulfate, nitrate, mercuric, magnesium, oxalate, and phosphate caused no interference. The ferric ion in a concentration above 1000 micrograms was found to interfere with the cobalt method.

The interference caused by the green ferrous complex can be eliminated by the oxidation of the ferrous to ferric ion. However, if the concentration of the ferrous ion is above 1000 micrograms, the cobalt method cannot be used.

The interference caused by the cupric ion can be eliminated either by the removal of this ion or by its determination. The cupric ion reacts with 3-nitrososalicylic acid at pH 4 to form a red-colored, water-soluble complex, whereas the nickel ion does not react below pH 5. A calibration curve can be prepared for the determination of copper throughout the range of 0 to 200 micrograms. By first adjusting the pH of unknown solution to pH 4, the copper ion can be determined. Analyzing another portion of the unknown solution at pH 5.6 to 6.0 according to the analytical procedure given above, the amount of cobalt ion can be determined from the colorimetric reading obtained from the combined petroleum ether layers, while the colorimetric reading of the aqueous solution will give the combined reading of both the nickel and copper ions. If the concentration of the copper ion which was determined at pH 4, and the reading of this copper concentration at pH 5.6 to 6.0 are known, the concentration of nickel present can be determined by subtraction and reference to the nickel calibration curve.

Several solutions were prepared containing known amounts of cobalt, nickel, and cupric ions (Table II).

The above procedure for the codetermination of cobalt and nickel and the modification for the determination of nickel, cobalt, and copper were tried with known standards of steel alloys. It was found satisfactory for cobalt and nickel codeterminations in alloys containing 5% and above of these ions. Copper could be determined in steel alloys containing 1% or more of copper. Further work on the determination of cobalt, nickel, and copper in steel alloys is being done.

SUMMARY

3-Nitrososalicylic acid was found more specific and more useful than *o*-nitrosophenol, reacting with ferrous, cobalt, nickel, and

cupric ions. Methods were also found whereby these metals could be determined in the presence of the other ions. A future publication will discuss the industrial applications of this reagent.

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Colorimetric Determination of Boron Using Carmine

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A colorimetric method is described for the quantitative determination of boron, based upon its reaction with a solution of carmine in concentrated sulfuric acid. The method is applicable in concentrations of boron from traces to several hundred parts per million and in such materials as waters, soil extracts, and plant materials. Interference of nitrates and nitrites is eliminated by the procedure. Germanium, molybdenum, cerium, silicate, phosphate, ammonium, fluoride, and the chlorides of calcium, magnesium, sodium, and potassium do not interfere. The method is expeditious and highly precise.

THERE is need for a rapid and accurate method for the determination of boron in irrigation waters, soils, and plants. The method should be suitable for small quantities of material and applicable to deficiency as well as to toxicity studies.

A number of colorimetric methods have appeared in the literature and several of the most promising were tested. In one of these (*2*), use of a carefully standardized reagent containing fuming sulfuric acid is somewhat inconvenient. In another (*1*), fluorides interfere and no way was found to remove them without a loss of boron. Zorkin (*6*) has reported a qualitative test for the detection of boric acid with a 0.05% carmine-red solution in concentrated sulfuric acid.

Since work started on this manuscript, Kazarinova-Oknina (*3*) has reported a method using a 0.005% solution of carmine red in concentrated hydrochloric acid. This method was found to be insensitive to small amounts of boron.

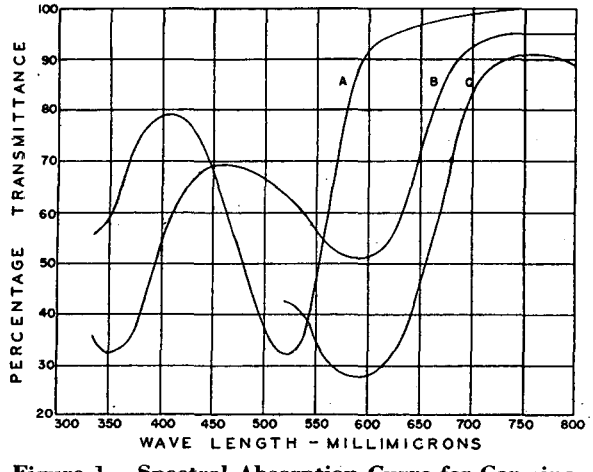

Figure 1. Spectral Absorption Curve for Carmine-Boron Complex

Reference solutions for *A* and *B* contain 0.0025% carmine and were compared against distilled water. For *C*, reference solution was undiluted reagent without boron

***A*. Dye solution only**
***B*. Dye-boron complex**
***C*. 10 p.p.m boron solution**

The method here proposed makes use of a solution of carmine in concentrated sulfuric acid. The reagent is an anthraquinone dye derived from cochineal and can be obtained in several different forms. Carmine No. 40 N. F. was used in this method. Carminic acid is entirely satisfactory, but is much more expensive. Carmine, presumably an impure form of the dye, and carmine red Ia, prepared by Dr. G. Grübler and Co., Leipzig, have been used. The color change is from a bright red, in the absence of boron, to a bluish red or blue, in the presence of boron. The reaction follows Beer's law over the range from 0 to 20 micrograms of boron. The interference of the more important anions and cations, ordinarily found in waters, soils, and plants, was tested. Nitrate and nitrite interfered but were eliminated by the procedure finally adopted. The method is presented in the belief that it will give accurate and reproducible results and will overcome some of the objections to other colorimetric methods.

Spectrophotometric curves of the carmine solution without boron (*A*) and of the dye-boron complex (*B*) are shown in Figure 1. These are more dilute solutions than the dye reagent and were compared against distilled water on the spectrophotometer. *C* represents a sample of 10 p.p.m. boron solution in the carmine reagent and is compared against boron-free carmine reagent.

APPARATUS

A spectrophotometer with matched square cuvettes. (A Coleman Model 14 Universal spectrophotometer with 13 × 13 × 105 mm. matched square cuvettes and filter No. PC-4 was used, but any good photoelectric colorimeter should be satisfactory.)

Centrifuge tubes, flasks, beakers, pipets, and burets (boron-free glass). Alkali-resistant (boron-free) glassware, porcelainware, platinum, or fused quartz dishes were found satisfactory. The use of borosilicate glassware was avoided. Equipment already in stock was used. Convenient sizes are: centrifuge tubes 15 ml., flasks 125 ml., beakers 100 ml., pipets 2 ml., and automatic burets 10 ml.

REAGENTS

Sodium hydroxide, dilute solution, boron-free.

Concentrated hydrochloric acid, C.P.

Dilute hydrochloric acid, 5 ml. of concentrated hydrochloric acid plus 95 ml. of water.

Concentrated sulfuric acid, reagent grade 95 to 96% sulfuric acid, specific gravity 1.84.

Carmine solution, 0.05% solution by weight of carmine in concentrated sulfuric acid (reagent grade 95–96% sulfuric acid,

specific gravity 1.84), shaken until completely dissolved. Carmine No. 40 N.F. was used.

Standard boric acid solution. Stock solution, made by dissolving 0.5716 gram of recrystallized boric acid in distilled water and diluting to 1 liter. One milliliter of this solution contains 0.100 mg. of boron.

PREPARATION OF STANDARD CURVE

Dilute portions of the standard boric acid solution to obtain standards over the range of 0 to 10 p.p.m. of boron. Treat 2 ml. of each solution, as described under procedure, and determine percentage transmittance. A typical curve is shown in Figure 2. For a reference, 2 ml. of distilled water are carried through the entire procedure and set at 100% transmittance.

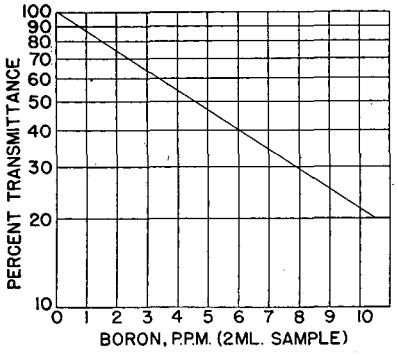

Figure 2. Concentration *vs.* Per Cent Transmittance for Carmine Solution

Procedure. Pipet 2 ml. of the sample into an Erlenmeyer flask and add 2 drops of concentrated hydrochloric acid. Add 10 ml. of concentrated sulfuric acid, mix, and cool. Add 10 ml. of carmine solution, mix, and allow to stand at least 45 minutes for color development. Determine the percentage transmittance at a wave length of 585 millimicrons against a reference solution of 2 ml. of distilled water carried through the entire procedure. Read the boron concentration from the concentration-transmittance calibration graph (Figure 2). Where the boron concentration is such that the measured transmittance value falls outside the recommended portion of the transmittance range (this method suggests 20 to 95%), either dilute the sample or concentrate it to meet the above conditions.

When boron concentration is too high, dilute the sample with distilled water to a known volume, mix, pipet 2 ml. into an Erlenmeyer flask, and proceed as directed above.

When boron concentration is too low, pipet a suitable aliquot of the sample into a beaker, platinum dish, or other suitable vessel. Make alkaline with sodium hydroxide solution and add a slight excess. (Add the same amount to all samples, including a reference.) Evaporate to dryness on a steam bath or in an oven at 95° C., cool, add 5 ml. of dilute hydrochloric acid, and triturate with a rubber policeman. Pour the solution into a conical centrifuge tube and centrifuge at 2000 r.p.m. Pipet 2 ml. of the clear solution into an Erlenmeyer flask and follow the procedure shown above, correcting the reading from the standard curve (Figure 2) to conform with the aliquot taken.

Procedure for Plant Material. PREPARATION OF SAMPLE. Remove all foreign matter from the green plant material, but avoid excessive washing. Dry at 70° C., grind, dry again to constant weight, and store in tightly stoppered bottles. If it is desired to express the results on the green weight basis, weigh the material before and after drying.

Weigh a portion of the dry sample and transfer to a glazed paper. The weight of material to be used will depend on the boron content of the sample. For each gram of the sample, add 0.1 gram of calcium oxide and mix well on paper. Transfer to a porcelain casserole or platinum dish, ignite as completely as possible in a muffle at 500° to 550° C., cool, and moisten with water. Cover with a watch glass, introduce 6 *N* hydrochloric acid, 15 ml. for a 5-gram sample, which should make the solution strongly acid, and heat on a steam bath for 30 minutes (*4*). Filter and wash the residue with distilled water. Dilute to a convenient volume. Pipet 2 ml. into an Erlenmeyer flask (boron-free glass) and follow the procedure given for water samples but add 2 drops of distilled water in place of the concentrated hydrochloric acid, since these samples are already strongly acid.

Example. When 5 grams of sample 2 (Table III), containing 37 p.p.m. of boron were ashed and the extract was diluted to 250 ml., 2 ml. taken for analysis gave a percentage transmittance of about 90.5.

Table I. Boron Found in Water Samples

Sample No.	Boron, Parts per Million: Electrometric titration method	Proposed method	Difference
1	0.37	0.40	+0.03
2	0.38	0.36	−0.02
3	0.38	0.40	+0.02
4	0.38	0.40	+0.02
5	0.39	0.40	+0.01
6	0.80	0.85	+0.05
7	0.96	0.86	−0.10
8	1.07	1.02	−0.05
9	1.66	1.64	−0.02
10	2.34	2.18	−0.16
11	2.87	2.70	−0.17
12	3.22	3.05	−0.17
13	4.65	4.65	0
14	8.44	8.45	+0.01

DISCUSSION

Interference tests were made using a number of different cations and anions. When hydrochloric acid is added, nitrate and nitrite do not interfere, but in the absence of the acid the results are high. With germanium, molybdenum, cerium, silicates, ammonium, fluorides, mixed chlorides of calcium, magnesium, sodium, and potassium, phosphates, and the ions common to natural waters and extracts of ashed plant material, no interference could be detected.

Results of analyses of several water samples are shown in Table I, along with the corresponding values determined by the electrometric titration method (*5*).

Table II shows results where the boron concentration was low and the sample had to be concentrated before development of color. Fifty milliliters of sample were evaporated and taken up in

Table II. Analyses of Water Samples

(Samples concentrated prior to colorimetric determination of boron)

Sample No.	Boron, Parts per Million: Electrometric titration method	Proposed method	Difference
Synthetic, 0.05 p.p.m. B	..	0.06	+0.01
Synthetic, 0.10 p.p.m. B	..	0.10	0
1	0.05	0.07	+0.02
2	0.09	0.06	−0.03
3	0.09	0.10	+0.01
4	0.09	0.10	+0.01
5	0.11	0.07	−0.04
6	0.15	0.14	−0.01
7	0.17	0.15	−0.02
8	0.19	0.15	−0.04
9	0.19	0.20	+0.01
10	0.20	0.18	−0.02
11	0.40	0.40	0
12	0.56	0.57	+0.01

Table III. Determination of Boron in Plant Samples

Sample No.	Boron, Parts per Million: Electrometric titration method	Proposed method	Difference
1	11	12	+1
2	37	37	0
3	55	58	+3
4	60	59	−1
5	64	63	−1
6	122	117	−5
7	144	138	−6
8	297	289	−8
9	528	526	−2

5 ml. of hydrochloric solution and 2-ml. portions (equivalent to 20 ml. of the original sample) were used for the colorimetric determination. Electrometric results are shown for comparison.

The results of analyses of several plant samples, shown in Table III, indicate that the method is applicable to plant material.

Temperature does not affect the results significantly over the range of 20° to 35° C.

Samples read after standing 45 minutes showed no appreciable change at the end of 4 hours.

Samples of standard boric acid were included with each set of analyses made over a period of a year. During this time several different lots of sulfuric acid and carmine were used but without effect on either the calibration curve or the recovery of boron from the standard solutions. This is interpreted to mean that the method is not sensitive to small changes in reagent concentrations.

The data obtained from standard boric acid solutions used in checking the precision of the method have been examined statistically. A high order of reproducibility is indicated by the following values on 15 such sets of calibrations.

Boron in standard boric acid solution, p.p.m.	1.0	5.0	10.0
Percentage transmittance, mean	86.2	47.7	23.3
Standard error of mean	±0.107	±0.097	±0.095

The accuracy of the method may be checked by the results in Tables I, II, and III. The standard error of the mean difference between the two methods shows that there is no significant difference at the 5% level.

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Determination of Chloroform and Bromoform

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A procedure for determining chloroform and bromoform is described. The haloform reacts with aniline in the presence of alkali and the halide ion formed by the reaction is determined.

METHODS have been published for the determination of chloroform by decomposing it with alcoholic sodium hydroxide and estimating the chloride by a silver nitrate method (*8*, *14*). Kunke (*5*) in a review states that pressure and heat are necessary for complete saponification. Stepanow (*12*) used metallic sodium and ethyl alcohol for the estimation of organic chlorine compounds. The accuracy of this procedure has been questioned, and modifications have appeared (*2*, *4*, *6*, *13*). Rauscher (*10*) introduced the use of ethanolamine with sodium and alcohol.

The main difficulty encountered in splitting off the halide with alkaline materials is incompleteness of reaction.

Determination of chloroform and bromoform using the Parr bomb method is also difficult; low results are usually obtained. This is due partially to the small sample necessary for an analysis because of the high halogen content and sometimes to the incomplete reaction in the bomb. Lime fusion methods have been used successfully, but these methods are time-consuming, and the technique has to be mastered before good results are obtained.

Colorimetric procedures include those involving the use of 2-naphthol for both chloroform and bromoform (*7*, *9*) and those using pyridine and sodium hydroxide for chloroform (*3*, *15*). The weight of cupric oxide precipitated from Fehling's solution by chloroform has been used as a quantitative measure (*1*).

As a qualitative test, haloforms are recognized by the odor of phenyl isocyanide when treated with aniline and alkali (*11*).

$$C_6H_5NH_2 + HCX_3 + 3NaOH \longrightarrow C_6H_5NC + 3NaX + 3H_2O$$

This reaction is the basis for the quantitative estimation of chloroform and bromoform described herewith.

In the development of the procedure an attempt was made to determine the residual alkali after completion of the reaction, but this indicated too high results. A determination of excess silver nitrate by titration with thiocyanate to the ferric alum end point was tried, but the deep color formed when the solution was acidified obscured the end point. Gravimetric determination of the silver halide yielded very satisfactory results for chloroform and bromoform. Low results were obtained for iodoform, the largest recovery being 91%.

Although the reaction is selective for haloforms, interference is caused by halogen compounds, from which the halogen can be split out by the alkali present in the analysis. Methyl-α,β-dichloropropionate and dimethyl chloroacetal are examples of this type of interference.

In general, no interference is encountered from phenols, carboxylic acids, and sulfonic acids. No silver precipitates were noted with the following acids: salicylic, stearic, maleic, tartaric, formic, acetic, succinic, caprylic, *o*-aminobenzoic, sulfanilic, and benzenesulfonic. Oxalic acid, however, causes serious interference because the silver oxalate is insoluble. Several naphthoic and naphthalenesulfonic acids, though they themselves do not precipitate a silver salt, interfere in that the silver salt will precipitate along with the silver halide.

The amides, esters, and nitriles of the above carboxylic acids should not interfere, because these materials are hydrolyzed by the alkaline solution to the corresponding acids.

Interference is sometimes encountered when acetylenic compounds with a free acetylenic hydrogen (RC≡CH) and mercaptans (thiols) are present. These materials yield insoluble silver salts, but the acidic solution keeps the acetylides and mercaptides from forming. Here again, these materials often coprecipitate with the silver halide.

In general, ketones, alcohols, and amines do not interfere. Aldehydes and acetals do not affect the silver nitrate, mainly because the solution is acidified with nitric acid before the silver nitrate is added, and no significant reduction of the silver ions take place under these conditions.

Table I. Analytical Results

	Chloroform, %	Bromoform, %
	99.4	99.8
	99.8	99.7
	100.0	100.1
		100.2
	Theoretical % Halogen	% Halogen Found by Bomb Method
Cl	89.11	89.1–88.6
Br	94.86	95.29

REAGENTS

The reagents used were C.P. aniline, 5% sodium hydroxide solution, C.P. methanol, and C.P. silver nitrate.

PROCEDURE

A sample containing about 0.0007 mole of chloroform or bromoform is placed in a 250-ml. condenser flask (S 24/40) containing 5 ml. of C.P. aniline, 25 ml. of 5% sodium hydroxide solution, and 50 ml. of C.P. methanol. Chloroform, because of its high volatility, is sampled by weighing an amount equal to tenfold the amount necessary for a determination into a glass-stoppered weighing bottle containing approximately 5 ml. of methanol. This is carefully washed into a 100-ml. volumetric flask and diluted to the mark with methanol. Ten milliliters of this solution are then pipetted into the alcohol-aniline-alkali mixture in the condenser flask with the tip of the pipet beneath the surface of the mixture. The flask is immediately attached to a condenser at least 60 cm. (24 inches) long in reflux position.

The mixture is gently refluxed for 1.5 to 2 hours. At 0.5-hour intervals, the inside of the condenser is washed down with a small amount of methanol. After 2 hours the flask is removed from the condenser, the mixture is neutralized with concentrated nitric acid, using litmus paper, and 5 ml. more of concentrated nitric acid are added. Ten grams of silver nitrate are dissolved in 25 ml. of water and added to the reaction mixture, which is heated to coagulate the silver halide precipitate. After cooling, it is filtered through a tared, 60-ml., medium, sintered-glass filter with suction. The precipitate is washed with methanol, then with diethyl ether, pulled dry with suction, and placed in an electric oven at 90° for 1 hour. The filter is reweighed, and the chloroform or bromoform originally present is calculated (Table I).

Because of the high percentage of halogen present in the compounds, a very small sample had to be used. For this reason these results by the bomb method are precise to ±1%.

The chloroform and bromoform were C.P. grade chemicals and were distilled once through a Podbielniak column to obtain the purity described above.

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Determination of Phenol Preservative

In Sera, Vaccines, and Protein Solutions

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A steam-distillation apparatus has been designed for the removal of phenol from biological and other protein solutions. Phenol was titrated with standard bromate-bromide solution. Sodium formaldehyde sulfoxylate, an interfering agent, is discussed. Excellent recoveries were obtained. The method is rapid and time-saving and can be performed by any trained analyst. Results are consistently reproducible.

PHENOL is determined in protein and biological solutions by numerous colorimetric methods (*15*). Theis and Benedict (*13*) employed Moir's reagent after precipitating the proteins by the Folin-Wu procedure. Folin and Ciocalteu (*5*) developed a colorimetric method for free and conjugated phenols. Diazotized sulfanilic acid and *p*-nitroaniline (*11*) have been utilized after deproteinizing phenolic solutions (*3*). Beshgetoor, Greene, and Stenger (*2*) added improvements to Gibbs's method by removing interfering substances in the determination of exceedingly low concentrations of phenol and its derivatives. Recently Ettinger and Ruchhoft (*4*) have introduced more refinements in Gibbs's procedure for the estimation of phenol in water with 2,6-dibromoquinonechlorimide (*6*). Proper hydrogen ion concentration is essential (*1, 14*). Without removing the protein from vaccines and sera, Sievers and Jännes (*10*) determined the phenol content colorimetrically with diazotized *p*-nitroaniline.

Turbidimetric and volumetric methods have been employed. Dilute solutions of pure phenol are assayed turbidimetrically by comparing standardized suspensions of brominated phenol with unknown suspensions of tribromophenol (*12*). Volumetric assays are likewise performed with standardized bromate-bromide solutions (*9*).

A review of the literature reveals the wide application of colorimetric methods. The author's experience with them has been unsatisfactory, particularly where protein solutions are involved, and interfering reactions between protein and reagents frequently caused erratic results. When the ratio of phenol to protein is sufficiently high, the undesirable effect of the proteins may be eliminated by dilution. Protein-free filtrates usually are satisfactory for colorimetric assay. Considerable time is required in their preparation, and this becomes more objectionable when numerous assays are to be performed.

The author has found the volumetric method with bromate-bromide solution, following steam distillation of phenol, the most advantageous. It utilizes a minimum of time, the preparation of standards for each day's assay is unnecessary, and results are

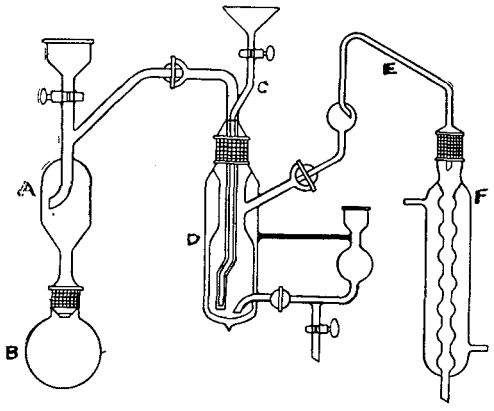


Figure 1. Schematic Drawing of All-Glass Still

easily reproduced. An important requirement in the method is the complete removal of interfering substances before titration of the phenol. The distillation is performed in an all-glass still especially constructed (Ace Glass Company, Vineland, N. J.). Initial experiments in apparatus assembled with rubber stoppers and unions produced erratic results. Volatile substances recovered in the distillate from the rubber reacted with bromine to give apparent phenol recoveries. Some precipitating agents fail to prevent foaming during steam distillation of proteins. The precipitant in the adopted method surpassed all others that were tried, by the complete prevention of foaming for all concentrations of protein. Recoveries of phenol from standardized solutions in the presence of protein ranged from 98.6 to 101.6%. Blood plasma, serum, bacterial toxin filtrates, toxoids, allergenic extracts, liver extract, bacterial vaccines, and rabies and smallpox vaccines include the protein solutions assayed. The method has been in constant use for 3 years in this laboratory.

APPARATUS

A schematic drawing of the all-glass still is shown in Figure 1. It consists of six different parts designed for quick assembly.

Steam is generated in the 500-ml. flask, *B*, which is fitted with a combination trap, funnel, and steam delivery tube, *A*. Part *C*, a continuation of the steam delivery tube, includes a sealed-in tube for the introduction of sample and reagents. The vacuum-jacketed distillation chamber *D*, is equipped with a siphon for draining and flushing after successive distillations. The bulb of this inner insulated chamber has a capacity of 75 ml. An inverted ground-glass stopper joins parts *C* and *D*. Trap *E* joins the vertical condenser, *F*, to the distillation chamber. Two ball and socket joints permit the removal of the distillation chamber for general cleaning. The entire assembly occupies a space of 18 × 18 × 4 inches (45 × 45 × 10 cm.).

REAGENTS

Solutions of sulfuric acid (33%) and hydrochloric acid (50%) are prepared from A.C.S. reagents on a volume basis. The following solutions are made on a weight-volume basis from analytical reagents: 12% silicotungstic acid (Eimer & Amend), 0.85% sodium chloride, 5% soluble starch solution prepared in boiling water and filtering through paper, and 10% neutral lead acetate.

A standard phenol solution is prepared as described by Hawk and Bergheim (*7*) except that the phenol concentration is adjusted to 1 mg. per ml. Eimer & Amend supply a phenol standard in 0.1 *N* hydrochloric acid containing 1 mg. per ml.

Potassium bromate, analytical reagent crystals, are dried for 30 minutes in a hot air oven at 100° C. To prepare a 0.01 *N* solution, 0.2784 gram is dissolved with 1.0 gram of potassium bromide in distilled water, to make 1000 ml.

Previously prepared 0.1 *N* sodium thiosulfate containing sodium carbonate (*8*) is properly diluted and restandardized to 0.01 normality.

PROCEDURE

With all stopcocks closed and all joints clamped, the apparatus is steam-flushed by boiling water in *B* for 5 to 10 minutes, and then stopcocks *A* and *C* are opened. An accurately measured sample, usually 1.0 ml. containing 0.25% to 0.50% phenol, is introduced through the funnel at *C* and rinsed with 2 ml. of 0.85% sodium chloride to prevent coagulation of adhering protein solution in the inner delivery tube. In the same manner, 2 ml. of 12% silicotungstic acid and 2 ml. of 33% sulfuric acid solution are introduced. The distillate is collected in a 250-ml. glass-stoppered Erlenmeyer flask, the stopcock at *C* is closed, and the distillation is begun. The stopcock at *A* is closed after steam is observed passing through it. The distillation is continued for 15 minutes after the first distillate is recovered. The rate of distillation is controlled to produce 40 to 50 ml. of distillate. Stopcocks *A* and *C* are immediately opened at the end of distillation to prevent back-flow of chemical solutions from *D* to the steam-generating flask and also to prevent clogging of the delivery tube *C* with the siliceous precipitate in the bottom of the distillation chamber. The residual 10 to 12 ml. of solution remaining in the chamber are drained through the siphon and the chamber is rinsed several times with distilled water. Four or five successive determinations can be made before removal of the siliceous precipitate. Thorough cleaning of the distillation chamber is essential after a day's operation.

EXPERIMENTAL

Various protein solutions were used in the recoveries of phenol by distillation (Table I). Distillation on unpreserved samples indicates that corrections are unnecessary.

Table I. Recovery of Phenol by Steam Distillation

Unpreserved Sample	Volume	Phenol Added	0.01 *N* Potassium Bromate Reacting with Phenol	Phenol Recovered	
	Ml.	*Mg.*	*Ml.*	*Mg.*	%
Normal horse serum	2.0	5.00	32.00	5.01	100.2
	2.0	5.00	32.15	5.04	100.8
Smallpox vaccine with brilliant green	2.0	5.00	31.45	4.93	98.6
	2.0	5.00	31.72	4.97	99.4
20% suspension of rabies virus brain tissue	1.0	2.50	16.22	2.54	101.6
	1.0	5.00	31.70	4.97	99.4
0.85% saline solution	2.0	5.00	31.88	4.99	99.8
	5.0	10.00	63.90	10.02	100.2
Diphtheria toxin filtrate	2.0	5.00	31.75	4.97	99.4
	2.0	5.00	31.70	4.97	99.4
Concentrated and refined diphtheria antitoxin	1.0	1.00	6.38	1.00	100.0
	1.0	2.50	16.20	2.52	100.8
	2.0	5.00	31.66	4.96	99.2
Canadian spruce bark extract	1.0	5.00	31.95	5.00	100.0
	1.0	5.00	31.80	4.98	99.6
Wool extract	1.0	5.00	31.86	4.99	99.8
Liver extract	1.0	5.00	31.80	4.98	99.6
Ragweed extract	1.0	1.00	6.45	1.01	101.0
	1.0	5.00	31.66	4.96	99.2
	1.0	10.00	63.50	9.95	99.5
Wheat extract	1.0	1.00	6.46	1.01	101.0
	1.0	5.00	31.80	4.98	99.6
Standard phenol solution	10.0	10.0	63.68	9.98	99.8
	5.0	5.0	31.95	5.00	100.0
0.85% saline solution	2.0	None	0.00	0.00	...
Diphtheria serum	1.0	None	0.00	0.00	...
	2.0	None	0.03	0.00	...
Normal horse serum	1.0	None	0.00	0.00	...
	2.0	None	0.02	0.00	...
Ragweed extract	2.0	None	0.00	0.00	...
	3.0	None	0.02	0.00	...

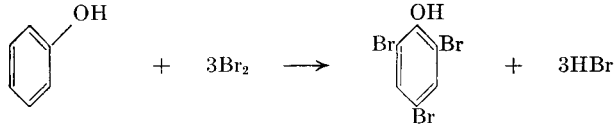
The distillate is titrated by introducing the proper volume, usually 50 ml. of 0.01 *N* potassium bromate solution, into the glass-stoppered Erlenmeyer flask together with 10 ml. of 50% hydrochloric acid. The flask is stoppered tightly and thoroughly agitated. After standing 10 minutes, 0.5 gram of crystalline potassium iodide is added and the remaining free iodine is titrated with 0.01 *N* sodium thiosulfate solution. Just before reaching the end point, 1 ml. of starch solution indicator is transferred to the flask. Each milliliter of 0.01 *N* potassium bromate utilized in the reaction is equivalent to 0.1568 mg. of phenol.

Table II. Effect of Sodium Formaldehyde Sulfoxylate in Presence of Lead Acetate

Sample	Volume	10% Lead Acetate Added	Phenol Added	0.01 *N* Potassium Bromate Reacting	Phenol Recovered	
	Ml.	*Ml.*	*Mg.*	*Ml.*	*Mg.*	%
5% Formopon	1.0	None	None	15.80	2.48 (apparent)	...
	1.0	2.0	None	None	None	...
	2.0	2.0	None	None	None	...
	1.0	2.0	5.00	32.00	5.01	100.2
	1.0	2.0	10.00	63.78	10.00	100.0
Apple extract and 5% Formopon	2.0 1.0	2.0	5.00	31.82	4.99	99.9
	2.0 2.0	4.0	5.00	31.80	4.98	99.6
Potato extract and 5% Formopon	1.0 1.0	2.0	5.00	32.00	5.01	100.2
	1.0 2.0	4.0	5.00	31.75	4.97	99.4

Several equations express the reactions involved.

$$KBrO_3 + 6HCl + 5KBr \longrightarrow 6KCl + 3Br_2 + 3H_2O$$



$$Br_2 + 2KI \longrightarrow 2KBr + I_2$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

Sodium formaldehyde sulfoxylate (Formopon) is occasionally used in allergenic extracts to prevent oxidation and discoloration of the solution. Upon distillation, it decomposes and yields hydrogen sulfide, which interferes with the titration. This is circumvented by distilling the extract in the presence of lead acetate (neutral). After the sample is introduced into the distillation chamber, 2 ml. of 10% lead acetate solution are added and the distillation is continued as previously outlined. The addition of sulfuric and silicotungstic acids is unnecessary in this procedure. Sulfuric acid precipitates the lead, which is an interfering and undesirable reaction. Table II shows the behavior of distilled sodium formaldehyde sulfoxylate solutions in the presence of lead acetate.

The results on pure solutions indicate that lead acetate eliminates the interference produced by the decomposition of sodium formaldehyde sulfoxylate. An apparent recovery of phenol occurs in the absence of lead acetate, which is completely rectified upon the addition of lead acetate. Extracts containing sodium formaldehyde sulfoxylate yielded satisfactory phenol recoveries when treated in this manner.

Quantities of phenol from 1 to 20 mg. have been quantitatively recovered by this method. With larger amounts of phenol, it is advisable to transfer 25 ml. of distilled water to the Erlenmeyer flask and distill directly into it to avoid loss of phenol by vaporization in the initial stages of distillation.

ACKNOWLEDGMENT

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Quantitative Determination of Aromatic Nitro Groups with Tin

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THE reaction between tin and aromatic nitro groups in aqueous hydrochloric acid solution has been used primarily as a preparative method. The several suggestions (*2–4*) of its use for the quantitative determination of nitro groups involve methods and conditions which are not optimum from the standpoint of accuracy and simplicity.

In order to relate the amount of tin used accurately to the amount of nitro compound, the side reactions involving atmospheric oxidation of the tin and evolution of hydrogen gas must be kept negligible. Under the conditions suggested by Kamm (*3*), using an open flask and concentrated hydrochloric acid, neither is achieved. According to Centnerswer (*1*), the rate of solution of tin in hydrochloric acid is proportional to the fourth power of the acid concentration. Gnehm (*2*) proposed measuring the hydrogen gas evolved in the side reaction and applying a correction, at the same time avoiding atmospheric oxidation by using an atmosphere of carbon dioxide. In the present study it is shown that satisfactory results can be obtained with very simple apparatus and procedure under conditions such that the influence of both main side reactions is kept very small.

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A simple procedure has been developed for the gravimetric determination of aromatic nitro compounds containing a variety of additional groups. The accuracy of the method is approximately 5 parts per 1000, comparing favorably with other methods of determining nitro groups. The method is not elaborate; no special equipment or materials are needed. A single determination requires a reasonably short time. Moreover, operational time is short, so that several determinations may be made at once. The method cannot be used in the presence of a few interfering groups.

PROCEDURE

The reaction is carried out in a 250-ml. Erlenmeyer flask fitted with a short reflux condenser, using a clean rubber stopper in preference to cork (Figure 1). A piece of small-bore glass tubing inserted through the condenser serves as a gas delivery tube for carbon dioxide.

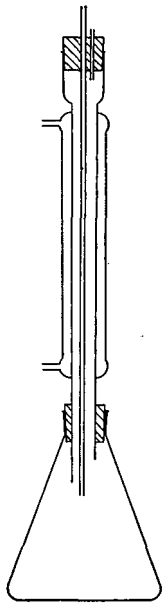

Figure 1. Apparatus

The surface of the tin is originally cleaned by shaking the tin 10 minutes in a solution consisting of approximately 50 ml. of methanol and 50 ml. of 0.75 *M* hydrochloric acid, containing 0.5 to 1 gram of *p*-nitrotoluene or nitrobenzene (or 1 to 2 ml. of nitric acid). The tin is filtered, washed with water followed by methanol, then dried. The surface will stay bright and clean for a considerable period of time.

Approximately 10 grams of clean granulated tin, reagent grade, 30-mesh, are placed in a clean sintered-glass crucible of medium porosity. The crucible and tin are dried at 75° C. and weighed. The tin is then placed in the reaction flask, along with a weighed amount, 0.2 to 0.4 gram, of the nitro compound. From 5 to 25 ml. of methanol, preferably free from formaldehyde, are added, depending on the solubility of the nitro compound. The flask is connected to the reflux condenser and warmed over a hot plate while the air is swept out with carbon dioxide. Then 35 ml. of 0.75 *M* hydrochloric acid (C.P.) are added through the condenser, followed by sufficient distilled water to make the total volume of solution 75 ml. The reaction mixture is heated gently to boiling for 1 hour, then filtered with suction through the original sintered-glass crucible, using a stream of water from a wash bottle to flush the residual tin from the flask into the crucible. The tin is washed thoroughly with water, then with methanol, and the crucible and tin are dried at 75° C. and weighed. From the amount of tin reacted, the amount of nitro group is calculated. The crucible and tin may be used for successive determinations.

After optimum conditions had been approached, runs were made to determine the effect of the several factors. When air was not excluded, the results were erratic, especially when the flask was shaken. The introduction of a slow stream of carbon dioxide through the gas delivery tube eliminated this difficulty.

The most important source of error was the side reaction of the tin with the hydrochloric acid, which was found to be highly dependent upon the acid concentration. The results of varying the hydrochloric acid concentration from 0.3 to 4.0 *M* are given in Figure 2, in which the excess of tin consumed over the theoretical amount required for the reduction of the nitro group is plotted against the final acid concentration. At low acid concentrations, especially below 0.5 *M*, the error is small, whereas at the higher concentrations, sometimes recommended, serious errors are involved.

Most nitro compounds are so insoluble in water that a certain amount of organic solvent is needed to increase the solubility. Methanol was selected as a solvent readily obtainable in a pure state. The results shown in Figure 3 indicate that the use of large amounts of the alcohol as solvent will increase the experimental error, an effect possibly due to the lowering of the hydrogen overvoltage on the tin surface.

The effect of sample size and small variations in the final acidity and stannous concentration has been studied and the findings are listed in Table I. They show that for all practical pur-

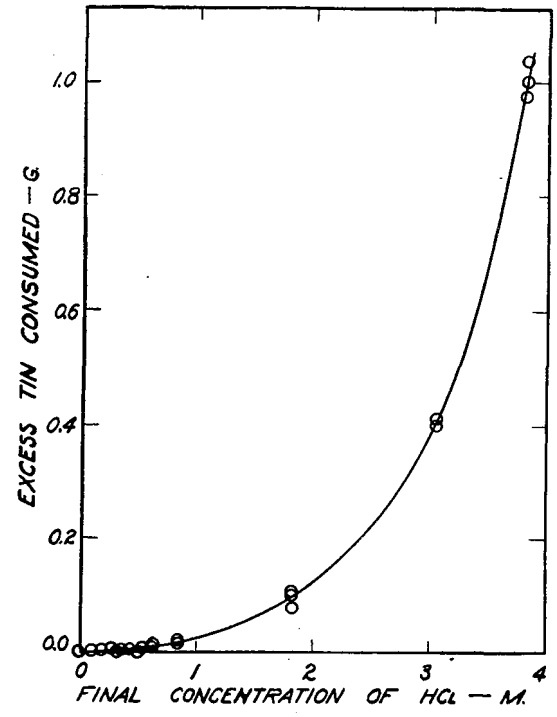

Figure 2. Variation of Excess Tin with Hydrochloric Acid Concentration

All runs were for 1 hour with 10 grams of tin, using 30% methanol as solvent

Table I. Effect of Final Acidity, Final Stannous Ion Concentration, and Sample Size

(Total tin each run, 10.0 grams. 25 ml. of CH_3OH, 50 ml. of HCl solution. All runs 1 hour. Compound, *p*-nitrotoluene)

Wt. of Nitro Compound G.	Final Acidity Eq./l.	Final Csn^{++} M./l.	Wt. of Tin Reacted G.	Excess Tin Reacted G.	% Reacted
0.07149	0.35	0.021	0.1896	0.0040	102.2
0.07149	0.25	0.021	0.1886	0.0030	101.6
0.07149	0.15	0.021	0.1899	0.0043	102.3
0.07149	0.10	0.021	0.1880	0.0024	101.3
0.1430	0.31	0.042	0.3752	0.0039	101.1
0.1430	0.11	0.042	0.3709	(−0.0004)	99.9
0.2302	0.29	0.067	0.6013	0.0035	100.6
0.2827	0.11	0.083	0.7355	0.0014	100.2
0.3695	0.13	0.11	0.9604	0.0009	100.1
0.1287[a]	0.26	0.12	0.3353	0.0011	100.3
0.0717[a]	0.20	0.11	0.1881	0.0019	101.0
0.0657[a]	0.10	0.10	0.1727	0.0021	101.2

[a] To these three runs 1.5 grams of fresh clean crystals of $SnCl_2.2H_2O$ were added.

Table II. Per Cent Completeness of Reaction

	Wt. of Nitro Compound G.	Wt. of Tin Reacted G.	Theoretical Tin %
m-Dinitrobenzene	0.3401	1.4415	100.1
	0.2576	1.0900	99.9
	0.3422	1.4406	99.1
p-Nitrobenzoic acid	0.2894	0.6233	101.1
	0.4114	0.8745	99.8
	0.1898	0.4076	100.8
Nitrobenzene	0.6848	1.9718	99.5
	0.3073	0.8929	100.4
	0.3988	1.1428	99.1
p-Nitrotoluene	0.3286	0.8536	100.0
	0.3217	0.8376	100.3
p-Nitroaniline	0.4459	1.1487	99.9
	0.2444	0.6320	100.3
β-Nitronaphthalene	0.2905	0.6029	100.9
	0.3368	0.6822	98.5
	0.3873	0.7895	99.1
2,4-Dinitrochlorobenzene	0.2147	0.7562	100.2
	0.2436	0.8587	100.3
m-Nitrocinnamic acid	0.3888	0.7186	100.2
	0.3740	0.6918	100.3
p-Nitrobenzyl cyanide	0.4155	0.9138	100.1
	0.3971	0.8709	99.8
p-Nitrophenol	0.3577	0.9189	100.4
	0.3500	0.8988	100.3
	0.3524	0.9036	100.2
	0.3209	0.8244	100.4
Picric acid	0.2031	0.9518	100.5
	0.1936	0.9084	100.6

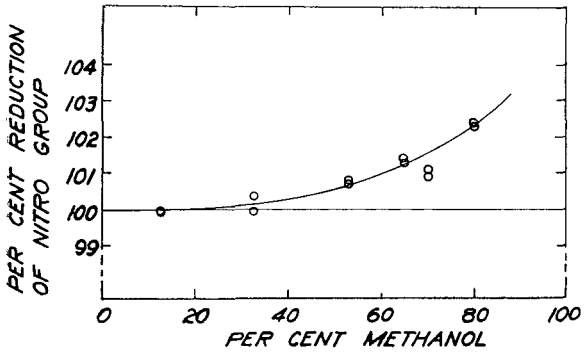

Figure 3. Influence of Concentration of Methanol as Solvent

All runs were for 1 hour with 10 grams of tin, using *p*-nitrotoluene equal to 0.4882 gram of tin and final acidity of 0.27 *M* HCl

poses the absolute error, as measured by the excess amount of tin reacted, is constant. Consequently, the relative error increases with decreasing sample size.

One factor of primary importance remains: the consequences of altering the reaction time. This is important because of its bearing upon the possibility that the above results are obtained by balancing a positive error due to hydrogen evolution against a negative error due to incomplete reaction of the nitro compound. This question was investigated by varying the reaction time from 5 minutes to 4 hours using *p*-nitrotoluene as the test substance. The findings given in Figure 4 show that the reaction is essentially complete in 30 minutes and that considerable latitude in the reaction time is possible after this initial period. The "leveling off" of the curve indicates that the side reaction between the tin and hydrochloric acid proceeds only very slowly under the conditions used—i.e., low acid and alcohol concentration.

Kinetic studies (*5*) made with several nitro compounds show that, proportional to the amount of stirring, a small fraction of the nitro compound escapes from the tin surface as an intermediate reduction product and subsequently reacts very rapidly with the stannous chloride, so that a few per cent of the tin is oxidized to the stannic state. This rapid reduction of the intermediates normally prevents any errors due to their rearrangement. On the other hand, the reduction of the stannic compounds by tin is relatively much slower than the reduction of the nitro compounds; hence the 30 to 60 minutes' time required for a complete reduction.

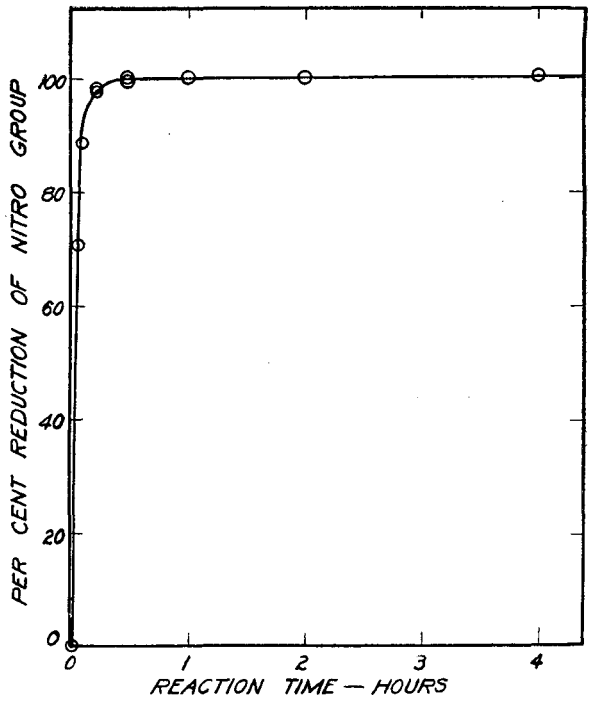

Figure 4. Variation of Per Cent Completeness of Reaction with Time

All runs were made with 10 grams of 30-mesh tin, using *p*-nitrotoluene equal to 0.8409 gram of tin; solvent contained 30% methanol, final acidity 0.5 *M* HCl; total volume of solvent 75 ml.

In the light of the above experimental data, it is desirable to use a sufficiently large sample of the nitro compound to cause reaction of 0.6 to 0.8 gram of tin, to use no more methanol than necessary, and to adjust the hydrochloric acid concentration so that its final concentration is approximately 0.15 molar, allowing the reaction to proceed at least 30 minutes in the absence of air. The directions for the analysis given at the beginning of this paper achieve these conditions.

Eleven pure nitro compounds with a variety of additional groups were analyzed by these directions, with the results shown in Table II. The results obtained are consistently good, the accuracy being approximately 5 parts per 1000. This compares favorably with other methods.

A few groups, when present, interfere with the analysis. Thus *p*- and *m*-iodonitrobenzene gave results 3 to 6% high, indicating possibly some replacement of the iodine atom by hydrogen. With *m*-nitrobenzaldehyde condensation took place, forming an insoluble yellow coating on the surface of the tin. The results for 1,3,5-trinitrobenzene were consistently 7 to 10% low.

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Separation and Determination of Sodium Oxide

In Presence of Lithium Oxide, Phosphorus Pentoxide, and Potassium Oxide

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The interference of lithium oxide, phosphorus pentoxide, and potassium oxide in determining sodium oxide with zinc uranyl acetate is eliminated by a single, easily performed separation. Sodium oxide is determined by precipitation with zinc uranyl acetate without regard for interferences, solution of the precipitate in 1-butanol–21 to 23% hydrochloric acid that separates the sodium as sodium chloride but dissolves lithium salts and phosphates, and reprecipitation of the sodium oxide with fresh zinc uranyl acetate. The double precipitation in itself eliminates potassium oxide interference.

NUMEROUS investigators have shown that appreciable quantities of lithium oxide salts interfere in the uranyl acetate methods for sodium (*1–3, 5, 7*). Although the amount of lithium oxide necessary to cause interference will depend upon the sample and reagent volumes and type, the threshold of serious interference is, generally, about 1.0 mg. This fact has made mandatory application of complex methods (*9*) for determining sodium oxide in lithium salts and minerals. Several methods for removing lithium before determining sodium oxide have been proposed.

Nydahl (*8*) separated lithium oxide by simple reprecipitation of the triple acetate salt; but later data show that this method is limited in scope. Adams, Benedetti-Pichler, and Bryant (*1*) precipitated lithium as the carbonate; Barber and Kolthoff (*2*) removed lithium with alcoholic ammonium fluoride; Sumuleanu and Botezatu (*10*) used aqueous ammonium fluoride. The use of washes to remove lithium from the dry triple acetate precipitate, as suggested by Kolthoff (*6*), cannot be expected to yield exact quantitative data. All these methods for removal of lithium are difficult to apply and may coprecipitate sodium oxide.

Collins (*4*) lists 187 references in his excellent review on the determination of sodium oxide with uranyl acetate reagents. He wrote that "in the analysis of inorganic or biological materials for sodium oxide with uranyl acetate reagents, the effect of the phosphate ion is probably the most troublesome..." Collins (*4*) lists some 70 references that indicate interference by phosphorus pentoxide. Before precipitation of sodium oxide the phosphate ion has been removed with salts of uranium, barium, zinc, lead, magnesium plus ammonia, calcium, and iron, as well as by heat and electrodialysis.

Collins (*4*) lists 47 references which indicate that above certain limits potassium oxide interferes. Various methods for eliminating the potassium oxide interference are proposed, such as precipitation with perchlorate or tartrate, readjustment of sodium–potassium ion ratio, or simple reprecipitation of the triple acetate precipitate.

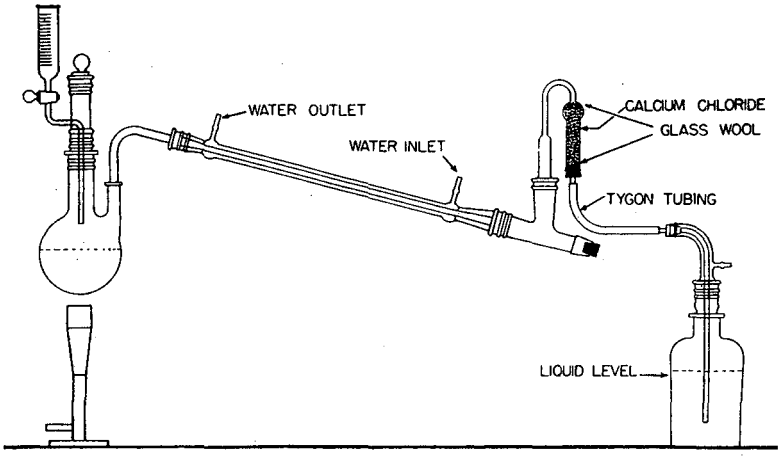

Figure 1. Apparatus for Preparation of 1-Butanol–21 to 23% Hydrochloric Acid

REAGENTS

Zinc Uranyl Acetate. This reagent is essentially that which has been described by other investigators. To 200 grams of uranyl acetate dihydrate add 980 ml. of water. In another beaker put 600 grams zinc acetate dihydrate, and add 640 ml. of water. Stir frequently, and heat each separately on the hot plate for 30 to 45 minutes. Keep covered with watch glasses. Add 120 ml. of 30% acetic acid to the first beaker (uranium) and 60 ml. of 30% acetic acid to the second beaker (zinc). In 45 minutes, most of the uranium salt will have dissolved. Whether it is dissolved or not, heat the zinc solution to boiling, and add to the hot uranium solution (probably cloudy). Stir and pour back into the beaker that originally contained the zinc acetate. The salts should dissolve completely to give a clear solution. Transfer to a 2-liter acid bottle when sufficiently cool, add 50 mg. of sodium chloride, stir, and allow to stand at room temperature for 24 hours. The clear supernatant liquid only is used as the reagent. Care must be used to prevent stirring up the precipitate when pipetting from the bottle.

Ethyl Alcohol, 95%, Saturated with Sodium Zinc Uranyl Acetate. Prepare several grams of sodium-zinc uranyl acetate by precipitating from a solution of pure sodium chloride with zinc uranyl acetate reagent, collecting on a fritted-glass filter, and washing with 95% ethyl alcohol. Transfer the precipitate to a 2-liter acid bottle, fill with 95% ethyl alcohol, and shake occasionally over a period of several days. For use, filter fresh each time, or keep previously filtered solution in a tightly stoppered bottle to exclude moisture.

1-Butanol–21 to 23% Hydrochloric Acid. This reagent is a solution of dry hydrogen chloride gas in anhydrous 1-butanol. The hydrogen chloride gas may come directly from a cylinder or from the action of sulfuric acid on sodium chloride. All of the hydrogen chloride gas employed in this investigation was prepared by heating sodium chloride in a borosilicate glass flask while drops of sulfuric acid entered continually. The hydrogen chloride gas that evolved was led through a water condenser and a calcium chloride tower. The dried gas was bubbled into the 1-butanol (Figure 1) to form the reagent. The 1-butanol was kept cool with ice. Any turbidity of the reagent may be sodium chloride and must be removed by centrifuging. The density (25°/4°) of the reagent should be between 0.91 and 0.93. Adjust to these figures

Table I. Effect of Lithium Oxide on Sodium Oxide Recovery by a Single Precipitation

Li_2O, Mg.	Na_2O Taken, Mg.	Na_2O Found, Mg.	Li_2O in Ppt., Mg.[a]
0.00	3.00	2.96	...
0.00	3.00	3.00	...
0.33	3.00	3.04	0.02
0.66	3.00	3.08	0.04
1.32	3.00	3.16	0.08
2.65	3.00	3.45	0.22
5.00	3.00	5.42	1.18
8.00	3.00	8.44	2.65
15.00	3.00	14.72	5.72
25.00	3.00	21.68	9.10
2.65	0.00	[b]	[b]
2.65	0.00	[b]	[b]

[a] Amount of precipitate above Na_2O calculated to Li_2O.
[b] No precipitate.

by adding anhydrous butanol or by passing more hydrogen chloride gas into the solution. The 1-butanol–21 to 23% hydrochloric acid is stored in a borosilicate glass bottle in such manner that no water is gained, and very little hydrochloric acid is lost. The solution was satisfactory for 3 weeks, but after 3 months had lost one third of its hydrochloric acid. Therefore the reagent should be regarded as suitable for use for not over 1 month, at ordinary room temperature.

PROCEDURE

Decomposition of the sample may be accomplished by any ordinary method, including the J. Lawrence Smith and Berzelius methods, or by solution in acid without separation of other elements.

The sodium oxide is obtained in a clear solution of 5-ml. volume, in a 50-ml. centrifuge tube (conical bottom, Corning No. 8120). The amount of sodium oxide allowable is 0.0 to 11.0 mg., using the suggested volume of sample and reagent.

Cool and then precipitate the sodium oxide as triple acetate with 20 to 25 ml. of the zinc uranyl acetate reagent. Immediately stir thoroughly, particularly in the bottom cone section of the tube. Remove, police, and wash the rod with 1 to 2 ml. of reagent from a small wash bottle. Stir once again at the end of 10 minutes. Usually so little precipitate sticks to the rod the second time that a very slight wash will suffice. Except when stirring, keep tube covered with a rubber cap of appropriate size. Let set for 30 minutes. With cap still on, centrifuge at a rate and time sufficient to settle thoroughly and to pack the precipitate. An International No. 2 centrifuge was satisfactory when operated at 2000 r. p. m. for 10 minutes (900 × gravity). Let the centrifuge coast to a stop to prevent swirling of the liquid.

Some of the precipitate invariably appears to float, so that filtration of the liquid is essential to complete recovery of the sodium oxide. Filter by decanting the liquid through a medium-porosity fritted borosilicate glass filter. Suction is necessary. Immediately add 30 ml. of the saturated 95% ethyl alcohol to the tube and swirl slightly to dissolve the water clinging to the walls. As soon as the first solution has gone through the filter, pour all the ethyl alcohol into the crucible and pull through. Reserve the crucible with its small precipitate for later solution. If any salts are present that might be precipitated by the 95% ethyl alcohol of which aluminum is an example, preliminary decantation with 10 ml. of zinc uranyl acetate reagent may be made. This must be followed by the usual 30-ml. wash with 95% ethyl alcohol.

Pour into the centrifuge tube 12 to 30 ml. of 1-butanol–21 to 23% hydrochloric acid. The amount to add is judged by the volume of the precipitate. Immediately stir to solution of the original triple acetate precipitate, cover the tube with the dry rubber cap, and place a small beaker over tube and cap. To exclude moisture, the tube should then be placed in a beaker and covered with tin foil, aluminum foil, or paper. A precipitate of sodium chloride will form simultaneously with solution of the original triple acetate. Although not proved necessary, setting of the tubes and beaker in a refrigerator is desirable to reduce the solubility of sodium chloride. Let sit 1 hour. To gather the sodium chloride in the bottom of the tube, rotate in a centrifuge until a clear solution is obtained (2000 r.p.m. for 20 minutes proved satisfactory). Decant the liquid into a dry beaker, and let the tube drain for a few seconds. Examine the liquid in the beaker for clearness and, if clear, discard.

Dissolve the small precipitate in the fritted-glass crucible with 10 drops of concentrated hydrochloric acid; then filter by suction into a small test tube placed under the funnel. Wash with 5 ml. of water, also catching this in the test tube. Mix and pour the contents of the test tube into the centrifuge tube holding the bulk of the sodium chloride. Set the centrifuge tube in a 400-ml. beaker containing 100 ml. of hot water, and boil on the hot plate for 10 minutes. Transfer the liquid from the centrifuge tube to a 30-ml. beaker. Evaporate the liquid to 5-ml. volume and cool. For small amounts of sodium oxide, evaporate to 2 to 3 ml.

Precipitation of sodium oxide should be at or near the same temperature at which the reagent solution was saturated with the triple salt. A corollary is that the zinc uranyl acetate reagent should not be allowed to become excessively cool, as by standing overnight in an unheated laboratory. Precipitate the sodium oxide as triple acetate by adding 20 to 25 ml. of zinc uranyl acetate reagent. Stir immediately. Cover with a watch glass and let set 30 minutes, stirring twice in the meantime. Filter by suction through a weighed, medium-porosity, fritted-glass crucible (borosilicate glass with nominal maximum pore size of 14 microns). Stir the precipitate and pour the entire contents of the beaker into the crucible. Immediately wash down the sides of the beaker with a small quantity of alcoholic wash solution. As soon as all the liquid in the filter has been pulled through, wash the sides, and precipitate once with the alcoholic solution. Police the beaker, and transfer all the precipitate to the crucible. Again wash down the sides of the crucible. Stop the suction and thoroughly stir the precipitate from the bottom of the crucible with a stream of the alcoholic wash. Suck all the liquid through, and wash twice from the inside top all the way around. Suck away excess alcohol. Remove the crucible from the suction and wipe the crucible, including the top and bottom flange, with a damp cloth. Dry for 20 minutes at 80° C., desiccate until cool, and weigh. The sodium oxide factor is 0.02015.

DATA AND DISCUSSION

Lithium Oxide. The extent of interference from lithium oxide by one precipitation only is shown in Table I. Here the sodium oxide is precipitated once only with zinc uranyl acetate in the presence of various amounts of lithium oxide, and is weighed as triple acetate without the separation with 1-butanol–21 to 23% hydrochloric acid.

Lithium oxide in amounts over 4 mg. cannot be eliminated by simple reprecipitation of the triple acetate. Less than 4 mg. of lithium oxide probably could be eliminated successfully by reprecipitation. In lithium minerals, salts, and unknown samples, however, the lithium oxide is or may be too high for successful analysis by such method.

Table II. Effect of Lithium Oxide on Sodium Oxide Recovery, Using Directed Procedure

Li_2O, Mg.	Na_2O Taken, Mg.	Na_2O Found, Mg.
1.00	3.00	3.00
3.00	3.00	2.96
5.00	3.00	2.94
10.00	3.00	2.98
15.00	3.00	3.10
20.00	3.00	2.98
25.00	3.00	3.07
30.00	0.30	0.27
30.00	9.00	9.14
50.00	3.00	3.03
100.00	3.00	3.04
200.00	3.00	3.01

To determine the upper limit of lithium oxide allowable when the analysis is made as directed in procedure, a series with constant sodium oxide and variable lithium oxide was prepared and analyzed. The data are summarized in Table II. Lithium oxide was added as lithium carbonate. When the lithium content was high, a correction had to be made for the sodium oxide content of the lithium carbonate. As the data show, recovery of 3.00 mg. of sodium oxide, from amounts of lithium oxide up to 200 mg., was complete and accurate within experimental error.

The data of Table III present a reverse view of the same problem. Here the data are presented when lithium oxide is held constant at 15 mg., an amount to be expected from a 200-mg.

sample of lithium-containing mineral. The sodium oxide was varied widely. Again, within experimental error, the recovery of sodium oxide was complete in all samples. Eleven to 12 mg. of sodium oxide are about the upper limit of sodium oxide allowable with 20 ml. of zinc uranyl acetate reagent.

To determine the upper limit of recovery of sodium oxide in the presence of large quantities of lithium oxide, a series was prepared with lithium oxide held constant at 100 mg. and the sodium oxide varied from 0.3 to 10.0 mg. The data are in Table IV. Recovery of sodium oxide was complete with 0.30 and 1.00 mg. of sodium oxide but was slightly low with 7.00 and 10.00 mg. Undoubtedly the proper approach for correct results in such an unusual combination would be merely to increase the amount of reagent and sample volume used, even to as much as 50 ml. of reagent and 10 ml. of sample volume.

Table III. Effect of Constant Lithium Oxide on Recovery of Wide Limits of Sodium Oxide, Using Directed Procedure

Li_2O, Mg.	Na_2O Taken, Mg.	Na_2O Found, Mg.
15.0	0.20	0.19
15.0	0.40	0.37
15.0	0.80	0.76
15.0	1.60	1.54
15.0	3.00	3.10
15.0	5.00	5.01
15.0	7.00	7.02
15.0	9.00	9.02
15.0	11.00	11.12

The data of Table I indicate that an error of 0.1 mg. of sodium oxide is found when 1.4 mg. of lithium oxide are present with 3.0 mg. of sodium oxide. To determine if a simple increase in volume of both reagent and sample would extend the threshold of lithium oxide interference, two samples of 3.00 mg. of sodium oxide and 6.6 mg. of lithium oxide in 25 ml. of water were precipitated with 100 ml. of reagent. The results are tabulated in Table V. Evidently, increased volumes will tolerate more lithium oxide. However, the larger volumes will make the sodium determination much less sensitive and will assume previous knowledge of the amount of lithium oxide present. In short, preventing lithium oxide interference by increased volumes alone is applicable only in special samples and has not the virtually universal application of the outlined procedure.

Phosphorus Pentoxide. To test the effectiveness of the directed procedure on phosphate interference, sodium oxide was precipitated in the presence of 100 mg. of potassium dihydrogen phosphate. Even to the eye, it was evident that, in the first sodium oxide precipitate with zinc uranyl acetate, the phosphate had formed a huge precipitate. Attempts to filter this mass led to plugged crucibles which effectively stopped filtration. The results obtained by use of the directed procedure on such a discouraging mass of precipitate are listed in Table VI. Sodium oxide was recovered accurately and interference from phosphorus pentoxide was eliminated.

Table IV. Effect of Large Quantities of Lithium Oxide on Recovery of Sodium Oxide, Using Directed Procedure

Li_2O, Mg.	Na_2O Taken, Mg.	Na_2O Found, Mg.
100	0.30	0.31
100	1.00	1.04
100	7.00	6.88
100	10.00	9.70

Table V. Effect of Simple Increase in Volume of Reagent and Sample, with Single Precipitation as Triple Acetate

Li_2O, Mg.	Sample Volume, Ml.	Na_2O Taken, Mg.	Reagent Volume, Ml.	Na_2O Found, Mg.
6.60	25	3.00	100	2.96
6.60	25	3.00	100	3.03

Table VI. Effect of Phosphorus Pentoxide on Recovery of Sodium Oxide, Using Directed Procedure

P_2O_5 (as KH_2PO_4), Mg.	K_2O, Mg.	Na_2O Taken, Mg.	Na_2O Found, Mg.
52.2	34.6	1.00	0.94
52.2	34.6	3.00	2.95
52.2	34.6	3.00	2.99
52.2	34.6	7.00	6.95

Potassium Oxide. Potassium is not effectively eliminated by the 1-butanol–21 to 23% hydrochloric acid reagent, because potassium chloride also is insoluble. However, double precipitation of the sodium oxide as triple acetate did eliminate the potassium oxide interference. The fact is shown in Table VI. The presence of 34.6 mg. of potassium oxide in each sample caused no difficulties. To explore further the upper limits of allowable potassium oxide, sodium oxide was precipitated and carried through the directed procedure in the presence of 200 mg. of potassium chloride (126.3 mg. of potassium oxide). The results appear in Table VII. The large quantity of potassium oxide did not cause interference. After addition of the zinc uranyl acetate reagent, the solution should be stirred immediately.

General. Application of the method is easy; no particular manipulative skill is required. Results may be obtained in one day.

Table VII. Effect of Potassium Oxide on Sodium Oxide Recovery, Using Directed Procedure

K_2O, Mg.	Na_2O Taken, Mg.	Na_2O Found, Mg.
126.3	1.00	1.02
126.3	4.00	4.04

Use of a centrifuge is mandatory. With the centrifuge tubes, moisture may be successfully excluded, the precipitate may be handled without dissolving and redrying, and the sodium chloride, which separates as a very fine grain, may be quantitatively collected with ease.

CONCLUSION

A procedure is presented for eliminating lithium oxide, phosphorus pentoxide, and potassium oxide interference in the zinc uranyl acetate method for the determination of sodium. The procedure is rapid and easily applied; it should give wider application to the uranyl acetate method for determining sodium oxide.

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Titration of Bases in Dioxane

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The titration of various organic bases in dioxane with a dioxane solution of perchloric acid is described. Modified methyl orange and methyl red are satisfactory indicators. Most nitrogen heterocyclic bases and aliphatic amines may be accurately titrated; aromatic amines are too weak to be titrated. Water and alcohol interfere if present in much more than trace amounts.

MANY organic bases cannot be titrated directly in aqueous solution because they are either too weak to give a sharp end point or only slightly soluble in water. For these reasons the use of nonaqueous solvents has been advocated. Various alcohols and alcohol mixtures have been suggested (*4, 6, 8, 11*). A disadvantage in the use of alcohol is that most bases are weaker in alcohol than in water. Palit (*10*) titrated salts of weak acids and several nitrogen bases in various glycol mixtures to either a potentiometric or visual end point. Aniline was accurately titrated, but very poor results were obtained in the titration of pyridine and related compounds. Other solvents which have been used for the titration of bases are acetic acid (*1, 3, 9*), formic acid (*5*), and benzene (*7*).

Dioxane serves as an excellent solvent for the titration of most organic bases. The titrating acid is a solution of perchloric acid in dioxane which may be kept for several weeks with little change in titer. Modified methyl orange (xylenecyanol) or methyl red serves as indicator, giving sharp end points. The titration of most bases may thus be quickly and conveniently carried out.

NITROGEN HETEROCYCLIC BASES

Pyridine ($K_b = 1.4 \times 10^{-9}$), although too weak to be titrated accurately in water, can be easily determined by titration in dioxane to the modified methyl orange end point. During the titration, pyridine perchlorate comes down as a slightly soluble white precipitate. This precipitate in no way interferes with the end point—in fact, it is chiefly responsible for the sharpness of the end point because the pyridinium ion is thus effectively removed from solution.

2,2′-Bipyridine and 1,10-phenanthroline may be titrated as monoacid bases in dioxane to the modified methyl orange end point or in ethyl ether to the methyl red end point. The perchlorate salt of these bases precipitates during the titration. Brucine ($K_1 = 9 \times 10^{-7}$, $K_2 = 2 \times 10^{-12}$) is insufficiently soluble in water to be titrated directly, but in dioxane may be conveniently titrated as a monoacid base. Brucine monoperchlorate is precipitated. 2,6-Lutidine gives an extremely sharp end point with modified methyl orange; an emulsion is formed during the titration. Hexamethylenetetramine ($K_b = 8 \times 10^{-10}$) can also be successfully titrated in dioxane with modified methyl orange indicator. It is usually difficult to get hexamethylenetetramine completely in solution without using excessive amounts of dioxane. However, if the titration is carried out slowly with efficient stirring, accurate results are obtained even if solution of the original sample was not complete.

Quantitative results for the above titrations are given in Table I.

Table I. Titration of Heterocyclic Bases with Perchloric Acid in Dioxane

Base	Wt. Taken *G.*	$HClO_4$ Used *Ml.*	$HClO_4$ *N*		Purity %
Pyridine	0.1987	24.87	0.0994		98.39
	0.1483	18.64			98.81
	0.2373	29.70			98.39
	0.1622	20.30			98.39
				Av.	98.50
2,6-Lutidine	0.2179	20.00	0.0992		97.58
	0.2613	23.98			97.57
				Av.	97.58
2,2′-Bipyridine	0.2105	13.65	0.0988		100.01
	0.3000	19.43			99.89
	0.3167	20.50			99.83
	0.3175	20.59			100.02
				Av.	99.94
1,10-Phenanthroline	0.3596	18.20	0.0994		99.67
	0.4168	21.03			99.36
	0.3700	18.70			99.53
				Av.	99.51
Brucine	0.4700	12.20	0.0976		99.88
	0.7590	19.72			99.97
	0.7486	19.47			100.07
				Av.	99.97

Table II. Titration of Benzylamine with Perchloric Acid in Dioxane and Water

Solvent	Wt. Taken *G.*	$HClO_4$ Used *Ml.*	$HClO_4$ *N*		Purity %
Water	0.2075	19.48	0.0977		98.31
	0.2330	21.83			98.11
				Av.	98.21
Dioxane	0.2342	21.55	0.0996		98.24
	0.2561	23.52			98.06
Ether	0.2262	20.86			98.46
				Av.	98.25

AMINES

The titration of aniline in dioxane was attempted, but both the modified methyl orange and methyl red end points are very poor. No precipitate appears during the titration. Aliphatic amines can be successfully titrated in dioxane, even though the perchlorate salt of the amine does not precipitate. As an example, benzylamine was titrated in both dioxane and ethyl ether using modified methyl orange and methyl red, respectively, as indicators. The results obtained by this titration agree with those obtained by titrating benzylamine in water with aqueous perchloric acid (Table II).

INTERFERENCES

Water and alcohols interfere with all of the previously described titrations. The indicator blank with both modified methyl orange and methyl red in 90% dioxane–10% water, for example, amounts to several milliliters of 0.1 *N* perchloric acid. The conversion of these indicators to their acid colors is very gradual. Alcohols interfere in a similar manner to water, but not to such a great extent. Ketones, aldehydes, hydrocarbons, nitrobenzene, and most carboxylic acids do not interfere. In Table III, the results obtained by titrating hexamethylenetetramine in the presence of various impurities are given.

Table III. Titration of Hexamethylenetetramine in Presence of 0.5 to 1 Gram of Added Impurities

Wt. Taken G.	Impurity	$HClO_4$ Used Ml.	$HClO_4$ N	Purity %
0.2716	None	19.93	0.0972	99.99
0.3271	$CH_3COCH(CH_3)_2$	24.00	0.0972	99.98
0.2464	None	18.05	0.0972	99.82
0.2771	*tert*-Butyl alcohol	20.50	0.0972	100.80
0.2862	Nitrobenzene	21.01	0.0972	100.03

PROCEDURE

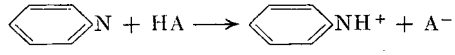
A sample of the proper size is weighed out and dissolved in dioxane or ethyl ether (25 to 50 ml. of solvent are usually sufficient). Two drops of indicator (modified methyl orange or methyl red for dioxane; methyl red for ether) are added and the solution is titrated with perchloric acid. One drop or less of 0.1 *N* acid is usually sufficient to give a sharp color change at the end point. In titrations where a precipitate is formed, the use of a magnetic stirrer is recommended but not required.

The perchloric acid solution is prepared by dissolving approximately 8.4 ml. of 72% perchloric acid in 1 liter of dioxane. This solution is standardized against diphenylguanidine, prepared according to the directions of Carlton (*2*). Diphenylguanidine is an excellent primary standard because it is readily available, easily purified, nonhygroscopic, easily soluble in dioxane and ether, has a high equivalent weight, and is a strong base.

DISCUSSION

The samples of 2,2′-bipyridine, brucine, and hexamethylenetetramine were known to be of very high purity. The fact that their purity was in each case very close to 100%, as determined by titration in dioxane, indicates that this method is capable of great accuracy. This would also seem to confirm the advisability of using diphenylguanidine as a primary standard.

The ionization of most acids and bases dissolved in dioxane and other solvents with low dielectric constants is very slight. (An exception would be solvents' possessing pronounced acid or basic properties. The ionization of acids in pyridine, for example, would be comparatively great.) In such media, an acid-base titration involving ions would, therefore, be expected to proceed in a sluggish fashion to give a very poor end point. All the bases that have been titrated successfully in dioxane, however, are neutral and do not react as ions. A strong acid, HA, will react readily with such a neutral base



Even with acids as strong as methanesulfonic acid, this titration is poor because the anion liberated acts as a base in dioxane and partially reverses the reaction. With perchloric acid, however, a sharp end point is obtained because the perchlorate ion possesses only extremely weak basic properties and the perchlorate ion is largely removed from solution in most titrations by the formation of a slightly soluble perchlorate salt.

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Separation and Analysis of Polynuclear Compounds by Countercurrent Distribution

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The partition coefficients of eighteen polynuclear compounds have been determined in the system, cyclohexane–80% ethyl alcohol. Partial saturation of ring structures and introduction of alkyl side chains increase the partition coefficients of parent compounds. Ring systems containing hetero nitrogen and oxygen atoms have appreciably lower partition coefficients than corresponding carbocyclic structures. These effects permit application of the countercurrent distribution method to separation and analysis of polynuclear compounds. The countercurrent distributions of phenanthrene, acenaphthene, and a mixture of carbazole homologs are reported as typical examples.

THE Craig countercurrent-distribution technique (*3*) is now recognized as a powerful tool for analysis of mixtures of closely related compounds (*6–8*). In this report the application of this technique to polynuclear compounds is described.

In a previous study of the separation of polynuclear hydrocarbons by countercurrent distribution (*4*), a solid phase (activated alumina) was used as one of the immiscible phases because it was thought that the spread among β-values (ratio of partition coefficients) of polynuclear hydrocarbons in systems composed of two liquid phases would be too small to make clean-cut separations. Although the procedure employing a solid phase successfully resolved a mixture of anthracene and chrysene, it did not lend itself to exact mathematical interpretation in terms of binomial expansion (*9*) (a necessary requisite for analysis and homogeneity determinations) because of the tendency of partition coefficients to change unduly during the development of the fractionation procedure. With the advent of improved distribution instruments capable of distinguishing between pairs of compounds with β-values as low as 1.1 (*1*, *5*), it appeared worth while to examine possibilities for separation and estimation of polynuclear compounds by countercurrent distribution between immiscible liquid pairs. The partition coefficients of a number of common polycyclic aromatic compounds in the system, cyclohexane–80% ethyl alcohol, were measured and correlated with structure.

Table I. Distribution of Polynuclear Compounds between Cyclohexane and 80% Ethyl Alcohol

Compound	Initial Concentration, Mg./Ml.	Partition Coefficient
Diphenyl	0.5	4.2
Diphenylene oxide	0.5	3.1
Naphthalene	0.5	3.6
1-Methylnaphthalene	0.5	3.9
2-Methylnaphthalene	0.5	4.8
Acenaphthene	0.1	3.7
Anthracene	0.1	3.3
Fluorene	0.1	3.7
9-Methylfluorene	0.1	4.4
Phenanthrene	0.1	3.3
9-Methylphenanthrene	0.1	4.2
9,10-Dihydrophenanthrene	0.1	4.6
Carbazole	0.1	0.26
9-Ethylcarbazole	0.1	3.0
9-Butylcarbazole	0.1	5.6
Phenanthridine	0.1	0.41
Pyrene	0.1	3.7
1-Ethylpyrene	0.1	5.5

MATERIALS

The polynuclear compounds were obtained from various commercial and academic sources. All had been purified by customary procedures such as crystallization, codistillation with ethylene glycol, chromatography, salt formation, and distillation over sodium.

PARTITION COEFFICIENTS OF POLYNUCLEAR COMPOUNDS

The partition coefficients of 18 polycyclic compounds distributed in the system, cyclohexane–80% (by weight) ethyl alcohol are listed in Table I. From these data, the following observations may be made:

Partition coefficients of condensed aromatic ring systems, containing one to four benzenoid rings, are nearly identical in the solvent pair employed. Thus, the partition coefficients of naphthalene, phenanthrene, anthracene, and pyrene fall within the range 3.5 ± 0.2.

An increase in this partition ratio may occur under the following conditions: when the ring systems are not condensed (diphenyl); when an alkyl group is introduced into a condensed ring structure (methylnaphthalenes, 9-methylphenanthrene, and alkylcarbazoles); and when aliphatic linkages are part of the ring system (9,10-dihydrophenanthrene).

The presence of a hetero oxygen or nitrogen atom in the ring system results in a decrease in the partition coefficient. This effect is particularly striking with carbazole and probably is due in part to hydrogen bonding between the carbazole and water molecules in the aqueous alcohol phase.

The spread of partition coefficients among the compounds listed in Table I is large enough to permit separation of the components of the following mixtures by 50- to 100-plate countercurrent distributions: phenanthrene and 9-methylphenanthrene; phenanthrene and dihydrophenanthrene; naphthalene and 2-methylnaphthalene; carbazole or phenanthridine and any other polynuclear compound listed in Table I; carbazole, 1-ethylcarbazole, and 1-butylcarbazole. However, mixtures containing phenanthrene, anthracene, naphthalene, acenaphthene, fluorene, and pyrene cannot be separated.

Some exploratory experiments, employing 1-methylnaphthalene and 2-methylnaphthalene as test compounds, were carried out to find a solvent pair which would give a larger β-value than that (1.23) found for these compounds in the cyclohexane–80% ethyl alcohol system. The solvent systems thus far tested (Table II) offer no advantage over the cyclohexane–80% ethyl alcohol system. However, possibilities along this line have not been exhausted and experiments are continuing.

DETERMINATION OF PARTITION COEFFICIENTS

Cyclohexane (spectrographic grade) and 80% ethyl alcohol are mixed in the proportion 12 to 10 by volume. After equilibration, an immiscible solvent pair of equal volumes is present. Standard solutions of the polycyclic compounds made up in the cyclohexane phase are equilibrated at 25° C. with an equal volume of the aqueous alcohol layer. The partition, k, is then calculated by the expression:

$$k = \frac{C_1}{C - C_1}$$

where C and C_1 are the concentrations of polynuclear compound in the cyclohexane phase before and after equilibration, respectively. Concentrations are measured by means of optical densities obtained with the Cary recording ultraviolet spectrophotometer at wave lengths of maximal absorption.

COUNTERCURRENT DISTRIBUTION PROCEDURE

The countercurrent distributions were carried out in the 54-tube stainless steel distribution machine of Craig and Post (*5*). Cyclohexane and 80% ethyl alcohol (mutually saturated) were employed as the upper and lower phases (10 ml. of each), respectively. Only the upper phase was analyzed after distribution. In most instances, complete ultraviolet absorption spectra of the upper phase of each tube were obtained by means of the Cary recording spectrometer. From these curves, the distribution patterns were plotted.

The methods for calculating composition from countercurrent distribution data have been reported in considerable detail (*8*, *9*). Warshowsky and Schantz (*8*) have shown by specific examples how to calculate the total amount of solute in a tube from measurements on one phase in each of two adjacent tubes.

ANALYSIS OF TECHNICAL-GRADE PRODUCTS

When phenanthrene, carbazole, anthracene, or fluorene is isolated from coal tar, each compound is usually contaminated with varying amounts of one or more of the others. By countercurrent

Table II. Partition Coefficients of 1-Methylnaphthalene and 2-Methylnaphthalene in Various Systems

System	Lighter Phase	Heavier Phase	Partition Coefficient[a] 1-Methyl-naphthalene	2-Methyl-naphthalene	Ratio, β
1	Heptane	Aniline	0.62	0.68	1.10
2	Cyclohexane	98% acetic acid	1.67	1.73	1.04
3	Benzene	80% acetic acid	11.8	10.1	0.86
4	Iso-octane	87% ethyl alcohol	2.1	2.3	1.09

[a] Initial concentration, 0.5 mg./ml.

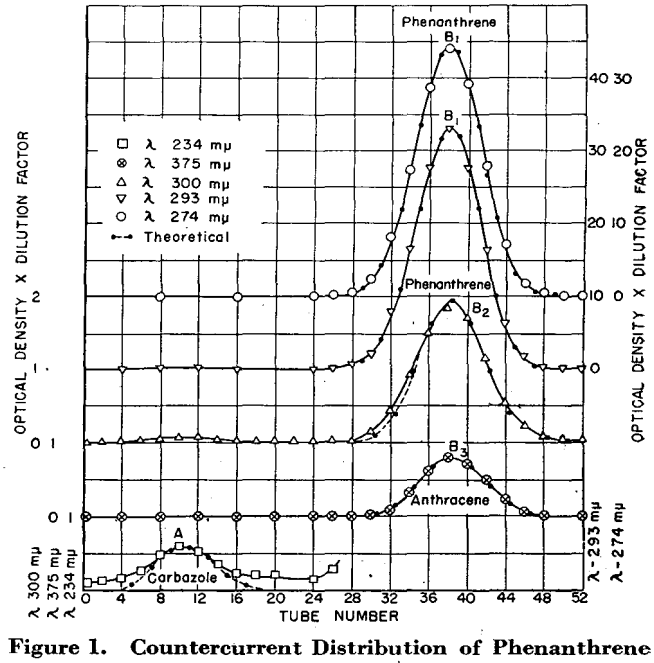

Figure 1. Countercurrent Distribution of Phenanthrene

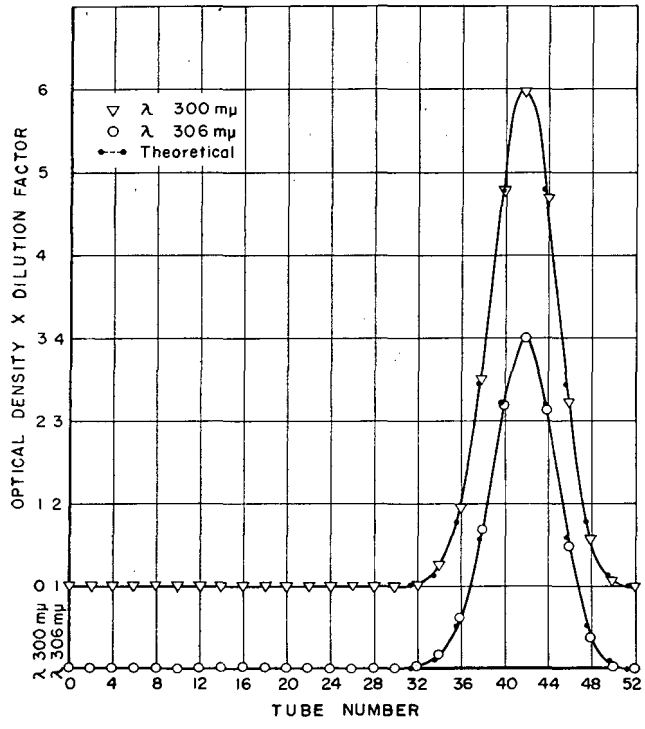

Figure 2. Countercurrent Distribution of Acenaphthene

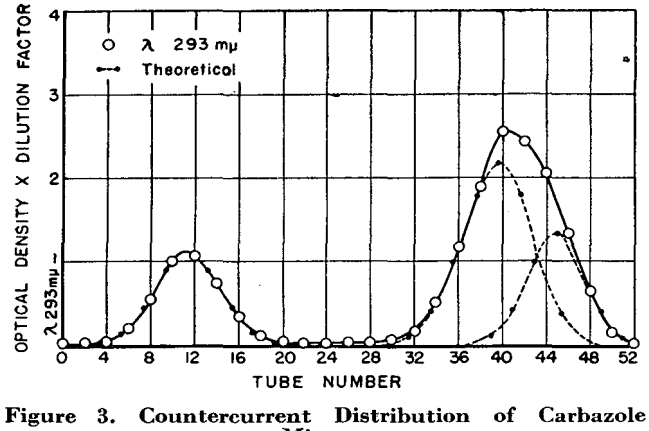

Figure 3. Countercurrent Distribution of Carbazole Mixture

distribution, the extent of such contamination can often be determined and some purification effected, if desired. In Figure 1, the results of a 53-plate distribution of a commercial sample (50 mg.) of phenanthrene (listed purity of 90%) are plotted. The distribution was conducted in the cyclohexane–80% ethyl alcohol system. The distributed sample was analyzed by ultraviolet measurements at wave lengths where the compounds suspected of being present had maximal absorption. The cyclohexane layers of tubes 4 to 16 give the ultraviolet absorption spectra of carbazole, and those of tubes 30 to 48, the ultraviolet spectra of a mixture of phenanthrene and anthracene. Theoretical distribution curves were calculated for these compounds by the method of Williamson and Craig (*9*) and were found to agree closely with the experimental ones. No appreciable amount of fluorene was present; the characteristic peaks of fluorene were not observed among the ultraviolet absorption spectra of the contents of tubes 28 to 48.

From the optical density value at the maximum of band B_1, the phenanthrene band, the amount of phenanthrene in the sample was calculated (*8*) and found to be 40.2 mg. As anticipated from the results of Table I, phenanthrene and anthracene (band B_3) did not separate; nevertheless, they could be determined in the presence of each other because anthracene, alone, has appreciable absorption at a wave length of 375 mμ. It was found that carbazole (band A) separated completely from phenanthrene and anthracene.

The carbazole and anthracene impurities calculated by the method previously described (*8*) comprised 1.9 and 4.7%, respectively; these values compare favorably with values of 1.9 and 4.8% obtained by independent methods of analysis (Table III). The observed optical density values at 300 mμ (band B_2) were higher than the sum of the densities of phenanthrene and anthracene at this wave length. If the difference is considered to be due to fluorene, a value of 1% is obtained for the fluorene content of the sample. As can be seen from the results in Table III, 98% of the weight of sample can be accounted for in the distribution analysis.

HOMOGENEITY TESTS

The use of countercurrent distribution for testing purity of polycyclic compounds is illustrated by the results obtained with acenaphthene. A commercial sample of this compound (listed purity of 98%) was distilled in vacuo through a Podbielniak column operating at an efficiency of 15 plates. That the distillate was pure acenaphthene was indicated by its physical constants and ultraviolet absorption spectrum. The results of a 53-plate distribution of 20 mg. of this material in the cyclohexane–80% ethyl alcohol system confirmed its homogeneity (Figure 2); nearly perfect agreement was obtained between experimental and theoretical curves.

SEPARATION AND ANALYSIS OF HOMOLOGS

Woolfolk, Orchin, and Storch (*10*) have shown that condensed ring structures with alkyl substituents of various lengths and types are present in the heavy-oil fraction of coal-hydrogenation product. To separate and analyze this complex mixture, a variety of methods and techniques, such as chromatography, precise fractional distillation, infrared and ultraviolet spectroscopies are necessary. The data of Table I indicate that countercurrent distribution may be a useful adjunct to these methods, inasmuch as the introduction of side chains into a condensed ring system has an appreciable effect on partition coefficient.

To illustrate this application, a mixture containing 4 mg. of carbazole, 2 mg. of 9-ethylcarbazole, and 1 mg. of 9-butylcarbazole was subjected to 53-plate distribution in the cyclohexane–80% ethyl alcohol system. Results plotted in Figure 3 show that carbazole readily separated from its homologs. Only a partial separation of ethyl- and butylcarbazole is obtained by a 53-plate distribution. Nevertheless, the theoretical curves of these components (curves 2 and 3, respectively) show that there are regions, free of overlapping bands, which can be employed for calculating the amount of each homolog. The portion of the experimental distribution pattern comprising the ethyl- and butylcarbazole

Table III. Analysis of Technical-Grade Phenanthrene

(Sample taken, 50 mg.)

Compound Determined	Amount Found, Mg.	Method
Phenanthrene	40.2	Countercurrent distribution
Anthracene	4.7	Countercurrent distribution
	4.8	Optical density at 375 mμ of original sample
Carbazole	1.9	Countercurrent distribution
	1.9	Chromatographic separation on alumina followed by ultraviolet determination
Fluorene	1.0	Countercurrent distribution
Other impurities	1.0	Countercurrent distribution
Total	48.9	

Table IV. Analysis of Carbazole Mixture

Compound	Amount Present, Mg.	Tube No.	Amount Found, Mg.	Error, %
Carbazole	4.0	12	4.15	
		13	4.12	
		14	4.06	
		Av.	4.11	+2.8
9-Ethylcarbazole	2.0	34	2.14	
		35	2.07	
		36	2.12	
		Av.	2.11	+5.5
9-Butylcarbazole	1.0	48	0.84	
		49	0.99	
		50	0.90	
		Av.	0.91	−9.0

components agrees closely with the sum of the two theoretical curves (2 and 3) calculated for these components. The agreement between calculated carbazole contents and the amounts subjected to fractionation are listed in Table IV. Although further tests would be needed to determine the limitations of the method, it is apparent that milligram amounts of carbazole and its ethyl and butyl homologs can be determined to an accuracy of 0.1 mg.

The separation of 9-ethylcarbazole and 9-butylcarbazole could have been greatly improved by use of an all-glass countercurrent distribution apparatus, which more than doubles the number of transfers that can be applied (*5*). Adjustment of the volume ratio of the two phases to the optimum value according to Bush and Densen (*2*), followed by the "completion of the square" method of fractionation, is another possible means of increasing the efficiency of separation of the homologs.

ACKNOWLEDGMENT

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Determination of Sodium and Potassium, Employing Ion-Exchange Separation

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An accurate method for determining sodium and potassium, employing ion exchange as a means of separation, is proposed. The method and results of separating sodium, potassium, and magnesium from mixtures of the three with subsequent determination of the sodium and potassium are given. Some elution variables and theoretical aspects are also considered.

ALTHOUGH the possibilities of ion exchange as a tool in inorganic analytical chemistry are many, few applications have been reported to date, and little has been reported with regard to ion-exchange separations of cations in macroquantities.

The proposed method consists essentially of two steps: separation of the sodium and potassium from each other and from all other constituents of the mixture by means of elution through a cation exchanger, and evaporation of the separate fractions of the eluate to dryness and titration of the alkali chloride residues.

This paper describes the separation of synthetic mixtures of sodium, potassium, and magnesium, and the subsequent determination of the sodium and potassium. (Of the common polyvalent cations, magnesium is the most difficult to separate from the alkalies by ion exchange, and for this reason its separation was studied.) The investigation is being continued, and the technique is being applied to silicates.

APPARATUS AND REAGENTS

The column finally selected was of borosilicate glass, 3.80 sq. cm. in cross-sectional area, containing 59.5 grams of oven-dried colloidal Dowex 50 which rested on a sintered-glass filter of medium porosity. This resin filled the column to a height of 59 cm., giving a bed volume of 224 ml. The resin was prepared for use by mixing it with about 1 liter of water, allowing the resin to settle, then decanting the liquid above the resin. This procedure was repeated five or six times until the liquid above the resin was clear. This procedure was necessary to prevent subsequent clogging of the glass filter by minute resin particles. After introduction into the column, the resin was washed with dilute hydrochloric acid to ensure complete conversion to the hydrogen form.

Preliminary experiments were performed with columns of other dimensions and Dowex 50 of other particle size.

Reagent grade sodium chloride, potassium chloride, magnesium oxide, and hydrochloric acid were used without further purification.

EXPERIMENTAL PROCEDURE

Elutions were generally performed at room temperature with 0.70 *M* hydrochloric acid at flow rates of about 0.6 ml. per minute per sq. cm. Samples containing sodium and potassium chlorides and magnesium oxide were dissolved in 5 ml. of 0.70 *M* hydrochloric acid and introduced into the column with a minimum amount of washing. The exchanger was previously saturated with the acid to be used during the elution. After introduction of the sample, and before beginning the elution, the column was drained until the level of liquid coincided with the level of the exchanger. The fractions of eluate were collected in graduated cylinders. The first 370-ml. portion of eluate was discarded. The next 160 ml. contained the sodium and the following 190 ml. contained the potassium. Under these conditions, magnesium does not appear in the eluate until at least

1100 ml. have been eluted. When as much as 36 me. of sulfate were included in the sample, it was found to be removed from the column before 180 ml. had been eluted, thus offering no interference in the separation.

The fractions were evaporated to dryness on a steam bath, and the residues were heated in an oven at 140° C. to remove most of the hydrogen chloride. The evaporations were hastened with infrared lamps. The residues, consisting of alkali chlorides and small amounts of retained hydrogen chloride, were then dissolved in water. Titration with standard base gave the amount of hydrogen chloride retained. The solutions were then analyzed by means of Mohr titrations to find the total chloride. The amount of alkali chloride was obtained from the difference between the two titrations.

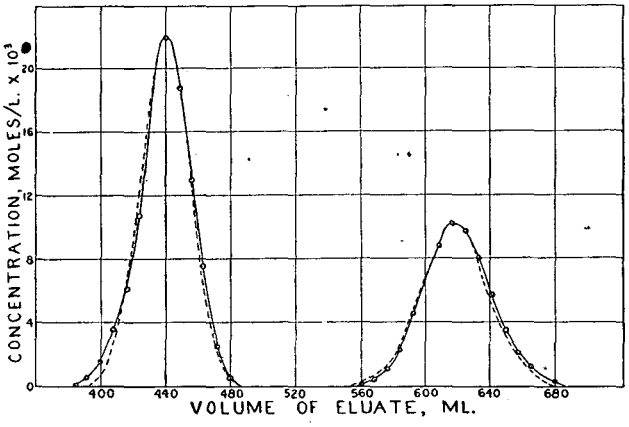

Figure 1. Elution of Sodium and Potassium

Column, 3.80 sq. cm. × 59.0 cm.
Exchanger, 59.5 grams of colloidal Dowex 50 (oven-dried basis)
Elutrient solution, 0.701 molar HCl
Flow rate, 0.60 ml./min./sq. cm.
Elution of 1.00 millimole of sodium and 0.50 millimole of potassium
Temperature, 32° C.
One V unit = 186 ml.

About 5 hours are required for an average elution (flow rate = 0.60), from the time of introduction of the mixture into the column until the completion of the potassium elution. However, very little of the analyst's attention is required during this period.

In the course of this investigation, it became desirable to known how closely equilibrium conditions were approached during elution. The symmetry of the elution curves was used as a criterion of equilibrium. These curves are obtained by plotting the concentration of alkali metal in the eluate as ordinate and volume of eluate as abscissa. The concentration of alkali metal was determined on 8-ml. fractions with a Perkin-Elmer flame photometer.

RESULTS

Typical data for the separation and recovery of sodium and potassium are listed in Table I. Typical elution graphs are shown in the solid curves of Figure 1, which illustrates both symmetry and good clear separation of the alkalies. The graphs indicate a better separation than has been attained previously by ion exchange (*2*, *3*).

Magnesium, which was varied in these mixtures from 0.5 to 0.9 me., consistently made its first appearance in the eluate at about 1100 ml.

DISCUSSION

By combining the equations of Mayer and Tompkins (*4*) with the probability equation, it can be shown that

$$U_m = CV \qquad (1)$$

$$p = 2\left(\frac{C+1}{C}\right)\left(\frac{U_m}{U_a - U_m}\right)^2 \qquad (2)$$

$$\log M = \log M_m - 0.217p\left(\frac{C}{C+1}\right)\left(\frac{U-U_m}{U_m}\right)^2 \qquad (3)$$

where M = molarity of alkali cation in any fraction of the eluate
U = volume of eluate in milliliters
M_m = maximum value of M
U_m = U when $M = M_m$
V = "free volume" or interstitial volume of the column, ml.
p = number of theoretical plates
C = "distribution ratio" of the alkali cation—i.e., ratio of the quantity of alkali cation in the resin in any plate to the quantity of alkali cation in the liquid in this plate at equilibrium

$$U_a = U \text{ when } M = \frac{M_m}{e}$$

The dashed graphs of Figure 1 were calculated by Equation 3 where C is 2.37 and 3.32, and p is 1.21×10^3 and 1.19×10^3 for sodium and potassium, respectively. These values were obtained by solving Equations 1 and 2 from the data of Figure 1. The close agreement between the solid and dashed curves indicates the validity of Equation 3 and the close approach to equilibrium conditions during the elution.

From these data, it is readily calculated that the average height of a theoretical plate is 0.048 cm. The average height per plate was not found to be constant as the column length was changed, but varied randomly from 0.04 to 0.12 cm. as the column length varied from 15 to 59 cm. Good agreement was not always obtained between the number of plates calculated from the sodium and potassium curves of a given run.

Table I. Separation and Recovery of Sodium and Potassium

(All weights expressed in milligrams)

No.	Alkali Determined	Alkali Chloride Taken in Mixture	Molar Ratio of Na to K	HCl Found in Residue	Alkali Chloride Found in Residue	Error
1	Na	351.2	3	0.4	350.9	−0.3
	K	149.3		0.4	149.4	+0.1
2	Na	350.9	3	0.4	350.7	−0.2
	K	149.1		0.3	149.5	+0.4
3	Na	349.9	3	0.2	349.4	−0.5
	K	148.1		0.2	147.9	−0.2
4	Na	58.5	2	0.1	58.7	+0.2
	K	37.7		0.1	37.7	0.0
5	Na	350.6	30	0.8	350.1	−0.5
	K	15.1		0.3	15.7	+0.6
6	Na	35.3	0.3	0.1	35.9	+0.6
	K	149.4		0.5	149.2	−0.2
7	Na	352.8	265	0.5	352.4	−0.4
	K	1.7		0.2	1.7	0.0
8	Na	3.5	0.03	0.2	3.3	−0.2
	K	149.1		0.4	149.2	+0.1

The effect of varying the flow-rate from 0.36 to 0.66 ml. per minute per sq. cm. can be seen from the results given in Table II. Variations of this order have little effect on the position and size of the fractions.

Table II. Effect of Flow Rate

Column. 3.80 sq. cm. × 58 cm.
Exchanger. 59.5 grams of colloidal Dowex 50 (oven-dried basis)
Elutrient solution. 0.709 molar hydrochloric acid
Fractions analyzed at 8-ml. intervals

Quantity Taken, Millimoles		Flow Rate, Ml./Min./Sq. Cm.	Range of Eluate Volume in Which Cation Was Detected, Ml.	
Na	K		Na	K
6.00	2.00	0.36	384 to 496	544 to 688
5.99	2.00	0.56	392 to 512	552 to 704
6.00	2.00	0.66	392 to 512	544 to 696

Table III. Effect of Temperature on Separation

Column. 3.80 sq. cm. × 14 cm.
Exchanger. 25 grams of oven-dried Dowex 50, 200 to 270-mesh
Elutrient solution. 1.00 molar hydrochloric acid

Quantity Taken, Millimoles			Flow Rate, Ml./Min./Sq. Cm.	Temp., ° C.	Range of Eluate Volume in Which Cation Was Detected, Ml.			Size of Fraction, Ml., Containing:		
Na	K	Mg			Na	K	Mg	Na	K	Mg
1.8	1.7	2.1	0.42	24	172–288	399–719	426–715	116	320	289
1.8	1.7	2.0	0.37	70	139–244	260–494	543–775	105	234	232

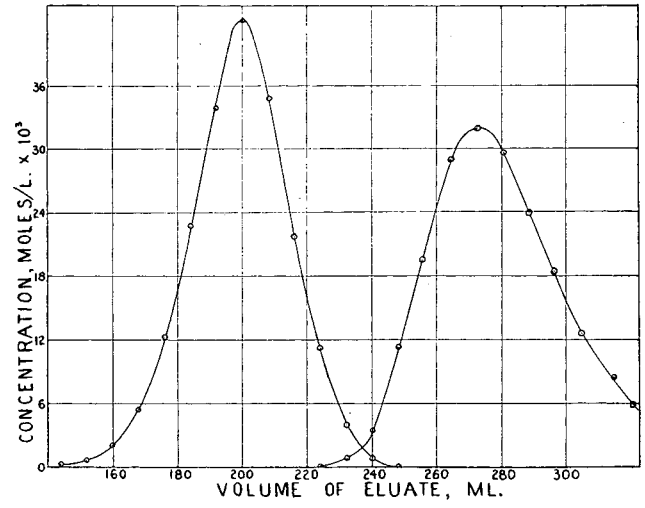

Figure 2. Elution Curves Showing Cross Contamination

Column, 3.80 sq. cm. × 21.1 cm.
Exchanger, 14.7 grams of colloidal Dowex 50 (oven-dried basis)
Elutrient solution, 0.407 molar HCl
Flow rate, 0.40 ml./min./sq. cm.
Elution of 1.80 millimoles of sodium and 1.82 millimoles of potassium
Temperature, 28° C.
One *V* unit = 70 ml.

In developing satisfactory conditions for separation, some elutions were obtained in which the two alkalies were not completely separated—i.e., a certain portion of the eluate contained both cations. One such elution is taken for consideration here to show the conformity with the method of Mayer and Tompkins (*4*) for calculating the point at which maximum cross contamination occurs. The elution considered is shown in Figure 2.

The number of theoretical plates calculated from Equation 2 is 244 and 222 for the sodium and potassium curves, respectively. The mean, 233, was used in the calculations that follow. The volume of liquid in each theoretical plate is designated by v, and n is the number of v's that have entered into a plate up to any given time. U_m is 200 ml. for sodium, and 272 ml. for potassium. Therefore, $C_{Na} = \frac{200}{70} = 2.86$ and $C_K = \frac{272}{70} = 3.88$. Substitution in Equation 8A of Mayer and Tompkins' article gives a value of $n = 800$ at the point of maximum cross contamination. As $v = V/p = 0.30$, the volume at which the maximum cross contamination occurs is $800 \times 0.30 = 240$ ml. This is in good agreement with the experimental value of 237 ml.

This investigation included the study of separations with Dowex 50 of 200- to 270-mesh. It was found that satisfactory separations, in which the eluate volumes and time required for elutions were comparable with those employing colloidal Dowex 50, could be achieved only at elevated temperatures. Elutions at elevated temperatures were performed by housing the column in a thermostatically controlled air bath. Table III shows the effect of increasing the temperature from 24° to 70° C.

Table III shows that a separation of sodium, potassium, and magnesium was achieved at 70°, while at 24° the magnesium was not separated from potassium. The sizes of the respective fractions were diminished with higher temperature. The higher temperature brings the sodium and potassium closer together, indicating an upper temperature limit for these conditions.

For a given column, the products of U_m and the molarity of elutrient acid are nearly constant for sodium and potassium; the product of U_m and the square of the molarity is nearly constant for magnesium. These relationships can be a useful guide in predicting the relative positions of the elution curve maxima after values of the constants have been evaluated from at least one run.

The equilibrium constant for the reaction

$$HR + Na^+ \rightleftharpoons NaR + H^+$$

is

$$K_{Na} = \frac{N_{NaR}\,[H^+]}{N_{HR}\,[Na^+]} \qquad (4)$$

where N denotes the mole fraction of the appropriate ion in the resin and the brackets denote molarities in the liquid phase. The distribution coefficient of sodium may be defined as

$$D_{Na} = \frac{L_R v}{L_S m} \qquad (5)$$

where L_R and L_S are the millimoles of sodium in the resin and liquid phases, respectively, when m grams of hydrogen resin are equilibrated with v ml. of solution. Substitution in Equation 4 of

$$[Na^+] = \frac{L_S}{v}$$

and

$$N_{NaR} = \frac{L_R}{Qm}$$

where Q is the capacity of the resin in milliequivalents per gram, yields

$$K_{Na} = \frac{L_R\,[H^+]v}{N_{HR}QmL_S}$$

Combination of this equation with Equation 5 yields

$$D_{Na} = K_{Na}\frac{N_{HR}\,Q}{[H^+]}$$

If the hydrogen ion concentration is sufficiently high so that N_{HR} is almost unity,

$$D_{Na} = K_{Na}\frac{Q}{[H^+]}$$

Mayer and Tompkins (*4*) have reported the following relation which applies to column behavior:

$$C_{Na} = D_{Na}\frac{M_c}{V}$$

where M_c is the mass of resin in the column. Therefore,

$$C_{Na} = K_{Na}\frac{Q}{[H^+]} \times \frac{M_c}{V} \qquad (6)$$

and analogously,

$$C_K = K_K\frac{Q}{[H^+]} \times \frac{M_c}{V} \qquad (7)$$

The capacity of the exchanger used for Figure 1 was determined as 4.77 millimoles per gram of oven-dried resin. Substitution of this value along with 0.700 for the hydrogen ion concentration and Bauman and Eichhorn's (*1*) values of 1.20 for K_{Na} and 1.50 for K_K in Equations 6 and 7 yields $C_{Na} = 2.66$ and $C_K = 3.26$. These are in fair agreement with the values

2.37 and 3.32, respectively, from the data of Figure 1. The mean values for C obtained from five other elutions are 2.39 for sodium and 3.28 for potassium, with mean deviations of 0.03 and 0.05, respectively.

CONCLUSIONS

A simple, accurate method for the separation and determination of sodium and potassium is described. The ion-exchange elution curves of sodium and potassium, under the recommended conditions, follow closely the theoretical curves based on the normal curve of error. The effects of some variables such as flow rate and temperature are shown. The relation between distribution coefficients and column behavior and the observed and calculated points of maximum cross contamination have been found to check the predictions of other authors. The success of these separations, along with the absence of tedious precipitation techniques, indicates possible application of this method to the determination of these alkalies in silicates such as glasses, clays, and feldspars.

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Iodometric Determination of Resorcinol

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This volumetric method for resorcinol is based on selective iodination in a buffered solution. Relatively few other phenols are reactive under the conditions chosen. An iodination time of 1 minute at pH 5.0 is used. Fifty milligrams of resorcinol may be determined with an accuracy of 5 parts per 1000 or 1 mg. with an accuracy of 10 parts per 1000.

METHODS for the macrodetermination of resorcinol have been based principally on bromination (*2, 3, 5–7*) or iodination reactions (*1, 4, 6*), but as used do not distinguish resorcinol from any of the other phenols. Methods based on the oxidation of resorcinol by alkaline permanganate are even less selective.

The resinous precipitate formed by the reaction of resorcinol and furfural in an acid solution forms the basis of a selective method (*9*). Phloroglucinol, pyrogallol, cresol, xylenol, and orcinol interfere. The method is not adapted to rapid determinations and requires an empirical factor. This determination may be concluded gravimetrically or volumetrically.

Resorcinol may be titrated in very dilute solutions with nitrous acid. Phenol does not interfere. The titration is continued until a permanent (30-minute) end point is obtained with starch-iodide paper. The product is 2,4-dinitroresorcinol.

The present procedure is based on the selective iodination of resorcinol in a buffered solution. Soper and Smith (*8*) have investigated the iodination of phenol as a function of pH, and conclude that the phenate ion is very much more readily iodinated than the nonionized phenol molecule. It is probable that the present method is possible because of the large ionization constant of resorcinol.

Very few of the common phenols interfere with this procedure. *m*-Dihydroxy phenols, such as phloroglucinol and orcinol, also absorb iodine and thus interfere. *o*-Dihydroxyphenols, such as catechol, interfere by the formation of exceedingly dark flocculent precipitates which obscure the end point. Catechol may be removed by the lead acetate method of Jones *et al.* (*5*).

Resorcinol samples of 50 mg. may be determined with an error of less than 5 parts per 1000 and samples of 1 mg. with an error of less than 10 parts per 1000.

REAGENTS

Iodine. A 0.1 N iodine solution was prepared by weighing 6.5 grams of iodine and 10 grams of potassium iodide into a beaker and adding 20 ml. of water. The mixture was stirred until solution was complete and then was diluted to 1 liter. The iodine solution was standardized against arsenious oxide using starch as an indicator.

Sodium Thiosulfate. A 0.1 N sodium thiosulfate solution was prepared by dissolving 24.85 grams of sodium thiosulfate in 1 liter of freshly boiled water containing 0.1 gram of sodium carbonate. It was allowed to stand in a stoppered bottle for 2 days before being standardized against potassium iodate.

Starch Solution. A 1% starch solution in distilled water containing 2% potassium iodide.

Buffer. The buffer was acetic acid–sodium acetate and was 1 molar in acetate ion. A solution of 120 ml. of acetic acid in about 1700 ml. of water was neutralized with concentrated sodium hydroxide until the pH rose to about 4.5. The solution was cooled to room temperature and the neutralization was continued with dilute sodium hydroxide until the pH rose to 5.0. The buffer is stored in a rubber-stoppered bottle and the pH should be frequently rechecked.

PROCEDURE

A sample containing about 0.05 gram of resorcinol is dissolved in a little water and 50 ml. of buffer are added. Fifty milliliters of 0.1 N iodine are added from a pipet. After 1 minute the excess iodine is titrated with standard 0.1 N sodium thiosulfate and starch.

CALCULATIONS

Because the reaction is

$$C_6H_4(OH)_2 + 3I_3 \longrightarrow C_6HI_3(OH)_2 + 3HI$$

the equivalent weight of resorcinol is one sixth of the molecular weight or 18.35.

Then

$$\%\ \text{resorcinol} = \frac{(B - T) \times N \times 1.835}{S}$$

where B = ml. of sodium thiosulfate required for 50 ml. of iodine
T = ml. of sodium thiosulfate used in titration
N = normality of sodium thiosulfate
S = weight of sample

EXPERIMENTAL

Effect of pH on Rate of Reaction. A series of determinations was made in which the reaction time and the pH were varied.

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Table I. Effect of pH on Rate of Iodination of Resorcinol

pH of Buffer	Reaction Time, Minutes	Resorcinol Reacted, %
2.p	1.00	11.4
2.0	2.00	16.9
2.0	4.00	24.8
3.5	0.50	37.5
3.5	1.00	41.3
3.5	2.00	48.2
3.5	4.00	55.7
3.5	7.00	65.9
4.0	0.50	58.5
4.0	1.00	70.8
4.0	2.00	84.1
4.0	4.00	94.9
4.0	7.00	98.6
4.5	0.50	89.1
4.5	1.00	97.2
4.5	2.00	100.0
4.5	6.00	100.0
5.0	0.50	100.4

The amount of resorcinol taken remained fixed at 2.725 milliequivalents. The temperature was 25.0° ± 0.1° C. The iodine added was 5.450 me., an excess of 100%. Results of these experiments (Table I, Figure 1) show that an iodination time of 30 seconds at pH 5.0 is sufficient. The iodination time of 1 minute, suggested in the procedure, was chosen to eliminate the necessity of actually timing the reaction.

Effect of Temperature on Rate of Iodination of Resorcinol. A pH of 4.0 was chosen for this series in order to show the effect of temperature over a wider range.

The resorcinol used was 2.725 me. An iodination time of 1.00 minute and a 100% excess of iodine were used. The results are found in Table II.

Effect of Other Phenols. Using the suggested procedure determinations were made in the presence of an equal amount of the second phenol (Table III).

Table II. Effect of Temperature on Rate of Iodination of Resorcinol

Temp., ° C.	Resorcinol Reacted, %
12.0	41.6
25.0	72.5
28.5	77.4
39.5	99.5

Table III. Effect of Certain Other Phenols on Determination of Resorcinol

Other Phenol	Resorcinol Reacted, %
Phenol	99.8
Mixed cresols	100.0
o-Phenylphenol	99.9
p-Phenylphenol	100.0
o-*tert*-Butylphenol	100.0
p-*tert*-Butylphenol	100.0
p-*tert*-Amylphenol	100.0
Catechol	Color too dark to see end point
Hydroquinone[a]	100.4
Pyrogallol	Color too dark to see end point
Phloroglucinol	Color too dark to see end point

[a] Modification described in discussion was used.

DISCUSSION

As shown in Table I, iodination is complete in 1 minute at any pH over 4.5. The pH 5.0 was selected for two reasons. Small changes in pH of the buffer in general cause large changes in the rate of reaction, but this is not true at 5.0. The iodination time is less critical at pH 5.0.

As shown in Table II, a change in temperature of 10° C. causes a change in the rate of reaction of about 25% under these conditions. Because a 1-minute iodination time is used, which is twice as long as is necessary, any room temperature should be suitable.

The iodination time need not be measured, but it is advisable not to allow much more than 1 minute. At too high a pH or too long a time the precipitate becomes dark red through aristol formation and the end point is difficult to see.

In the presence of hydroquinone a modification in the procedure is necessary. The hydroquinone consumes iodine under these conditions. This iodine, however, may be recovered by making the sample strongly acid with hydrochloric acid after the normal iodination period. After 1 minute's contact with the acid the sample is titrated in the normal manner.

Phloroglucinol, pyrogallol, orcinol, and the other *m*-dihydroxyphenols interfere through iodination and usually through aristol formation also.

In the presence of catechol a different type of interference occurs. A blue-black precipitate forms when resorcinol is iodinated in the presence of catechol. The catechol may be removed prior to iodination by the lead acetate method of Jones *et al.* (*5*).

Ten milliliters of freshly filtered 4% lead acetate are added to a sample containing not more than 0.05 gram of catechol. After 30 minutes the precipitate is filtered on a fine paper and washed five times with small portions of distilled water. The filtrate is buffered and iodinated in the normal manner. Ten milliliters of concentrated hydrochloric acid are added just prior to titration and a correction of 0.05 ml. is subtracted from the titration. With this procedure it is possible to determine resorcinol in the presence of an equal amount of catechol with an error of less than 1 part per 100.

Milligram samples of resorcinol may be determined by this method using 0.01 *N* iodine and thiosulfate. Five milliliters of buffer are used and a 10-ml. buret is used for the thiosulfate. The error on a 1-mg. sample is less than 1 part per 100.

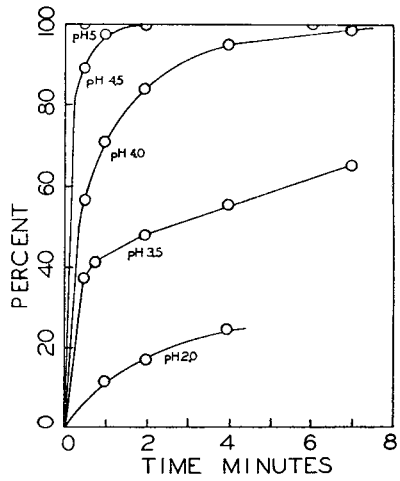

Figure 1. Effect of pH on Iodination

Erratic results obtained with any of these procedures usually mean incomplete reaction. This may be caused by too low a pH, too little buffer, too small an excess of iodine, or too short an iodination period. A very red precipitate means too high a pH, too long an iodination time, or too high a temperature.

This method has been used for 2 years in an industrial laboratory as a routine control method where it has proved to be of satisfactory value in the hands of experienced analysts.

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Improved Equipment for Engler-Type Distillations

Internal Electric Heater

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Distillation range is an important measure of purity or of general composition for many materials, particularly coal tar and petroleum distillates and various organic chemical intermediates. To minimize fire hazard and improve the laboratory efficiency of the distillation tests, an internal type of electric immersion heater was developed and is described. Excellent agreement has been obtained between distillation range tests conducted with this heater and those where gas is used as the heating source.

DISTILLATION range is an important measure of purity or general composition for many materials. It is of particular importance for coal tar and petroleum distillates and various organic chemical intermediates. Generally accepted methods for the determination of distillation range, such as that of the American Society for Testing Materials (*1–3*), use external heating sources such as a gas flame or an external electric resistance heater. Of the two, the gas flame is by far the more common. Heating by either of these methods is potentially hazardous because flask breakage may cause a laboratory fire or hydrocarbon vapors may be ignited when the tests are carried out in close proximity to production units. In order to minimize fire hazard and improve the laboratory efficiency of the distillation tests, an internal type of electric immersion heater was developed. The method described herein was developed primarily for the distillation of aromatic hydrocarbons, but has been found equally reliable for the distillation of petroleum distillates and organic chemical intermediates.

Excellent agreement in results is obtained between distillation range tests conducted with the internal electric resistance heater described herein and those where gas is used as the heating source. The internal electric immersion heater has three major advantages over external heating sources.

Efficiency. It is possible for as many as four tests to be run simultaneously by the same operator by properly staggering distillations. This contrasts with the relative difficulty encountered by the operator in adjusting the gas burner when test of only one distillation range is being conducted. With the electric immersion-type heater the adjustable autotransformer or rheostat can be set to a predetermined position and the distillation then allowed to proceed without further adjustment or periodic checking on the rate of distillation for a given material. The particular setting is established by the latent heat of vaporization and boiling temperature; the former determines the theoretical heat input, while the latter is the chief factor contributing to heat loss which must also be made up by the heater.

End or Dry Point. A very distinct and sharp dry point is ob-

Table I. Distillation Range Test of Benzene (° C.)

Material	Test	1st Drop	1 Ml.	2.5 Ml.	5 Ml.	10 Ml.	50 Ml.	90 Ml.	95 Ml.	Dry	Over-all Range
Benzene A	Electric										
	1	79.5	79.6	79.7	79.9	80.0	80.1	80.2	80.2	80.3	0.8
	2	79.5	79.6	79.7	79.9	79.9	80.1	80.2	80.2	80.2	0.7
	A.S.T.M. gas										
	1	79.6	79.7	79.8	79.9	80.0	80.1	80.2	80.2	80.3	0.7
	2	79.4	79.5	79.7	79.9	80.0	80.1	80.1	80.1	80.2	0.8
Benzene B	Electric										
	1	79.4	79.5	79.7	79.9	80.0	80.1	80.2	80.2	80.3	0.9
	2	79.4	79.5	79.7	79.8	79.9	80.0	80.1	80.2	80.3	0.9
	A.S.T.M. gas										
	1	79.5	79.7	79.8	79.9	80.0	80.1	80.2	80.2	80.3	0.8
	2	79.4	79.5	79.7	79.9	80.0	80.1	80.1	80.1	80.2	0.8

Table II. Distillation Range Test of Toluene and Xylene

Material	Test	1st Drop	1 Ml.	2.5 Ml.	5 Ml.	10 Ml.	50 Ml.	90 Ml.	95 Ml.	Dry	Over-all Range
Toluene 6,9415	Electric										
	1	110.0	110.1	110.2	110.3	110.4	110.6	110.7	110.8	110.9	0.9
	2	110.1	110.2	110.3	110.4	110.5	110.6	110.7	110.8	110.9	0.8
	A.S.T.M. gas										
	1	110.0	110.2	110.3	110.4	110.5	110.6	110.7	110.7	110.9	0.9
	2	110.1	110.2	110.4	110.5	110.5	110.6	110.7	110.8	110.9	0.8
Toluene 6,9400	Electric	110.2	110.3	110.4	110.4	110.5	110.6	110.7	110.8	110.8	0.6
	A.S.T.M. gas	110.2	110.3	110.4	110.4	110.5	110.6	110.7	110.7	110.8	0.6
Toluene 6,23664	Electric	110.2	110.3	110.4	110.4	110.5	110.6	110.7	110.8	110.9	0.7
	A.S.T.M. gas	110.3	110.4	110.4	110.5	110.5	110.6	110.7	110.8	111.0	0.7
Toluene SHPx10230	Electric	110.0	110.1	110.2	110.3	110.4	110.6	110.7	110.7	110.8	0.8
	A.S.T.M. gas	109.9	110.0	110.1	110.3	110.3	110.6	110.7	110.7	110.7	0.8
Xylene 393	Electric	138.3	138.5	138.6	138.7	138.8	139.0	139.6	139.8	140.3	2.0
	A.S.T.M. gas	138.3	138.4	138.7	138.8	138.9	139.3	139.9	140.2	140.4	2.1
Xylene 413	Electric	137.8	137.9	138.2	138.4	138.5	139.0	139.6	140.0	140.4	2.6
	A.S.T.M. gas	137.6	138.1	138.3	138.4	138.5	139.1	139.7	140.1	140.3	2.7
Xylene 451	Electric	130.8	131.4	132.2	132.7	133.2	136.7	140.3	141.1	142.3	11.5
	A.S.T.M. gas	131.5	132.2	132.6	133.1	133.7	136.7	140.2	140.9	142.7	11.2

Table III. Distillation Range Tests

Material	Test	1st Drop	1 Ml.	2.5 Ml.	5 Ml.	10 Ml.	50 Ml.	90 Ml.	95 Ml.	Dry	Over-all Range
Chloroform	Electric	60.25	60.42	60.56	60.80	..	61.26	..	..	61.51	1.3
	A.S.T.M. gas	60.21	60.31	60.41	60.76	..	61.26	..	..	61.49	1.3
Ethyl alcohol	Electric	78.50	78.50	78.50	78.50	..	78.59	..	78.90	79.1	0.60
	A.S.T.M. gas	78.50	78.50	78.50	78.53	..	78.57	..	78.70	78.9	0.40
Aniline	Electric	183.86	184.18	184.29	184.34	..	184.40	..	184.54	185.16	1.3
	A.S.T.M. gas	183.95	184.21	184.28	184.33	..	184.40	..	184.46	185.30	1.4
Dimethyl-aniline	Electric	193.29	193.35	193.39	193.41	..	193.50	..	193.86	195.10	1.8
	A.S.T.M. gas	193.37	193.43	193.47	193.50	..	193.50	..	193.81	195.25	1.9
Diethyl-aniline	Electric	216.23	216.36	216.60	216.68	..	216.80	..	216.89	217.05	0.8
	A.S.T.M. gas	216.38	216.43	216.66	216.71	..	216.80	..	216.85	217.05	0.7
Monoethyl-aniline	Electric	204.44	204.48	204.51	204.61	..	204.70	..	205.25	205.30	1.9
	A.S.T.M. gas	204.37	204.50	204.55	204.58	..	204.70	..	205.28	206.30	1.9
Carbon tetra-chloride	Electric	76.54	76.64	76.66	76.69	..	76.75	..	..	77.02	0.50

tained with the electric immersion heater. Practically all superheating effects, so common with the gas method of heating, are absent. When the dry point is reached the heat supply can be shut off instantly. The end point is much sharper, and the distillation flask is not overheated at the end of the test.

Safety. There is far less danger of flask breakage, because the temperature extremes across the glass between the heating source and the boiling liquid are absent. Heat is transferred directly from the heating source to the boiling liquid. If a flask breaks when the immersion heater is being used, the boiling liquid falls to the bottom of the enclosing insulating jacket, and not to the hot heating surface where air would be available for combustion. With the internal electrical heater the heat input can be stopped immediately, whereas with other methods of heating, there is considerable heat stored in either the burner or the electric resistance heating unit.

DISCUSSION OF DATA

Tables I, II, and III show the excellent agreement that is obtained in distillation range tests conducted with the electrical immersion-type heater and the conventional gas heating method.

In Table I duplicate tests on two different benzene samples are compared. The reproducibility is excellent, the maximum deviation being only 0.1° C. in boiling range.

In Table II, similar comparative data are given for toluene and xylene. The greatest difference between the two methods in these tests is only 0.1° C.

In Table III, data are given for various industrial organic chemicals, many of which boil as high as 200° C. Here again, agreement is excellent, the maximum deviation being 0.2° C. for ethyl alcohol.

These results fall well within the range usually allowed for distillation range tests. With the gas heating method it is difficult to obtain results where the over-all range does not differ by at least 0.1° C. for duplicate tests on the same material (*4*).

The thermal efficiency of the distillation setup using the electrical immersion type of heater is high. However, as the boiling point of the material being tested rises, the heat loss becomes greater and the thermal efficiency falls.

Thermal equivalent of electrical input equals heat of vaporization plus heat losses.

Data are given in Table IV for a test on thermal efficiency when benzene was tested.

A glass shield insulates the distillation flask from air currents within the room, and eliminates much of the convection difficulties associated with the gas flame type of heating. Convection currents around the insulating jacket are greatly reduced, because the heating source is located within the flask. The temperature of the flask surface is no higher than that of the boiling liquid. The air around the flask within the jacket serves as an excellent insulator, being of low specific heat and low conductivity.

For a definite material with the same boiling point and the same latent heat of vaporization, the electrical heating requirement is approximately the same from one test to the next. This permits preadjustment of the autotransformer to the exact position for the required heat input and thereby eliminates much of the attention and adjustment required with other methods of heating. A very considerable increase in the operator's efficiency is thus obtained. By properly staggering the distillation range tests, one operator can conduct as many as four tests simultaneously.

As will be noted in Table III, there is no noticeable difference in results between the tests heated externally by gas and those heated internally by electricity, even up to temperatures as high as 217° C. (diethylaniline boiling point). This indicates that the increased heat loss at higher temperatures and any accompanying refluxing on the neck of the flask have little effect in so far as difference between the two methods of heating is concerned. At temperatures below 150° C., the glass jacket is not essential to obtaining comparable results between the electrical immersion and the gas heaters. The thermal efficiency is obviously less when no jacket is used for the distillation.

It has been found impossible to obtain the correct rate of distillation (5 to 7 ml. per minute) for liquids which have high

Table IV. Thermal Efficiency of Electrical Immersion Heater

Liquid	Boiling Point, ° C.	Heat Input		Heat of Vaporization, Cal./min.	Efficiency, %
		Watts	Cal./min.		
Benzene	80.1	48.8	700	560	84.2

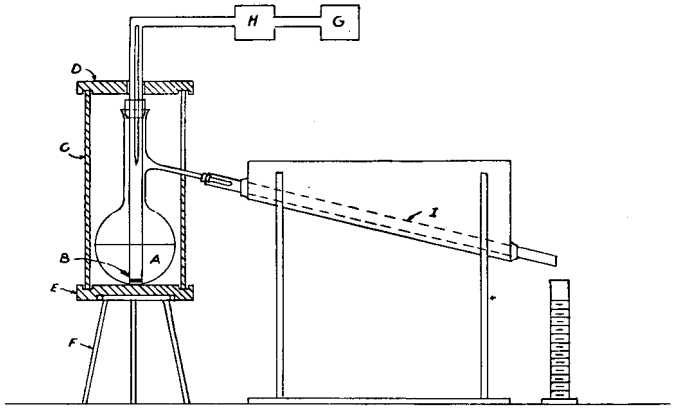

Figure 1. Diagram of Equipment Assembly

A. 200-ml. distillation flask
B. Immersion heater (see Figure 2)
C. Glass shield
D. Split Transite top disk
E. Bottom Transite disk
F. Tripod
G. Autotransformer, 5 amperes, 110 volts
H. Stepdown transformer, 115 to 7 volts
I. A.S.T.M. condenser

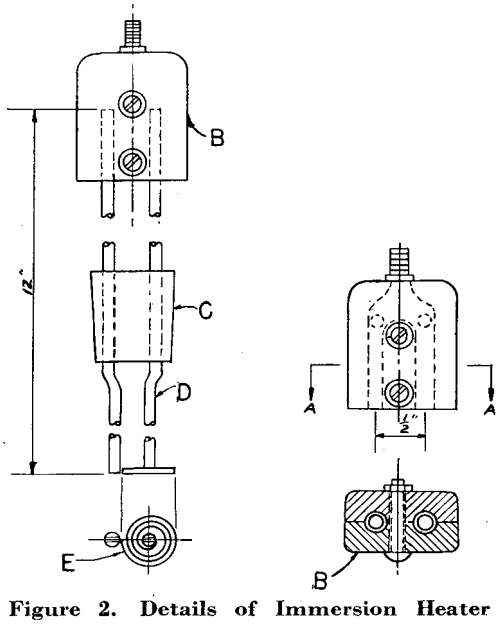

Figure 2. Details of Immersion Heater

A. Cross section
B. Appliance plug
C. Cork
D. 0.125-inch bronze welding rod 12 inches long
E. Nichrome resistance tape, 8 inches long, 6 turns. 0.0253 × 0.625 inch heating element

latent heats of vaporization and/or which tend to vapor-seal over the heating element and thereby very appreciably decrease the rate of heat transfer to the boiling liquid. Difficulty has been encountered with water and methanol in this respect, but not with any of the other materials tested.

The internal heater is not recommended for the distillation of materials that leave appreciable residues of pitch or tar. Materials that are thermally unstable may be decomposed or polymerized, owing to the high local temperature of the heating element. No difficulty has been encountered with any of the normal coal tar or petroleum distillates or organic chemical intermediates tested.

APPARATUS

The general assembly of the distillation apparatus is shown in Figure 1. It differs basically from the standard A.S.T.M. methods (*1*, *3*) in the mode of heating and the method of insulating the flask.

Immersion Heater. The detail of the immersion heater is shown in Figure 2. The heating element is made of Nichrome resistance tape, 0.0253 by 0.0625 inch, with a resistance of 0.35 ohm per foot. The ends of the resistance tape are brazed to the two leads made of 0.125-inch bronze welding rods, No. 25, 12 inches long. The two leads are held in position and are connected to the electrical circuit by the receptacle table shown in Figure 2.

Electrical Control. The electrical input to the immersion heater is controlled by a variable-adjustment autotransformer followed by a fixed-ratio stepdown transformer. For these tests, a 5-ampere Variac autotransformer with a scale from 0 to 135 was used on the 110-volt alternating current supply circuit, followed by a fixed-ratio 115-volt to 7-volt stepdown transformer. For ordinary laboratory distillation the equipment setup shown in Figure 1 is used. For location in hazardous areas both the autotransformer and the fixed ratio stepdown transformer are oil-immersed and situated in a common steel box. In so far as possible, all wiring is made to conform to explosionproof requirements.

A rheostat may be used as a substitute for the autotransformer. However, the large amount of heat that must be dissipated is a distinct disadvantage with the rheostat.

Distillation Flask. A 200-ml. distillation flask is used (*4*). No attempt has been made to apply the procedure using the A.S.T.M. D-86-46 flask (*2*). The authors believe that such an application is feasible if the heating element is modified slightly.

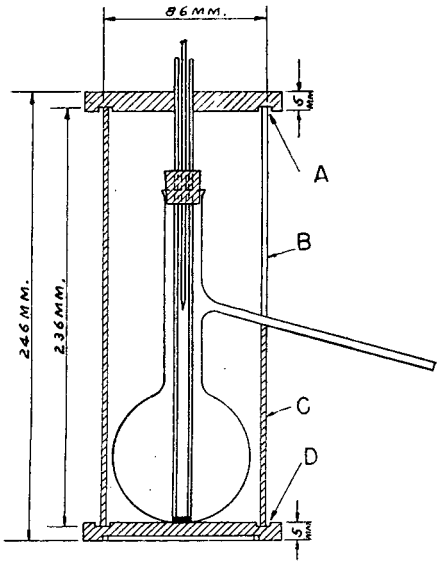

Figure 3. Details of Flask Assembly

A. Split Transite disk groove, 4 mm. wide and 1 mm. deep
B. Groove in glass shield, 12.4 mm. long and 10 mm. wide
C. Glass shield
D. Transite disk groove, 4 mm. wide and 1 mm. deep

Insulating Jacket. The distillation flask is centered within the insulating glass jacket shown in Figure 3, supported by a short length of 1-inch (2.5-cm.) inside diameter borosilicate glass tubing, fire polished and rounded on the ends. The cylinder is made of borosilicate glass 86 mm. in diameter by 236 mm. long, closed at the bottom end. A slit 4.5 inches long extends down from the top to accommodate the vapor take-off line leading to the condenser.

The glass insulating shield fits into a circular cutout section in a disk of 0.75-inch Transite. The Transite bottom disk sits on top of an ordinary laboratory tripod. The top of the glass cylinder is closed by a split 0.25-inch Transite disk with a hole in the center to allow the thermometer and the lead wires to pass through. A circular groove is cut in the split disk to fit over the insulating shield, thus ensuring close fit.

In place of the open-end cylinder shown in Figure 3, a further refinement is the use of a glass cylinder with the bottom end closed. In case of breakage of the distillation flask the contents are thus retained in the insulating jacket.

The remainder of the apparatus is essentially the same as that described in the standard A.S.T.M. methods (*1*, *3*).

Thermometer. A.S.T.M. thermometers of the desired range are used.

Condenser. The condenser tube is made of glass, being approximately 610 mm. long and having an inside diameter of 12 mm. It is mounted in a conventional cooling trough, 16 inches long inside and 6 inches wide, to which it is sealed with suitable corks. Condenser water ranging between 10° and 20° C. is used.

Receiver. A calibrated 100-ml. cylinder, graduated in single milliliters, is used. This is the same graduate used to measure out the 100-ml. distillate sample.

OPERATION

The distillation apparatus is assembled as shown in Figure 1. Operation is patterned after that of the A.S.T.M. method for aromatic hydrocarbons.

The distillation thermometer is adjusted in the cork at the top of the neck of the flask, so that the top of the expansion bulb is level with the lowest point of the side arm of the flask. The leads on the immersion heating element are adjusted in the same cork used for the thermometer, so that the heating coil rests flat on the bottom at the center of the flask. The thermometer is centered and does not touch the bronze heating leads. The heating leads must not touch the side of the flask.

A 100-ml. sample of the material to be tested is measured into a clean, dry 100-ml. graduated cylinder. The contents are carefully transferred to the distillation flask, allowing at least 15 seconds for complete drainage.

The flask is next connected securely to the end of the condenser tube through a cork, after which the insulating jacket and the flask-supporting glass section are fitted up from the bottom around the flask. The previously adjusted tripod shield and the entire assembly are centered and adjusted; the distillation flask must be centered and must not touch the walls of the insulating jacket.

The 100-ml. graduated cylinder used to measure out the sample is placed under the discharge end of the condenser tube to receive the distillate.

The cork containing the distillation thermometer and the immersion heater leads is fitted into the neck of the flask. (The thermometer must touch neither the leads nor the sides of the flask.)

The autotransformer is adjusted to a predetermined setting for the particular material or test being run. This setting must be sufficient to have the flask contents boiling within 3 to 3.5 minutes. As soon as ebullition has begun, the electrical input control is readjusted so that the ring of condensing vapor on the wall of the flask reaches the lower edge of the side arm in not less than 90 seconds, and preferably at 120 seconds.

As soon as the distillation starts the heater is again adjusted to a predetermined setting, so that a distillation rate of 5 to 7 ml. per minute (about 2 drops per second) is obtained. This rate is maintained to dryness.

Temperature readings are recorded when the first drop falls from the condenser tube discharge and when 5, 10, 50, 90, and 95% of the material have distilled over. In the case of material of wide boiling range, readings are made each 10 to 90%. A final temperature reading, the dry point, is taken just as the liquid disappears from the bottom of the flask. In the case of crude materials, a decomposition point rather than a dry point may be obtained. At the decomposition point the tempera-

ture ceases to rise and then begins to fall. The decomposition temperature is considered to be the maximum temperature reached. With the electric immersion heater these end points are very sharp.

SUMMARY

The internal electric immersion heater and the external gas method of heating gave the same distillation test results when used for aromatic compounds boiling below 220° C. Excellent agreement was obtained for many industrial organic chemicals, such as aniline, dimethylaniline, diethylaniline, nitrobenzene, chloroform, carbon tetrachloride, and ethyl alcohol.

In the internal electrical heater, the chemist has a tool for standard empirical distillation tests which is more efficient and safer and gives more precise end points than the commonly used external gas heater. The uniformity of vaporization made possible by the ease and exactness of adjustment assures reproducibility of results, while the ease of operation permits a high labor efficiency in analytical laboratories.

The electrical immersion heater has been used for Engler distillation tests at the Calco Division of the American Cyanamid Company for over 13 years.

This modified distillation apparatus may also be used with petroleum products. Such an application is logical, but no attempt has been made to construct a heater for the 125-ml. flask commonly used by the petroleum industry.

ACKNOWLEDGMENT

Acknowledgment is made to G. L. Berry and A. P. Beardsley, who first conceived of the use of internal heater as an analytical tool, when it was necessary to avoid the use of gas in light oil production units.

Credit is due to H. J. Rodenberger, who contributed to the development of the electrical immersion heater on many chemicals other than light oil products.

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Preparation of Iridosmine for Analysis by Dry Chlorination

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The corrosive action of dry chlorine on refractory platiniferous alloys at high temperatures, in the presence of sodium chloride, is shown to be an efficient means of conversion to soluble products and introduces a minimum of impurities. A new procedure for the gravimetric microdetermination of iridium is outlined, and has been found capable of good precision.

THE analysis of platiniferous materials is frequently hindered by the lack of an effective solvent. In the ordinary course of fire assay, residues that resist corrosion by aqua regia are generally classified as iridosmine or iridium. Caustic fusions attack some of these refractory materials but invariably introduce large amounts of undesirable metallic impurities such as gold, silver, nickel, iron, sodium, and barium, depending on the composition of the vessel and flux. Furthermore, the authors have found that certain naturally occurring alloys such as Tasmanian iridosmine are not attacked by caustic agents under the most drastic conditions, despite the claims of Leidie (*9*) and Zvyaginzev (*16*). Deville (*2*), Karpov (*8*) and Gilchrist (*4*) have advocated a preliminary fusion with zinc or lead, followed by leaching with acid, as a means of obtaining the noble metal in a more finely divided and reactive state. These methods necessarily leave the material contaminated by significant amounts of the foreign metal.

During the present investigation, a new procedure was developed for the complete corrosion of Tasmanian iridosmine in gaseous chlorine, in the presence and absence of sodium chloride. Although the reaction has been described previously by many authors, there is no record that it was ever before used successfully for the complete conversion of this highly resistant alloy to soluble products. The present procedure accomplished this in one operation with a specimen which had been found to resist corrosion by all conventional methods, under the most severe conditions. The authors' method was incorporated into a gravimetric microprocedure for the determination of iridium by hydrolytic precipitation. The individual reactions to chlorination of other members of the platinum group and a few minerals were observed, and indicated that the method is generally applicable to all refractory platinum residues.

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Recently, Wichers (*7*, *13*) has recommended a new alternative procedure for the corrosion of such "insoluble" alloys, establishing its ability to corrode pure iridium. As this macromethod of wet chlorination in sealed glass tubes also avoids the more undesirable features of caustic fusion, the authors undertook to compare it with dry chlorination on a semimicro scale, in determining known amounts of iridium metal. Both methods yielded quantitative results; the authors' procedure showed slightly better precision, under the conditions described.

APPARATUS AND CORROSION PROCEDURE

Boat Method. The apparatus used for all dry chlorinations is shown in Figure 1. It consisted of a U-shaped silica tube of 1-inch (2.5-cm.) bore with one end drawn out to a diameter of $^9/_{16}$ inch for a length of 4 inches. The bottom of the tube was flattened at the construction, to permit horizontal introduction of a boat without spilling the contents. This elongated section and about 3 inches of the shoulder projected from a rheostat-controlled electric muffle furnace in which the tube was heated. The door of the muffle was of Transite board, cut to fit the tube and split to permit its easy removal. A flat, ground joint connected the silica tube to a short, right-angled borosilicate glass adapter, held tightly in place by twine looped over projecting hooks on either side. The upper portion of Figure 1 represents a horizontal plane, while the portion below the broken line is to be considered as a vertical projection.

Cylinder chlorine was dried by first bubbling it through two successive towers, each containing 30 ml. of 98% sulfuric acid, then passing it over a freshly exposed surface of phosphorus pentoxide before introduction at the shorter end of the ignition tube. Chlorine and associated vapors issuing from the other end were led through a train of absorbing solutions, usually 50-ml. portions of 1 to 1 hydrochloric acid.

In each determination, the metallic sample was weighed directly into a micro porcelain boat, $^5/_8$ inch in length. Any sodium chloride to be added was weighed on glazed paper and transferred to the boat so that it covered all of the metal. Experiment showed this convenient method to be particularly

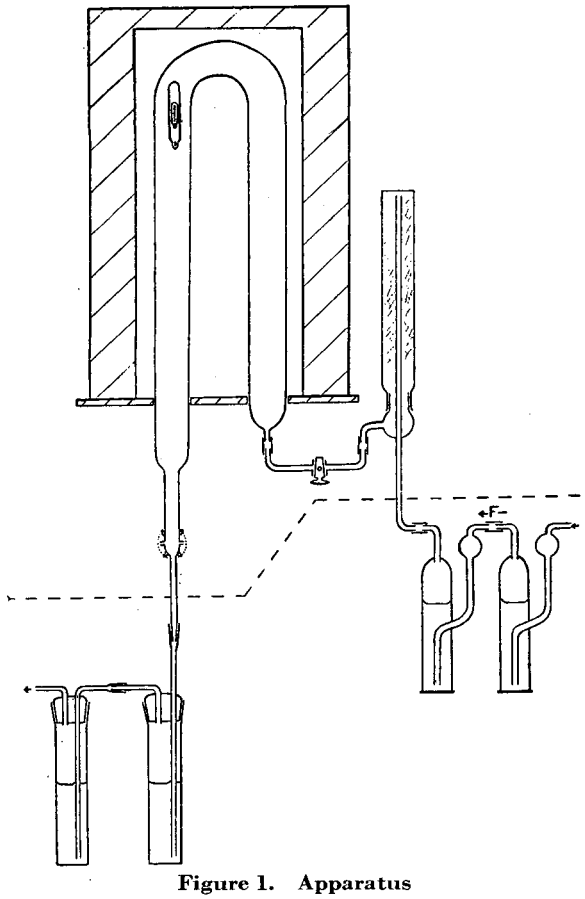

Figure 1. Apparatus

suitable for the handling of micro quantities, where trituration with salt and subsequent transfer of the reaction mixture to the boat, as recommended by Wöhler (*14*) and Claus (*1*), are likely to result in significant losses of material. The boat and charge were supported in a larger porcelain boat and inserted well to the back of the cold ignition tube, which was then flushed with chlorine and placed in the preheated muffle. The receiving train was connected, and passage of chlorine was commenced immediately, to avoid oxide formation. At the end of the reaction period, the silica tube was closed and removed from the furnace, allowing the contents to cool in an atmosphere of chlorine.

Bomb Method. For wet chlorination of iridium by the Wichers method, the reaction vessels were sealed borosilicate glass tubes of 5-mm. outer diameter and 3-mm. bore. Twenty-centimeter lengths, 1.65 ml. in capacity, were charged with 1.00 ml. of hydrochloric acid and 21.0 mg. of sodium chlorate, quantities based on the data recorded by Wichers on tube strengths and internal pressures (*7*) and optimum ratios of oxidant to hydrochloric acid (*13*). The technique of filling consisted in transferring the weighed sample of metal from a square of glazed paper into the tube, which had previously been sealed at one end. The acid was added by pipet, and the tube was cooled in dry ice to freeze the liquid contents. Sodium chlorate was added from a piece of glazed paper, and the tube was kept in a small cylinder of dry ice while the open end was sealed in the flame of a blast lamp.

The tubes were enclosed in asbestos-lined metal shields during oven-heating, as recommended by Wichers (*13*).

CHLORINATION OF ELEMENTS

The preliminary step, before chlorination of complex minerals and concentrates, was to establish the behavior of the individual constituents. For this purpose, reagent grade metals, obtained from the Baker Platinum Company, were chosen, except where otherwise specified. The receiving solutions were two 50-ml. portions of 1 to 1 hydrochloric acid, saturated with sulfur dioxide in the case of osmium, to ensure retention of volatile products.

Two sets of experiments are summarized in Table I. In one series, the pure metal was exposed to chlorine alone, while in the other it was first covered with dry sodium chloride.

Qualitative examination was made of the products of reaction left in the boat, deposited as sublimate on the cooler end of the ignition tube, and retained in the receivers. The tube deposit was easily removed by rinsing with dilute hydrochloric acid. The metals were detected by various tests, identified in parentheses in Table I.

(*a*) **For Iridium.** The solution was evaporated on the steam bath to 1-ml. volume, before applying Pollard's test (*10*), using perchloric acid and acid lithium sulfate. The authors found it sensitive to 0.005 mg. of iridium; the confirmatory test with dichlorobenzidine would detect 0.002 mg., but was less specific.

(*b*) **For Osmium.** The receiving solutions were concentrated, separately, by evaporation over steam to 1 ml., then 1 ml. of thiourea reagent solution was added and heating was continued for a few minutes. A pink color developed in the presence of osmium. The reagent solution was prepared by dissolving 25 grams of solid thiourea in 250 ml. of hydrochloric acid, and diluting to 1 liter.

(*c*) **For Ruthenium.** To the sample, concentrated to 0.5 ml. by evaporation over steam, was added 1 ml. of thiourea–

Table I. Products of Chlorination of Various Elements[a]

Element	Material Mg.	Material State	NaCl Added	Time, Hours	Temp., °C.	Composition of Soluble Products: Boat residue	Tube deposit	Receiving solution
Ir	1.585	Reduction residue	No	24	660–720	Ir^{++} (*v*) (insol.)	Ir^{+} (*s*)	1st, Ir^{-} (*s*) 2nd, Ir^{-} (*s*)
	3.810	Sponge	Yes	8	680–720	Ir^{+} (*s*), Ir^{+++} (*v*)	Ir^{+} (*s*)	1st, Ir^{-} (*a*), (*s*)[b] 2nd, Ir^{-} (*a*), (*s*)
Os	0.526	Sponge	No	67	650–710	None	Os^{-} (*b*), (*v*), tr. (*s*)	1st, Os^{++} (*s*) 2nd, Os^{+} (*s*)
	2.125	Sponge	Yes	5	640–670	Os^{+++} (*s*)	Os^{++} (*s*)	1st, Os^{+} (*s*) 2nd, Os^{-} (*s*)
Ru	14.403	Sponge	No	14	680–710	None	Ru^{+++} (*v*)	1st, Ru^{+} (*c*) 2nd, Ru^{+} (*c*)
	1.969	Sponge	Yes	8	670–710	Ru^{+} (*c*)	Ru^{+++} (*c*)	1st, Ru^{-} (*c*), (*s*) 2nd, Ru^{-} (*c*), (*s*)
Rh	1.241	Sponge	No	18	600–710	Rh^{+++} (*v*) (insol.)	Rh^{-} (*s*)	1st, Rh^{-} (*s*) 2nd, Rh^{-} (*s*)
	1.918	Sponge	Yes	5½	620–710	Rh^{+++} (*v*)	Rh^{-} (*s*)	1st, Rh^{-} (*s*) 2nd, Rh^{-} (*s*)
Pt	1.317	Sponge	Yes	8	680–710	Pt^{+++} (*d*)	Pt^{+} (*d*)	1st, Pt^{-} (*d*) 2nd, Pt^{-} (*d*)
Au	3.049	Sheet	Yes	8	680–710	Au^{-} (*e*)	Au^{+++} (*e*)	1st, Au tr. (*e*) 2nd, Au tr. (*e*)
Pd	1.499	Sponge	Yes	8	690–710	Pd^{+++} (*f*)	Pd^{-} (*f*)	1st, Pd^{-} (*f*) 2nd, Pd^{-} (*f*)
Ag	0.986	Sponge[c]	No	4	730	Ag^{+++} (*g*) (*v*)	...	1st, Ag^{+} (*s*) 2nd, Ag^{+} (*s*)
	2.012	Sponge[c]	Yes	4	730	Ag^{++} (*g*)	...	1st, Ag^{+} (*s*) 2nd, Ag^{+} (*s*)
Pb	4.042	Sponge[d]	No	18	630–710	None	Pb^{+++} (*s*)	1st, Pb^{+} (*s*) 2nd, Pb^{+} (*s*)

[a] Qualitative tests used are indicated in brackets; number of + signs roughly indicates comparative amounts
[b] Contents of both receivers from a similar chlorination of 2000 mg. of iridium also gave negative tests for Ir (*a*).
[c] Kahlbaum reagent.
[d] Merck reagent.

hydrochloric acid reagent, and warming was continued as in (*b*). The method was based on Wolbling's report (*15*); ruthenium was indicated by the appearance of a blue color. In the case of a negative test, it was repeated with the addition of stannous chloride.

(*d*) **For Platinum.** The stannous chloride test as described by Tananaeff and Michaltschischin (*11*) was found to be the most sensitive, especially in the presence of other platinum metals.

(*e*) **For Gold.** Feigl's procedure (*3*) with *p*-dimethylaminobenzalrodanine was used.

(*f*) **For Palladium.** In the absence of other platinum metals, palladium was indicated by a dark precipitate which formed on the addition of 1 ml. of a saturated solution of stannous chloride in 6 *N* hydrochloric acid to the sample, concentrated to 0.5 ml. on the steam bath.

(*g*) **For Silver.** The fused chlorination residues were identified as silver chloride by their insolubility in water and dilute acids, in contrast with their solubility in ammonia solution.

(*s*) Spectrographic evidence.

(*v*) Color of the residue and nature of the tube deposit were considered sufficient proof of the presence of the metal, in some cases, without the confirmation of a color reaction.

In connection with the iridium test (*a*), the authors' results were in disagreement with Pollard's, who claimed superior sensitivity over the old nitric-sulfuric test. Evidently the mauve color with perchloric acid and the blue color with nitric acid are both evidences of a higher oxidation state of iridium, and the authors found the methods equally sensitive. Furthermore, fuming with sulfuric acid alone, in the absence of added oxidant, invariably produced a strong violet coloration with iridium chloride solution.

From these and other confirmatory experiments, it was concluded that none of the platinum metals except osmium and ruthenium were ever carried out of the ignition tube. This information would facilitate subsequent analytical treatment of mixed chlorination products. However, lead, silver, and gold were all recovered from the receivers, in varying proportions. In the absence of sodium chloride, conditions could probably be adjusted to drive all of the osmium out of the ignition tube and boat, into the receiving solutions. The behavior of ruthenium was not consistent, in this respect. Further investigation is in progress to clarify the nature of the reaction between ruthenium and dry chlorine.

The sublimate was heavy in the case of ruthenium, lead, and gold, and light with osmium, iridium, and platinum, while palladium and rhodium were never detected in the tube rinsings. Osmium was sometimes deposited in finely divided, black form on ground-glass surfaces in the apparatus. This tendency was accentuated in the presence of organic matter, and when osmium was present it was never advisable to coat the flat adapter joint with wax, a device occasionally used to obtain a better seal.

Little difference was observed between the nature of the deposit obtained in the presence of sodium chloride and the product resulting from chlorination of the metal only. Sodium chloride alone sublimed very slightly, most remaining unfused in the boat, with little decrepitation.

The boat residues were tested for solubility in 50 ml. of 0.1 *N* hydrochloric acid. In the absence of sodium chloride, they were generally insoluble, but in its presence all residual chlorides dissolved readily, leaving no visible residue on filtering. There were indications that distinct complex chlorides with sodium chloride had formed with iridium, platinum, palladium, and rhodium. Osmium seemed to form a complex also, but it was apparently unstable and broke up into sodium chloride and a volatile chloride of osmium. If any complex chloride of ruthenium formed, it must have been unstable at 700° C.

Iridium. Because it was hoped ultimately to produce a method of determining the elementary constituents in iridosmines, the quantitative aspects of the chlorination procedure for iridium were investigated in a series of experiments starting with the pure metal sponge. In every case, the sample was covered with ten times its weight of reagent grade, dry sodium chloride and exposed to chlorine for 8 hours at about 700° C. The product was dissolved in 0.1 *N* hydrochloric acid and filtered before determining the iridium content. No insoluble residues were ever obtained after 8 hours' chlorination, but several preliminary trials showed 4 hours to be insufficient for the complete reaction of 5 mg. of iridium.

Table II. Recovery of Iridium from Soluble Products of Chlorination in Presence of Sodium Chloride

Expt. No.	Ir Added	Ir Recovered	Difference	
	Mg.	*Mg.*	*Mg*	%
1	5.336	5.362	+0.026	+0.5
2	4.453	4.496	+0.043	+1.0
3	3.052	3.083	+0.031	+1.0
4	3.810	3.850	+0.040	+1.1
5	2.171	2.186	+0.015	+0.7
6	2.819	2.825	+0.006	+0.2
7	2.865	2.875	+0.010	+0.3
8	3.233	3.259	+0.026	+0.8
9	3.854	3.880	+0.026	+0.7
				Av. +0.7 ± 0.2

A pinkish gray sublimate in the cold end of the ignition tube, which also contained some iridium, was readily removed by rinsing with dilute hydrochloric acid. As flecks of rubber from the connection occasionally entered the tube with the chlorine, the washings were filtered before being added to the bulk of the sample, bringing the combined volume to about 50 ml. Iridium was determined gravimetrically, as described below.

The receiving solutions were evaporated individually on the steam bath, and examined for iridium by Pollard's test. In no case was the characteristic mauve color obtained, but a faint yellow test with dichlorobenzidine was sometimes observed. This indicated that iridium was either absent, or present to the extent of 0.003 mg. or less, per receiver.

In Table II, the original sample weight of iridium is compared with the net weight of metal recovered in a series of nine chlorination experiments. Although the results were 0.7% high, on the average, good precision was obtained.

Determination of Iridium. Hydrolytic precipitation was considered to be the best method available for determining iridium. Owing to the tendency toward occlusion and colloidal formation, hydrolytic precipitation methods frequently do not lend themselves to microprocedures. However, the authors found that a modification of Gilchrist's macroprocedure (*5*, *6*) was suitable for samples of 10 mg. and less. Although it required exacting technique, tests with a standard solution showed that it was capable of a precision of ±0.1%, but invariably gave slightly high results.

The solution was heated nearly to boiling, then 10 ml. of a 10% solution of sodium bromate were added. Filtered, 10% sodium bicarbonate solution was added in small portions until the pH of the solution was about 6, using bromocresol purple as an external indicator. Two or 3-ml. excess of the bicarbonate solution seemed to have no ill effects, such as the tendency to peptize the precipitate. Another 5-ml. portion of bromate solution was introduced, and the solution was boiled for 5 minutes while the black suspension coagulated. The mixture was filtered, preferably while still hot, through 7-cm. Whatman No. 42 paper, and the residue was washed with 200 ml. of 1% ammonium chloride solution. The importance of this step was emphasized in a series of determinations from a standard iridium solution where washing with a smaller volume led to high and inconsistent results. The beaker was cleaned with two small pieces of filter paper, which were added to the other filter. Because of the tendency of the precipitate to creep, the top of the funnel was cleaned with another bit of filter paper, which was added to the others. These three filter scraps were always torn from the same ¼ filter paper, to maintain a consistent blank. This method is considered more efficient than application of a feather for removal of last traces of precipitate from the beaker.

The paper and precipitate were folded into a tared, porcelain crucible of 1.5-ml. capacity and "ashed" slowly in a muffle furnace. Heating was continued at 600° to 650° C. for a few minutes after ignition appeared to be complete. The crucible

was cooled, then ignited in hydrogen and weighed on a microbalance by the following schedule:

10 minutes in hydrogen at about 650° C.
5 minutes' cooling in hydrogen
5 minutes' cooling in nitrogen
15 minutes' cooling in a desiccator
10 minutes' equilibration in balance case

Saturated calcium nitrate solution was used in both desiccator and balance case to maintain 50% humidity, as recommended by Thiers and Beamish (*12*). An average experimental blank of 0.071 mg. (± 0.009) was subtracted from the residue, leaving the net weight of iridium recovered.

Heating Losses. In connection with the gravimetric determination of iridium, a study was made of the extent of loss by volatilization on igniting the metal in air, at different temperatures. The literature fails to suggest the fact that such losses may be a source of considerable error, particularly in handling microquantities.

A set of crucibles was selected whose weights proved to be constant over the range of conditions tested. Reduction residues from determination of iridium were heated at 650° to 675° C. in the crucibles for 4 hours, without appreciable decrease in weight. Above 800° C., however, significant losses occurred, as indicated in Table III. The ignitions were made in a muffle furnace with the door slightly ajar, to admit air, and the residues were reduced in hydrogen before each weighing.

Table III. Iridium Losses on Heating in Air

Time Hours	Temp. ° C.	Iridium Residue from Sample No. 1		2		3		4	
Initially		12.310		13.124		16.283		15.864	
			0.427[a]		0.195[a]		0.196[a]		0.183[a]
1.5	800–925	11.883		12.929		16.087		15.681	
			0.194		0.155		0.106		0.156
1	850–950	11.689		12.774		15.981		15.525	
			0.185		0.149		0.148		0.120
1	850–950	11.504		12.625		15.833		15.405	
			0.188		0.163		0.185		0.097
1	850–950	11.316		12.462		15.698		15.308	

[a] Mg. loss in weight after each ignition.

It was concluded that excessively high temperatures during ignition in air must be avoided in the gravimetric microdetermination of iridium. Temperatures below 650° C. may be used safely.

During the ignition in air, the iridium always changed from gray to black in color, and increased in weight. Attributing the gain to combination with oxygen, the composition of the black material corresponded approximately to the formula Ir_2O_3. Possibly the iridium that was lost during the high-temperature ignitions formed a higher, volatile oxide, such as IrO_4, whose existence has been postulated by analogy with the volatile octavalent oxides of osmium and ruthenium.

CHLORINATION OF IRIDOSMINE

Material was chosen which had completely resisted attack by caustic fusion and was only partially dissolved by a bomb method of wet chlorination. Qualitative analysis of the soluble portion had shown that iridium and osmium predominated, with some platinum and traces of ruthenium. This shiny, finely divided Tasmanian iridosmine was chlorinated in the presence of at least ten times its weight of sodium chloride, under the conditions listed in Table IV. A light tube deposit was obtained, but the major product was a dark brown cinder left in the boat. Both appeared to be readily soluble in 50 ml. of 0.1 *N* hydrochloric acid. The latter was rinsed into a Whatman filter in such a way that any insoluble residue would be transferred from boat to paper. The filter was rinsed with 0.1 *N* hydrochloric acid and distilled water, rinsed with 1% ammonium chloride, and "ashed" in a muffle furnace. In no case did the residual ash appreciably exceed the average blank determination of 0.041 (±0.008) mg.

The results were conclusive proof that the authors' procedure was successful in the complete conversion of "Tasmanian iridosmine" to soluble products.

Other Native Alloys. To test the effectiveness of the method with coarser material, an Alaskan native platinum alloy was chosen.

The metal was in the form of shiny granules, each weighing roughly 0.5 mg. A 4-mg. sample was covered with ten times its weight of sodium chloride and ignited in chlorine for 10 hours at 660° to 710° C. At the end of this period, the residue was black and well fused, and dissolved completely in 50 ml. of 0.1 *N* hydrochloric acid. The section of ignition tube between the furnace door and delivery tip was very lightly coated with a colored deposit, which was readily and completely soluble in 50 ml. of 0.1 *N* hydrochloric acid. A small black ring, also observed during all chlorinations of iridosmine, was visible inside the bubbling tip of the first receiver. This ring, found to be typical of osmium, redissolved on contact with the acidic receiving solution.

A coarse-grained variety of iridosmine was treated in an identical manner. The sample, which consisted of two shiny flakes and weighed 2 mg., appeared to react completely. Again, the residue dissolved completely in 50 ml. of 0.1 *N* hydrochloric acid. A dark tube deposit dissolved in dilute hydrochloric acid except for a small ring where it had extended just inside the furnace door. With samples not placed well to the back of the furnace, in the high-temperature zone, there was a risk of incomplete reaction, as demonstrated by partially insoluble residues.

These results with two native alloys not only illustrated the general applicability of the chlorination procedure to the corrosion of the platinum minerals, but also show that it is effective with the most inert type of alloy, that occurring in larger flakes.

The soluble products of the preceding chlorinations were examined with the aid of several qualitative tests, described in connection with Table I, with the following variations. The receiving solutions were decolorized by sulfur dioxide before evaporation for spectrographic analysis, to avoid loss of osmium. Osmium in the presence of relatively large amounts of other platinum metals was found by testing the vapors of a boiling solution to which hydrogen peroxide had been added, by passing them through an acidified solution containing thiourea indicator (*h*). The results are summarized in Table V.

The complexity of the above native alloys prevented a quantitative measurement of their composition, for there is available no dependable procedure for the separation of the platinum metals on a microscale.

Chlorination without Sodium Chloride. Chlorination of both coarse and fine varieties of iridosmine proceeded more slowly in

Table IV. Chlorination of Tasmanian Iridosmine in Presence of Sodium Chloride

Expt. No.	Iridosmine Mg.	NaCl Mg.	Time Hours	Temp. ° C.	Insoluble Residue Mg.	Blank Mg.	Net Insoluble Mg.
1	3.791	42.3	12	700–50	None visible	...	...
2	3.7	51.0	12	700–50	None visible	...	...
3	2.532	45.4	12	720–50	None visible	...	...
4	2.953	40.36	12	730–50	None visible	...	...
5	3.302	33.0	8	710	0.044	0.041	+0.003
6	2.448	24.5	8	710	0.040	0.041	−0.001
7	3.653	36.5	8	710	0.042	0.041	+0.001
8	2.836	28.4	8	710	0.031	0.041	−0.010

Table V. Products of Chlorination of Native Alloys in Presence of Sodium Chloride

Material	Boat Residue	Tube Deposit	Receiving Solutions
Alaskan platinum alloy	Os^{-} (*h*), (*s*) Ir^{+++} (*a*), (*s*) Pt^{-} ? (*d*), $^{+}$ (*s*) Ru^{-} (*s*)	Os^{-} (*h*), $^{+}$ (*s*) Ir^{+} (*a*), tr. (*s*) Pt tr. (*s*) Ru^{-} (*s*)	1st, Os^{++} (*b*) 2nd, Os^{+} (*b*)
Coarse-grained iridosmine	Os^{-} (*h*), (*s*) Ir^{+++} (*a*), (*s*) Pt^{-} (*d*), or tr. (*s*) Ru tr. (*s*)	Os^{-} (*h*), (*s*) Ir^{+} (*a*), tr. (*s*) Pt tr. (*s*) Ru^{++} (*s*)	1st, Os^{+++} (*b*) 2nd, Os^{++} (*b*)
Tasmanian iridosmine	Os^{+}, $^{-}$ (*h*)[a] Ir^{+++} (*a*), (*s*) Pt^{+} (*s*) Ru^{-} (*s*)	Os^{++} (*h*), (*s*) Ir^{+} (*s*) Pt^{+} (*s*) Ru^{+} (*s*)	1st, Os^{+} (*b*), (*s*) Ir^{-} (*s*) Pt^{-} (*d*), (*s*) Ru^{-} (*s*) 2nd, Os^{+} (*b*), (*s*) Ir^{-} (*s*) Pt^{-} (*d*), (*s*) Ru^{-} (*s*)

[a] Different results with products of different chlorinations.

the absence of sodium chloride, and tended to produce insoluble boat residues.

A sample of 4.074 mg. of the Tasmanian mineral was ignited in chlorine at about 700° C. During the first 24 hours, chlorine was absorbed, while the solid increased in bulk and turned reddish black. After this period, it gradually disappeared, until the boat was clean after a total of 217 hours of chlorination. The only products of reaction were a light, tan-colored tube deposit, and whatever had passed over into the (three) receivers. Most of the former was removed with dilute hydrochloric acid, but some proved insoluble. The evaporated tube rinsings showed spectrographic evidence of iridium, osmium, platinum, and a trace of ruthenium. Only osmium was detected in the receiving solutions, and never beyond the first two receivers.

A second experiment, in which 2.293 mg. of the same type of alloy were treated, confirmed the conclusion that Tasmanian iridosmine can be converted, on prolonged treatment with dry chlorine, into products which are appreciably volatile at 700° C.

With the coarser variety of iridosmine, samples of 32.409 and 17.747 mg. were chlorinated at about 670° C., without sodium chloride. In both cases, after one week, there was a reddish brown residue in the boat and a dark brown tube deposit. Continued chlorination of the smaller residue for 25 days finally resulted in its complete conversion to volatile products. Although osmium, iridium, and traces of ruthenium and platinum were found in the sublimate, only osmium was detected with certainty in the receiving solutions, spectrographically.

SEALED TUBE METHOD FOR IRIDIUM

The procedure described by Wichers (*13*) was adapted to the treatment of milligram quantities of iridium, as described above. Samples of pure iridium sponge were chlorinated for 24 hours at 196° C. After opening, the tubes were rinsed thoroughly with acidified distilled water (10 drops of 12 *N* hydrochloric acid per 250 ml.) to transfer the products to a beaker. The combined washings were filtered to remove silica, and iridium was determined in the filtrate, by the authors' procedure.

The average amount of iridium recovered (Table VI) was within 0.3% of the charge, but the average deviation from the mean was three times this large. Iridium was recovered from the products of boat chlorination (Table II), on the other hand, with a precision of ±0.2%. The major advantage of the latter however, was the requirement of less exacting technique.

SUMMARY

Conclusive proof has been given, for the first time, of the complete conversion of Tasmanian iridosmine to soluble products by reaction with chlorine in the presence of sodium chloride, at elevated temperatures. Further evidence supports the prediction that the method is equally efficient for the corrosion of other refractory alloys of the platinum family, even when not in a finely divided state. The procedure has been proposed as the first step in a general method for the microanalysis of platinum metal residues, including assay "insolubles."

Toward this end, the individual response of all the platinum family of elements and other elements frequently associated with them in concentrates and assay residues was examined, with and without the use of sodium chloride as a chlorination aid. In its presence, only soluble products were obtained, largely in the form of double chlorides with sodium. Certain elements also gave volatile products, some in the form of sublimate and the rest as vapors mixed with the excess chlorine. In the absence of salt, residual products were always insoluble in dilute acid, and the same was true with alloys.

A satisfactory procedure was worked out, in detail, for the gravimetric microdetermination of iridium, based on the macromethod of hydrolytic precipitation. Recovery of iridium from chlorination products was dependable, but consistently slightly high. Losses incurred by heating iridium metal in air were found to be significant at temperatures above 800° C., but negligible below 650° C.

A micro adaptation of Wichers' bomb method was used to dissolve samples of pure iridium sponge, and iridium was recovered quantitatively from solutions prepared in this way. After a comparison of this method with dry chlorination, the latter was concluded to be more convenient and capable of somewhat higher precision.

There is the possibility that the dry chlorination procedure will prove valuable in a wider application, for the large-scale, commercial preparation of platinum metals.

Table VI. Recovery of Iridium from Soluble Products of Sealed-Tube Chlorination

Expt. No.	Ir Added	Ir Recovered	Difference	
	Mg.	*Mg.*	*Mg.*	%
1	4.288	4.279	−0.009	−0.2
2	6.838	6.877	+0.039	+0.6
3	6.492	6.292	−0.200	−3.2
4	7.983	7.989	+0.006	+0.1
5	4.971	4.904	−0.067	−1.4
6	8.071	8.145	+0.074	+0.9
7	7.531	7.613	+0.082	+1.1
8	9.771	9.806	+0.035	+0.4
9	6.211	6.384	+0.102	+1.6
10	5.696	5.694	−0.002	±0.0
11	8.656	8.728	+0.072	+0.8
12	5.764	5.946	+0.182	+3.1
			Av.	0.3 ±1.0

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Methadon Hydrochloride

Optical Properties, Microchemical Reactions, and X-Ray Diffraction Data

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Physical and chemical properties of methadon hydrochloride are presented. Seven reagents are listed which produce characteristic microscopic crystals from dilute solutions. Single crystals grown from aqueous solutions can be used for measurement of the optic axial angle, extinction angles, and refractive indexes and for observation of interference figures. X-ray diffraction data are useful in identifying the powdered material, and the ultraviolet absorption spectra of methadon base and hydrochloride may be relied upon for identifying small quantities in solution.

METHADON hydrochloride (4,4-diphenyl-6-dimethylamino-3-heptanone hydrochloride) has recently been placed on the market under the names dolophine, amidone, etc., as a substitute for morphine. Because of its habit-forming characteristics, it is classified by law as a narcotic and its sale is restricted. A report on its physiological effects and the history of its development has been published (*2*).

It is a white crystalline compound, soluble in water and ethyl alcohol and insoluble in ether. Its melting point has been found by various investigators to be 230° to 232° C. (*3*), 236° to 236.5° C. (*5*), and 241° to 242° C. corrected (*7*). The solubility in water has been reported to be about 5% (*2*); however, solutions of 10% or more at room temperature (20° to 25° C.) can be prepared without difficulty. From aqueous solutions of the hydrochloride, ammonium hydroxide and other alkalies precipitate the free base as an oily substance which can be extracted with chloroform, ethyl ether, or petroleum ether. Levo- and dextrorotatory isomers of methadon have been prepared (*2*); however, the hydrochloride salt (manufactured by Eli Lilly & Company) used in the following experiments was proved by crystallographic and polariscopic observations to be the optically neutral racemate.

MICROCHEMICAL REACTIONS

In making these tests, the methods and reagents described by Stephenson (*6*) were used. Aqueous methadon hydrochloride solutions of concentrations 1 to 10,000, 1 to 5000, 1 to 1000, 1 to 500, 1 to 200, and 1 to 50, and a saturated solution were mixed with approximately equal drops of reagent on a microscope slide and allowed to stand until crystals developed or all liquid evaporated. The drops were not stirred in the test described, although in some cases stirring hastens crystallization. The progress of crystallization was observed under a microscope at a magnification of 100. Of the 25 reagents listed by Stephenson (*6*), six produced satisfactory crystals. Good crystals were also obtained with uranium nitrate 20% and lanthanum nitrate 20%. Results of the tests are shown in Table I.

Table I. Microchemical Reactions

	Reagents Used	Reaction
1	Sodium carbonate, 5%	Oil droplets
2	Sodium nitroprusside, 5%	Oil droplets
3	Disodium phosphate, 5%	Oil droplets
4	Potassium hydroxide, 5%	Oil droplets
5	Potassium acetate, 5%	Oil droplets
6	Potassium iodide, 5%	Colorless crystals
7	Potassium chromate, 5%	Oil droplets
8	Potassium ferrocyanide, 5%	Colorless crystals
9	Potassium ferricyanide, 5%	Yellow crystals
10	Potassium permanganate, 5%	Amorphous precipitate
11	Gold chloride, 5%	Amorphous precipitate
12	Silver nitrate, 5%	Amorphous precipitate
13	Ammonium molybdate, 5%	Amorphous precipitate
14	Platinum chloride, 5%	Amorphous precipitate
15	Ferric chloride, 5%	No reaction
16	Zinc chloride, 5%	Oil droplets
17	Picric acid, saturated solution	Amorphous precipitate
18	Marme's reagent	Colorless crystals
19	Mayer's reagent	Colorless crystals
20	Millon's reagent	Amorphous precipitate
21	Wagner's reagent	Pale brown crystals
22	Phosphomolybdic acid reagent	Amorphous precipitate
23	Phosphotungstic acid reagent	Amorphous precipitate
24	Kraut's reagent	Amorphous precipitate
25	Sodium bisulfite	No reaction
26	Uranium nitrate, 5%	No reaction
27	Uranium nitrate, 20%	Colorless crystals
28	Lathanum nitrate, 20%	Colorless crystals

Table II. Crystallization from Solution

Reagent	Concentration of Methadon HCl
Potassium iodide, 5%	1:1000
Potassium ferrocyanide, 5% (fresh solution)	1:500
Potassium ferricyanide, 5% (fresh solution)	1:500
Marme's reagent (fresh solution)	1:10,000
Mayer's reagent	1:20,000
Wagner's reagent	1:1000
Lanthanum nitrate, 20%	1:20

These reagents were selected for trial because their reactions with most of the common alkaloids have been reported (*6*). Uranium and lanthanum nitrates are exceptions. However, when these two reagents were mixed, as described above, with solutions of morphine, codeine, heroin, novocaine, strychnine, brucine, pilocarpine, quinine, caffeine, dilaudid, dionine, peronine, stovaine, urotropine, and ethanolamine, no similar crystals were formed. Seven of the eight crystalline compounds observed were examined microscopically. Photomicrographs of typical crystals are reproduced in Figures 1 and 2. Some of these are undoubtedly sufficiently distinctive to be used for identification. Marme's reagent has been recommended by Schuldiner (*4*) and potassium ferrocyanide by Watson and Bowman (*9*) for this purpose. Table II shows the lowest concentrations of methadon hydrochloride solutions from which crystals were obtained.

PREPARATION OF METHADON HYDROCHLORIDE CRYSTALS FOR OPTICAL EXAMINATIONS

Methadon hydrochloride can be recrystallized from water, in which it is much more soluble hot than cold. This fact is useful in the preparation of crystals for optical examination and identification. A saturated solution can be made by crushing fragments of methadon hydrochloride in a drop of distilled water on a microscope slide until many small pieces remain in excess; a few large fragments may be left to hold up the cover glass, which should be large enough to prevent the solution from bulging out around the edges. A seal of paraffin oil or other similar oil should be run around the edge of the cover glass to prevent evaporation of the solvent. The sealed preparation can be warmed

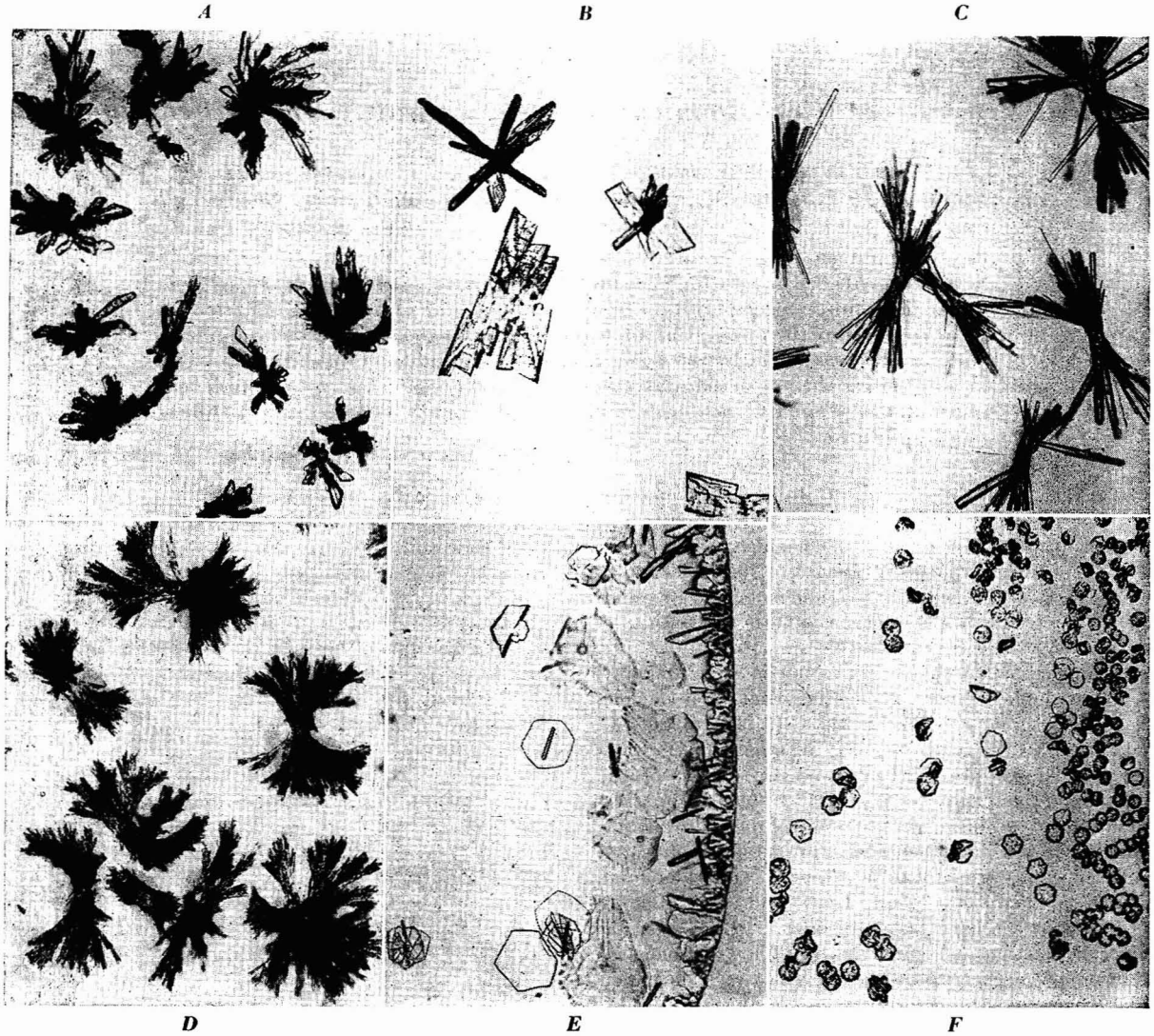

Figure 1. Photomicrographs of Typical Crystals (×80)

	Reagents	Concentration of Methadon HCl
A.	Potassium iodide	Saturated solution
B.	Potassium iodide	1–200
C.	Potassium ferrocyanide	1–50
D.	Potassium ferrocyanide	Saturated solution
E.	Potassium ferricyanide	1–50
F.	Potassium ferricyanide	1–50

cautiously over a microflame or hot plate to cause most of the small fragments to dissolve; the remaining fragments will grow slowly upon cooling the preparation. The crystals which result will look like those in Figure 2,*F*. An uncovered drop of solution evaporates too rapidly, forming a vitreous film without satisfactory crystals. Larger quantities of crystals can be grown by cooling a warm saturated solution in a covered weighing bottle or similar container. It is important to have a few particles of methadon hydrochloride present as seed in order to obtain good crystallization. Rapid evaporation must be avoided.

INDEX DETERMINATION

Single crystals grown as described above were immersed in various refractive-index liquids for determination of the refractive indexes (*1*). It was necessary to mount crystals on a stage goniometer in order to measure the principal refractive indexes, because the peculiar shape of the crystals causes them to lie with their principal optical directions oblique to the axis of the microscope in most cases. All angles of Figure 3 were measured by means of the rotating stage. Diamond-shaped crystals which are resting on an end face can be seen in Figures 2,*F*, and 3. Such crystals show symmetrical extinction. They give an interference figure showing the obtuse bisectrix at one edge of the field. From such crystals the refractive index, β, can be obtained and also an index, α' (Figure 3), intermediate between α and γ. The acute angle of 62° is a reliable diagnostic characteristic.

Crystals of the elongated type in Figure 2,*F*, show extinction within 1° or 2° of parallelism relative to the long edge. The maximum extinction angle found by measuring six different crystals was 1.5°; the average was 0.75°. The setting error was about 0.5°. The refractive index, γ, is obtainable for vibrations parallel to the long edge, as can be seen by reference to Figure 3. The elongated crystals with the broad dark borders shown in Figure 2,*F*, give an interference figure intermediate between the optic normal and the acute bisectrix, whereas the nearly corresponding drawing in Figure 3 is the optic normal view. The striated sides of the goniometer-mounted crystals caused by many narrow vicinal faces made accurate measurements of angles impossible; therefore, the angles shown on the optic

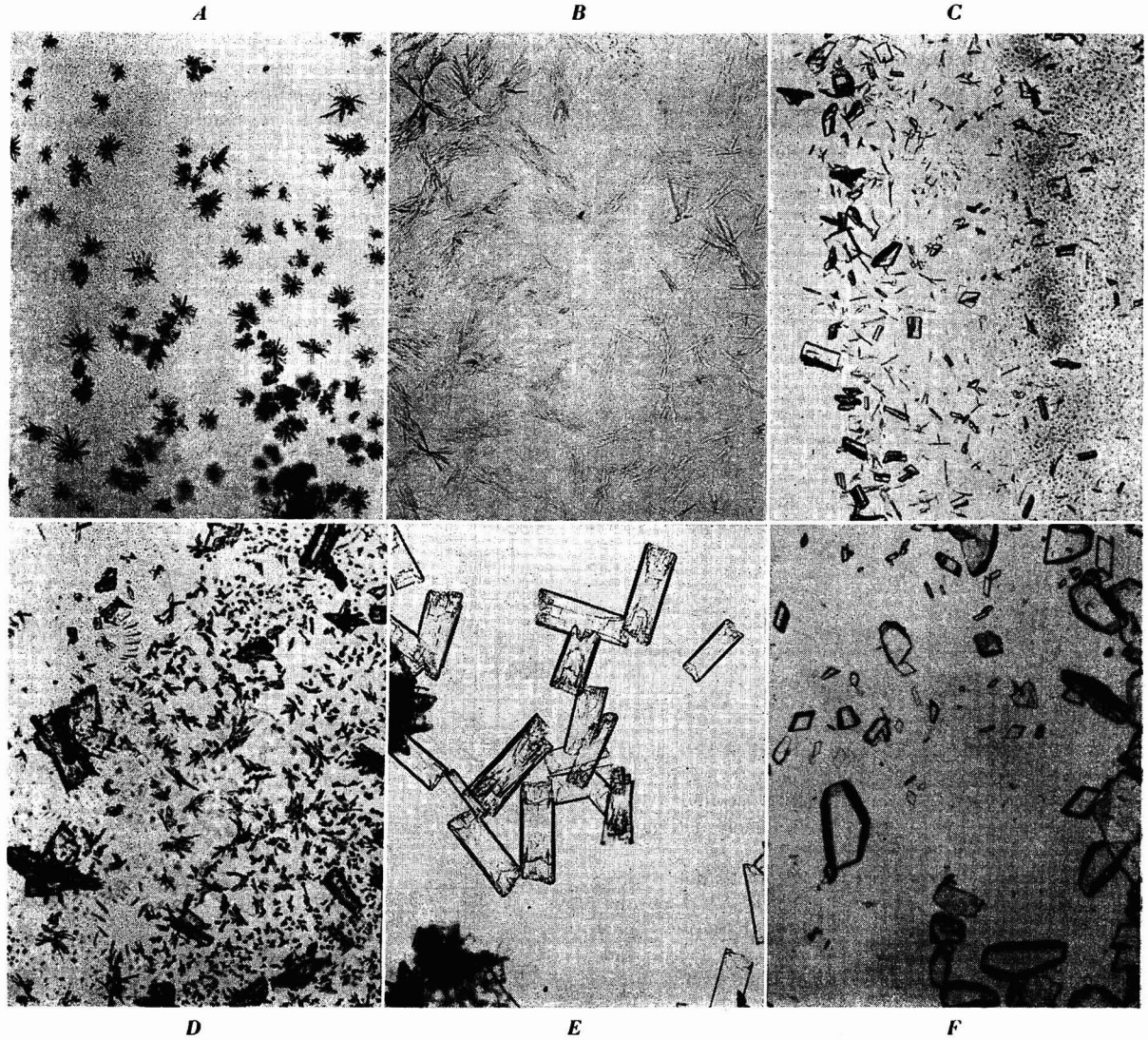

Figure 2. Photomicrographs of Typical Crystals

	Reagents	Concentration of Methadon HCl
A.	Marme's reagent	1–200 (×104)
B.	Mayer's reagent	1–1000 (×80)
C.	Wagner's reagent	1–200 (×80)
D.	Wagner's reagent	1–50 (×120)
E.	Lanthanum nitrate	Saturated solution (×80)
F.	Methadon HCl crystallized from saturated solution	

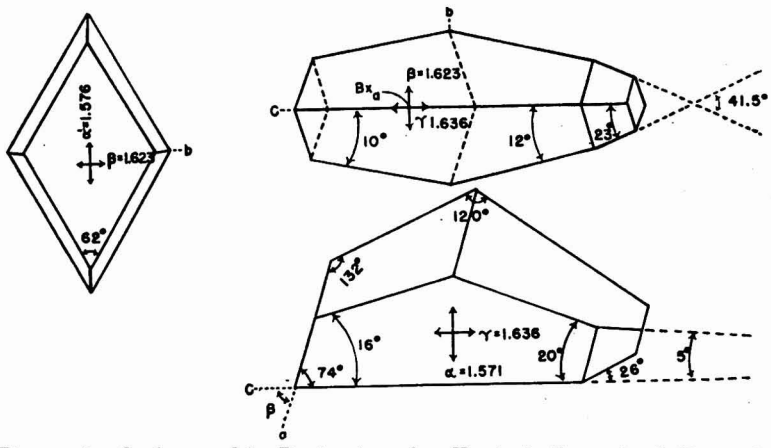

Figure 3. Orthographic Projection for Typical Crystal of Racemic Methadon Hydrochloride

normal and acute bisectrix views in Figure 3 are only approximate. The γ vibration direction was within 0.5° of parallelism with the long base edge on the crystal measured, but the edge was imperfect; consequently, slight obliquity may be observed on other crystals, as would be expected for a monoclinic substance. Solutions of this preparation cannot be optically active because the crystals are monoclinic and belong to Class 3 (Schoenflies, C_s) which has only a plane of symmetry. Polariscopic examination of a 10% aqueous solution showed no optical rotation. Table III and Figure 3 summarize the optical and crystallographic data.

Standard procedures for identifying crystalline compounds by the use of x-rays are applicable to methadon hydrochloride. Weissenberg x-ray diffraction photographs confirm the Class 3 symmetry of this substance. The photographs show that (h k l) reflections occur only

Table III. Optical and Crystallographic Properties of Racemic Methadon Hydrochloride

Crystal system	Monoclinic, Class 3, only a plane of symmetry; acute angle β = 74°
Optic orientation	β vibration direction is parallel to crystallographic axis b. Plane of symmetry contains axial plane. α direction is acute bisectrix which is nearly perpendicular to crystallographic axis c.
Refractive indexes, 5893 A.; 25° C.	α = 1.5713 ± 0.0005, β = 1.6232 ± 0.0005, γ = 1.6360 ± 0.0005, α' = 1.5760 ± 0.0005 from crystals resting on an end face
Optic axial angle	
Observed	$2E$ = 90° ± 1° by calibrated micrometer eyepiece
Calcd. from $\sin V = \frac{\sin E}{1.623}$	$2V$ = 52°
Observed	$2V$ = 52° by rotating from one optic axis to the other on goniometer
Calcd. from indexes. $\mathrm{Cos}^2 V = \frac{\gamma^2(\beta^2 - \alpha^2)}{\beta^2(\gamma^2 - \alpha^2)}$	$2V$ = 52° C.
Optical character	Negative
Dispersion	($r < v$) distinct on both optic axes

when $h + k = 2n$ and (h o l) reflections only when $h = 2n$ and $l = 2n$. From microscopic observations (Figure 3) it is evident, however, that the crystals do not possess a twofold axis of symmetry. The space group is therefore uniquely determined to be $C_s^4 - C_c$.

An x-ray photograph of powdered racemic methadon hydrochloride has been taken in a General Electric XRD powder camera with nickel filtered CuK_α (λ = 1.542 A.) radiation. The sample was ground to a very fine powder in an agate mortar and then placed in a cellulose acetate capillary about 1 mm. in diameter. The capillary was rotated during exposure. The results obtained are recorded in Table IV.

Table IV. X-Ray Powder Data of Racemic Methadon Hydrochloride CuK_α (λ = 1.542)[a]

d, A.	I[b]	d, A.	I[b]	d, A.	I[b]
12.33	MS	4.55	VVS	3.09	MS
8.27	M	4.33	S	2.96	M
7.46	VVS	4.13	MS	2.90	W
6.45	VS	4.00	MS	2.83	MW
5.91	MS	3.86	MS	2.74	M
5.65	MW	3.70	MW	2.67	M
5.38	VW	3.48	MS	2.59	W
5.04	VW	3.32	MW	2.52	M
4.70	MS	3.19	MS		

[a] Furnished by Merle Ballantyne, Western Regional Research Laboratories.
[b] Visually estimated intensities. S, strong; M, medium; W, weak; V, very.

The ultraviolet absorption spectra (*8*) of methadon base and methadon hydrochloride can also serve for identification (Figure 4). Alcoholic solutions of the hydrochloride exhibit two characteristic electronic absorption bands at wave lengths and molecular extinctions as follows: λ_{max} = 294 mμ, ϵ_{max} = 460; the phenyl band λ_{max} = 259 mμ, ϵ_{max} = 480. ($\epsilon = 1/cd \log_{10} I/I_0$. c = concentration in moles per liter. d = length of path in centimeters. $\log_{10} I/I_0$ = optical density.) The minimum between the two electronic bands occurs at λ = 275 mμ, ϵ_{min} = 300. In water solutions, the long wave-length maximum shifts to 292 mμ and the absorption rises, ϵ_{max} = 520. The absorption spectrum of the free base, methadon, in alcohol or hexane is essentially the same in the region of the 294 mμ band but is uniquely altered at wave lengths below 250 mμ owing to the appearance of a new strong absorption band; on the long wave-length wing of this band the phenyl 259 mμ maximum has an apparently enhanced value of ϵ_{max} = 760 in alcohol, ϵ_{max} = 830 in hexane

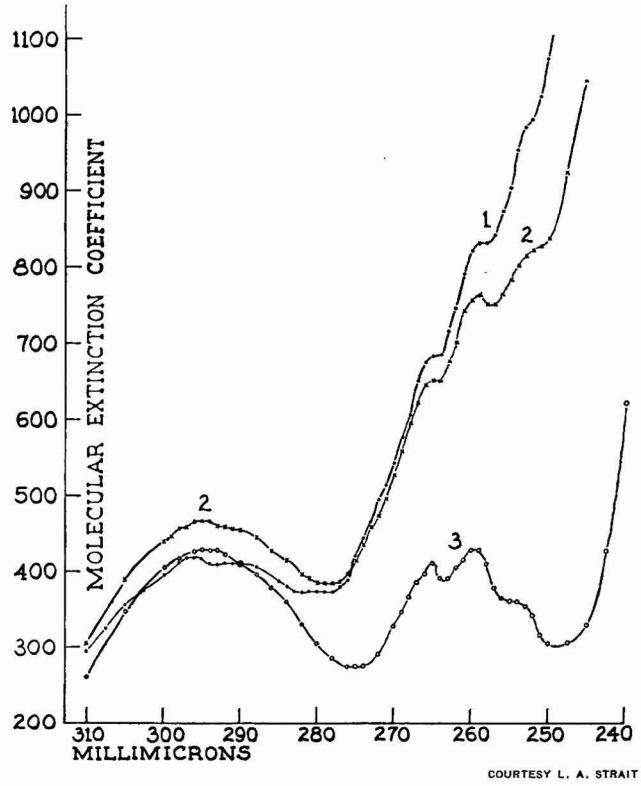

Figure 4. Ultraviolet Absorption Spectra of Methadon

1. **Methadon base in hexane**
2. **Methadon base in ethyl alcohol**
3. **Methadon hydrochloride in ethyl alcohol**

A 10 mg. % solution in a 1-cm. path length is adequate to reveal clearly the spectrum properties.

ACKNOWLEDGMENT

The assistance given by G. E. Mallory of the Alcohol Tax Unit Laboratory in the study of the microchemical reactions is gratefully acknowledged.

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Colorimetric Microdetermination of Rhodium with 2-Mercaptobenzoxazole

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A colorimetric procedure has been developed, using 2-mercaptobenzoxazole, for the determination of moderate amounts of rhodium. Interference of iridium is negligible even when present in the proportion of 2 parts to 1 of rhodium. The reactions of other platinum metals are described.

FOR the determination of rhodium, 2-mercaptobenzoxazole has been employed as a colorimetric reagent. The insoluble red mercaptobenzoxazolate of rhodium, which is precipitated from acetic acid medium, is dissolved in acetone to give a yellow-to-red solution, depending on the concentration of the metal. The platinum metals interfering most strongly are platinum and palladium. Iridium and gold in low concentration do not interfere.

Several organic monosulfides have been used for the determination of rhodium. Kienitz and Rombock (*4*) used thionalide (thioglycollic β-aminonaphthalide) for its volumetric estimation. Currah *et al.* (*1*) reported the gravimetric determination of rhodium with thiobarbituric acid. The use of 2-mercaptobenzothiazole for the separation of rhodium and palladium from platinum has been reported by Ubaldini and Nebbia (*5*); 2-mercaptobenzothiazole and 2-mercaptobenzoxazole were used by Haines and Ryan (*3*) to determine rhodium gravimetrically. In the present investigation the reaction of 2-mercaptobenzoxazole with other platinum metals and the use of this reagent for the colorimetric determination of rhodium have been studied.

REAGENTS

Stock rhodium chloride solution was prepared by dissolving rhodium chloride ($RhCl_3.x H_2O$) in 1 liter of an aqueous solution containing 1 ml. of concentrated hydrochloric acid. This solution, standardized by both the hydrogen sulfide (*2*) and mercaptobenzoxazole (*3*) procedures, contained 11.75 mg. of rhodium per 25 ml. of solution. Suitable concentrations were prepared as needed by diluting the stock solution with water.

Solutions of platinum, palladium, iridium, and gold were prepared by dissolving the pure metal or a suitable pure salt in aqua regia, hydrochloric acid, or water, removing nitric acid, if present, by evaporating to dryness in the presence of hydrochloric acid, and finally dissolving in a solution containing 1 ml. of concentrated hydrochloric acid per liter.

2-Mercaptobenzoxazole solution was made by dissolving 1 gram of the reagent (obtained from Eastman Kodak Company) in 100 ml. of 95% ethyl alcohol.

DEVELOPMENT OF METHOD

During the investigation of five organic mercapto compounds, it was found that rhodium could be precipitated quantitatively with 2-mercaptobenzoxazole or 2-mercaptobenzothiazole. Subsequent investigation indicated that these reagents might show colorimetric possibilities. It was found that the red 2-mercaptobenzoxazolate dissolved in acetone to give a colored solution suitable for the determination of rhodium; the 2-mercaptobenzothiazolate proved to be only partially soluble in acetone. The transmittancy curve for acetone solution of the rhodium compound is given in Figure 1.

The data for this curve were obtained with a Model DU Beckman spectrophotometer using a 1-cm. cell. The compound curve was obtained for a solution containing 24 micrograms of rhodium prepared in the same manner as for the colorimetric determination. Although maximum absorption occurs in the ultraviolet, good results are obtained using a blue filter. All reported results were obtained using a blue filter (maximum transmittancy at 420 mμ) with a Lumetron photoelectric colorimeter, Model 400A, and voltage stabilizer.

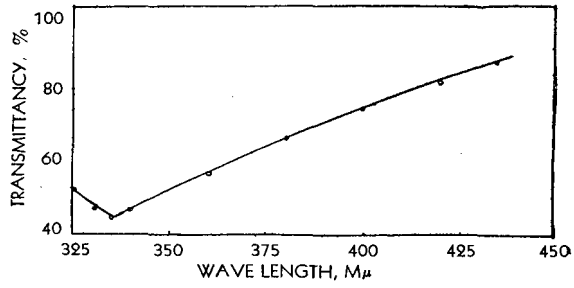

Figure 1. Transmittancy of Rhodium in Acetone Solution

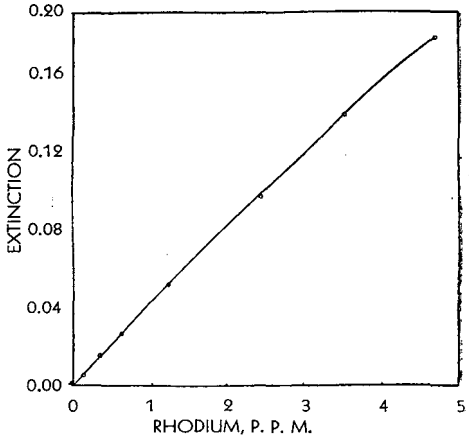

Figure 2. Determination of Rhodium

PROCEDURE

The following method may be applied in the determination of 0.01 to 1.0 mg. of rhodium.

Rhodium samples were measured into Erlenmeyer flasks fitted with short-stemmed funnels, 1 to 2 ml. of concentrated acetic acid and a few drops of the reagent were added, and the volume was made up to approximately 20 ml. The solutions were allowed to boil vigorously on a hot plate for 15 minutes and, after cooling to room temperature, the precipitates were separated from the 2 to 3 ml. of solution remaining by drawing off the supernatant liquid with a filter stick or by filtering directly through a fine filter crucible. The precipitates were dissolved in acetone, the volume was made up to 100 ml., and extinction was measured with colorimeter. A straight-line relationship is not obtained, denoting nonconformity to Beer's law (see Figure 2).

In order to obtain reliable results the solutions must be boiled vigorously for 15 minutes, so that complete precipitation of the

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rhodium is obtained. The acetone solution is stable, no perceptible change in color intensity being noted in 4 days.

REACTION OF 2-MERCAPTOBENZOXAZOLE WITH OTHER PLATINUM METALS

Under the same conditions of precipitation as with rhodium, Pt^{++++}, Pd^{++}, Ir^{++++}, and Au^{+++} give precipitates with 2-mercaptobenzoxazole. The reactions shown below were obtained using 5 mg. of the platinum metal in 25 ml. of solution.

Platinum. Immediate chocolate-brown precipitate changing to brownish yellow on heating; partially soluble in acetone.

Palladium. Immediate red precipitate changing to orange yellow on heating; partially soluble in acetone.

Iridium. Slight brownish red precipitate on heating; partially soluble in acetone.

Rhodium. Red precipitate on heating; readily soluble in acetone.

Gold. Purple-brown precipitate changing to light brown on heating; insoluble in acetone.

INTERFERENCE OF PLATINUM METALS

The platinum metals interfering most strongly are platinum and palladium. Iridium in low concentrations does not interfere. Large quantities of gold cause no interference, because the gold precipitate is insoluble in acetone. Table I shows typical results in the colorimetric determination of rhodium with 2-mercaptobenzoxazole.

The noninterference of iridium in at least equivalent amounts is particularly noteworthy, for rhodium is usually left with this element in the systematic analysis of the platinum group metals (*2*).

Solvents. Hexane, benzene, ethyl ether, methanol, ethanol, and carbon tetrachloride do not dissolve the mercaptobenzoxazolate. Methyl ethyl ketone and dioxane, although readily dissolving the rhodium precipitate, show no advantages over acetone.

Water in Acetone. Measurements of the extinction (at 420 mμ) of solutions varying from 1 to 30% in water were the same. Beyond this limit difficulty is encountered due to complex precipitating out of solution; precipitates appear if more than 35% water is present.

Table I. Determination of Rhodium with 2-Mercaptobenzoxazole

(Final volume 100 ml. Extinction measured using blue filter with Lumetron Model 400A)

Rh Present, γ	Rh Found, γ
12	11
25	26
60	58
120	120
94 + 120γ Pt	116
94 + 140γ Pd	150
94 + 0.5 mg. Au	94
94 + 1.0 mg. Au	96
94 + 50γ Ir	92
94 + 100γ Ir	89
94 + 200γ Ir	94
940 + 1.5 mg. Ir	937

Reagent Solution. The reagent is stable for at least 2 weeks. If reagent solution is allowed to stand, the rhodium precipitate obtained proves difficultly soluble in acetone. Complete transmittancy is obtained beyond 360 mμ for 10 mg. of the reagent in 100 ml. of acetone and excess reagent causes no interference.

Excess Acid. Variations in the acetic acid concentration from 1 to 30%, in the precipitation of the complex, showed no change in the extinction obtained.

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Fractional Sublimation on a Removable Transparent Film

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An apparatus is described for separating the components of a mixture of organic compounds by sublimation at reduced pressure. The sublimate is deposited on a removable transparent plastic film. Microscopic examination of the sublimate as well as chemical tests thereon may be performed without removing the sublimate from the film.

SUBLIMATION procedures have long been recognized as a means for separating and purifying those organic compounds which may, upon heating, undergo direct transition from the solid to the gaseous phase without decomposition. The number of sublimable compounds has been greatly increased by the use of reduced pressure. The advantages of sublimation over other methods of purification have been adequately discussed by Hubacher (*2*).

Many sublimation apparatus and techniques have been described (*2*), in which the sublimate is usually collected on the surface of a glass receiver. In order to perform subsequent chemical or microscopical tests, the crystalline sublimate must be removed either by a scraping process or by dissolution in a suitable solvent. If a scraping procedure is employed, the more or less well formed crystals are likely to be damaged. If two or more components of a mixture have been fractionally separated by a single sublimation, a subsequent dissolution procedure will obviously defeat the original purpose of the sublimation.

To overcome this difficulty, a procedure was devised whereby the sublimed crystals, without further manipulation, may be examined directly on the collecting surface. A sublimation tube consisting of two cylindrical sections connected by a ground-glass joint was designed and constructed as shown in Figure 1. The male ground-glass joint is of constant diameter throughout its entire length and has exactly the same diameter as the rest of the tubing to which it is connected. This feature eliminates the dead space at the joint usually found in the standard type of ground-glass joints. The use of this straight-walled sublimation tube permits the insertion of a transparent cellophane film (which serves as a condensing surface for the sublimate) without the presence of any dead space between the film and inner wall

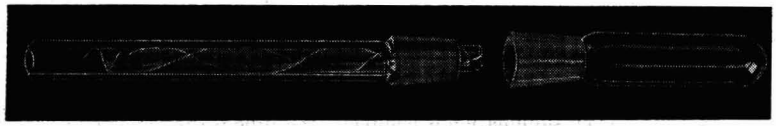

Figure 1. Sublimation Tube with Cellulose Film

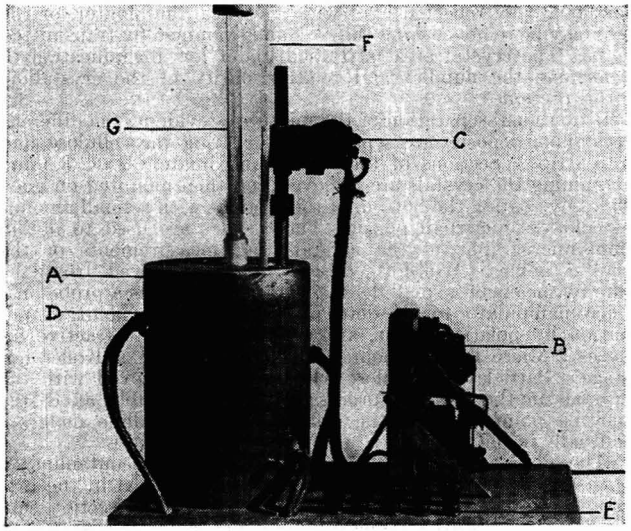

Figure 2. Sublimation Apparatus

A. **Aluminum block**
B. **Relay**
C. **Thermoregulator**
D. **Cartridge heaters**
E. **Binding posts**
F. **Thermometer**
G. **Sublimation tube**

of the tube. When sublimation is complete, the film is removed from the tube without disturbing the crystalline pattern of the sublimate. This procedure results in quantitative deposition of the sublimate on a flat, transparent surface, so that crystalline forms may be easily distinguished microscopically and individual crystals may be readily removed for physical and chemical examination.

Several sublimation devices (*1*, *3*) have been designed for depositing the sublimate on a removable collector. The latter, however, is in one plane, so that the deposit consists of aggregates rather than individual crystals. In the authors' apparatus the removable transparent film is in a vertical position during the sublimation procedure and hence individual crystals deposit in the uppermost part of the sublimate. Fractionation of two or more components is conducted in one uninterrupted sublimation. This cannot be done by methods previously described in the literature.

Mixtures which contain components that sublime at different rates can be fractionally separated during one sublimation step by controlling the temperature and rate of heating. Components that sublime under different conditions may be made to deposit at different levels on the film, and where the separation is not sharp, overlapping boundaries may be cut out and resublimed. The characteristic forms of the different crystals in the sublimed mixture can usually be recognized by their optical properties, even in mixtures where complete fractional separation is not attainable (Figures 8 and 9). Pure individual crystals to be used for the determination of melting point and other physical, as well as chemical, properties may be picked from the mass by the use of a micromanipulator. Quantities of organic material ranging from 0.05 to 50 mg. can be conveniently sublimed.

SUBLIMATION APPARATUS

The sublimation apparatus (Figure 2) may be readily constructed of materials available from any laboratory supply house.

The parts consist of a cylindrical aluminum block, *A*, 6 inches (15 cm.) high and 4.5 inches (11.25 cm.) in diameter, obtainable from the Aluminum Company of America; Cenco mechanical latch electrical reset relay, No. 98330, *B;* Cenco de Khotinsky single-pole double-lock bimetallic thermoregulator, No. 90025, *C;* four General Electric 120-watt 115-volt, 3 × 0.5 inch cartridge heaters, *D;* ten voltmeter-type binding posts, *E;* and a 300° C. thermometer, *F*.

The auxiliary equipment includes a vacuum pump, vacuum gage, freezing trap, and Dewar flask.

The aluminum block and assembly are mounted on a 0.5-inch Transite board with three 1-inch legs. The electrical connections for the thermoregulator and relay accompany the apparatus supplied by the manufacturer. The leads for each of the four cartridge heaters connect to a pair of binding posts and a 110-volt direct current supply, and the lines from the regulator and relay are connected to the two remaining binding posts. In this way, any combination of heaters with series or parallel connections can be made with jumpers across the binding posts. No thermal insulation is used on the heating block, as a constant temperature can be maintained with the thermoregulator. When a temperature differential is to be maintained within the block, insulation is unnecessary and is actually detrimental.

SUBLIMATION TUBE

The sublimation tube (Figure 1) may be obtained from Eck and Krebs, New York, N. Y., supplied as No. 5600. The outer diameter of the lower section is 1.8 cm., and the over-all length is 7.6 cm. including a No. 14/20 female ground-glass joint. The tube fits tightly into the hole, with the bottom edge of the joint at the upper level of the aluminum block. The top section of the sublimation tube is 18.5 cm. in length with constant inner diameter of 8 mm., and the wall thickness is 2 mm. The male joint is made by building up glass on the outside of the thick-walled tube and then grinding a 14/20 taper male joint. In this way the inside of the tube is of uniform diameter throughout its entire length.

Cellulose sausage casing (Visking Corporation, Chicago, Ill.) was found the most suitable lining to function as a condensing surface for the sublimate. This film will not char when the block is heated to 300° C. It is relatively alkali-resistant, insoluble in most organic solvents, and unaffected by cold concentrated hydrochloric or sulfuric acid. A 1.5 × 6 inch strip of the cellulose casing is cut from the roll, washed by dipping in

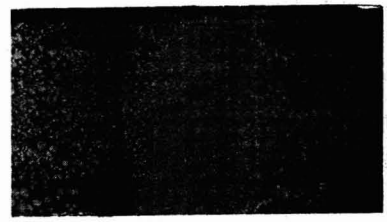

Figure 3. Separation by Sublimation of Mixture of Phenobarbituric, Acetylsalicylic, and Salicylic Acids

Left to right in order named (×2.5)

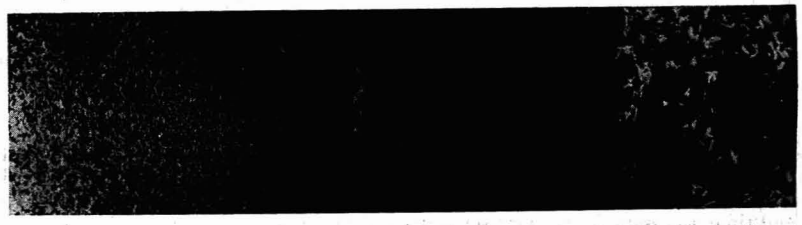

Figure 4. Wider Separation of Phenobarbituric and Salicylic Acids Produced by Higher Sublimation Temperature (×4.5)

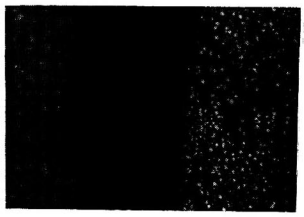

Figure 5. Sublimate from Mixture of Caffeine and Benzoic Acid (×3)

Left. Caffeine
Right. Benzoic acid

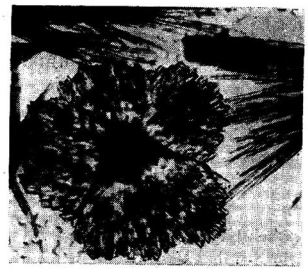

Figure 6. Phenobarbituric Acid Sublimate Shown in Figure 3 (×75)

Figure 7. Acetylsalicylic Acid Sublimate Shown in Figure 3 (×70)

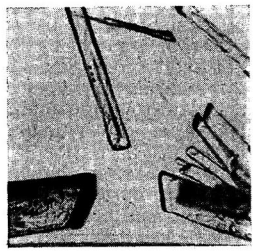

Figure 8. Salicylic Acid Sublimate Shown in Figure 3 (×70)

ethyl ether, and dried. The paper is rolled around a glass rod and inserted through the joint end of the upper section of the sublimation tube, about 0.25 inch of the paper projecting from the joint. The rod is then removed and the cellulose film is grasped by the 0.25-inch excess projecting above the joint. The roll of cellulose film is rotated in clockwise direction until it forms a spiral inside the tube, then in a counter-clockwise direction until the coil partially unwinds, causing it to expand and wedge tightly against the internal walls of the sublimation tube. Any excess of cellulose film extending beyond the ground-glass joint is trimmed flush with the end of the joint. Figure 1 shows the cellulose film properly inserted in the sublimation tube.

SUBLIMATION PROCEDURE

The following procedure was developed primarily for the investigation of substances extracted from unknown medicinal mixtures and biological materials by immiscible solvents.

The extracted substance or its solution is placed in the bottom section of the sublimation tube. Any solvent present is evaporated by heating on a hot plate. The upper portion of the tube is connected to a vacuum pump assembly capable of furnishing a pressure of 1 mm. or less. The ground-glass joints are connected while the vacuum is being applied. The rate of heating is controlled by the proper combination of the heating elements at the binding posts. For unknown mixtures the heating elements are connected in parallel with the thermoregulator set at about 150° C., causing the temperature to rise approximately 2° per minute. The cellophane film condensing surface is observed from time to time. When a sublimate begins to appear, the thermoregulator is cut back to maintain that temperature as long as crystals continue to deposit. It is then advanced to a higher level and further observations are made as the sublimation progresses. In this manner components of mixtures are deposited at different levels on the film.

The nature of the deposition levels is an indication of the possible number of components as well as the sublimation conditions that will give the best possible separation of the mixture. A preliminary trial sublimation of an unknown mixture will usually establish the conditions of temperature, rate of heating, and time necessary for the best separation of a component from a mixture. In subsequent sublimations, the thermoregulator can be set accordingly and the operation can proceed with but little attention.

EXAMINATION OF SUBLIMATE

When sublimation is complete, the tube is disconnected at the joint and the film is removed by hooking it with a dental probe. The film coil is carefully unwound, then fastened by thumbtacks to a cork pad for a few hours, after which time it will remain flat. The sublimate can be examined microscopically on the cork board by reflected light with a vertical illuminator, or the film may be removed from the cork and examined by transmitted light. The crystal area is studied under low magnification to determine the number and relative purity of the crystalline forms present.

If fractional separation of the mixture is evident, the different crystalline deposits are separated by cutting the cellulose film into strips. Sections of the film, approximately 2 × 3 mm., containing the crystals are removed and then mounted on glass slides by coating the bottom of the sections with a small amount of colorless fingernail polish. These slides are used to obtain photomicrographs of the crystals and measurements of the crystal angles. Well-formed crystals are removed from the film by means of a small dental scalpel mounted as a probe on a micromanipulator for the determination of melting point, examination by polarized light, and determination of refractive indexes. Micro melting points are determined on a Kofler hot stage. Particles of cellulose which may be removed with the crystals in the scraping process do not appreciably affect the melting point, because the cellulose and crystalline melt are mutually insoluble.

The sublimates from tissue extracts are generally contaminated with an oily deposit which is not entirely removed in the preliminary extraction process. In such cases a film section containing the crystals for melting point determination is cut out and washed by allowing petroleum ether or ethyl ether to flow across the film while it is held at an acute angle. Because of the relatively small exposed surface of the sublimed crystals, they can be washed several times without appreciable loss of crystalline material.

Cut film sections are advantageous in the chemical examination of sublimates. The resistance of the film to alkalies and cold concentrated acids permits the direct execution of color reactions and formation of crystalline derivatives on a small section of the

Figure 9. Sublimate from Mixture of Aminopyrine (*left*) and Allyl Isopropyl Barbituric Acid (*right*) (×75)

Overlapping of two substances has not interfered with crystalline form of either compound

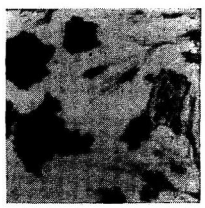

Figure 10. Sublimate from Mixture of Diethyl Barbituric Acid (*left*) and Phenobarbituric Acid (*right*) (×50)

Figure 11. Sublimate from Mixture of Allyl Isopropyl Barbituric Acid (*left*) and Ethyl Isopropyl Barbituric Acid (*right*) (×50)

Globules are oily deposit from tissues

film. Interference due to charring of the film occurs only in those color reactions which require hot concentrated sulfuric acid. For such tests, crystals are carefully removed from the film so that there is no contamination by cellulose particles, because any fibers that may dissolve in the hot acid will produce a brown coloration which will alter or mask the color of a particular reaction. Crystals must be removed from the paper for optical studies under polarized light. Although the crystalline forms are clearly defined when the film mounts are observed under crossed Nicols, the paper is birefracting and the optical constants of the crystals are altered accordingly.

In carrying out microprecipitation reactions for the production of characteristic crystals, the reagents may be added directly to cut film sections, inasmuch as the transparent film particles floating in the drop on a microscopic slide do not interfere with the formation or observation of the crystalline precipitate. Because the film is insoluble in most organic solvents, except such cellulose solvents as acetone and ethyl acetate, crystals can be dissolved from the film by immersion in suitable organic solvent.

In the preparation of derivatives where microcondensation-type reactions are to be carried out in nonaqueous solution, cut film sections are of a decided advantage because organic liquids have much less tendency to creep on the film than on a glass surface; consequently, the reaction mixture remains as concentrated droplets on the film surface. If resublimation is necessary, the sublimate may be transferred to the lower half of the sublimation tube by means of an organic solvent, or the film sections may be used directly. Charring of the film at the higher temperatures inside the heating block will not affect the nature of the sublimate. The fractional sublimation of a few drugs commonly encountered is illustrated in Figures 3 to 11.

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Ultramicrodetermination of Nitrogen

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Over the range of 0.1 to 10 micrograms of nitrogen, the present method is simpler than the Carlsberg micro-Kjeldahl procedures. A two-step digestion procedure is used to avoid bumping and the distillation tubes are coated with silicone in place of paraffin. The ammonia is received in potassium dihydrogen phosphate and titrated with acid to pH 4.6, using bromocresol green indicator.

THE procedure described is based on Carlsberg methods (*1*, *2*), with simplifying modifications and improved hydrophobic coating for distillation tubes. Although it does not achieve the ultimate accuracy nor lower limits of the Bruel method (*2*), it is sufficiently simple to warrant general use by technicians moderately skillful in microchemistry. For the past year it has given uniformly consistent results in the range 0.5 to 5 micrograms of nitrogen, providing better accuracy and fewer lost determinations than have been hitherto obtainable. Bruel *et al.* (*2*) have discussed related micro-Kjeldahl procedures and Glick (*3*) has described Carlsberg procedures and basic apparatus.

A major difficulty in micro-Kjeldahl destruction of organic material using small volumes (<10 μl.) of digestion mixture has been the high probability of loss by sputtering or bumping. This was overcome at Carlsberg by the use of a hot sulfuric acid bath or sealed ampoules. The present method employs two heated metal blocks as digestion racks; one serves to eliminate most of the water, the second to complete destruction at 250° C.

APPARATUS AND REAGENTS

Destruction tubes, 6 × 50 mm. (Kimble 45060).

Coated distillation tubes, 6 × 25 mm. (Arthur H. Thomas Company 2463-M). The tubes are coated by filling with a 5% solution of G.E. Dri-film 9987 in chloroform and then inverting to drain off the excess. The hydrophobic film is set by heating in a drying oven at 110° C. for 2 hours or overnight. The tubes are boiled in three changes of redistilled water to remove residual acid, after which they are dried in the oven and stored until used. Such coatings are inert to enzymes and appear to resist the strong alkali used in the distillation for at least three determinations.

Digestion Blocks. Aluminum blocks 5 cm. thick and 7.5 cm. square are cut from 2 × 3 inch (5 × 7.5 cm.) stock with 25 holes 7 mm. in diameter and 15 mm. deep to receive the destruction tubes. A hole is drilled horizontally to receive a thermometer and the block is heated with a gas micro burner or an electric hot plate.

Teflon Transfer Plate. Du Pont polytetrafluoroethylene polymer, 5 cm. in diameter and 5 mm. thick with a polished upper surface, is ruled into several segments. Alternatively, a piece of $^1/_{16}$-inch Teflon sheet or a piece of glass covered with 0.002-inch Teflon tape may be used. The tape is translucent.

Micropipets, Carlsberg model and specification (*3*), 2 of 5, 3 of 10, 1 of 20, 1 of 50, and 1 of 100 μl.

Microburet, of 0.05- or 0.1-ml. capacity, or alternatively a colorimeter with microcuvettes (<1.0-ml. capacity).

Stirring Magnet and Magnetic Stirring Beads. An electromagnet with current interrupter (Arthur H. Thomas Company) (*3*) is applied to the side of the titration tubes to actuate the magnetic stirring beads or "fleas." The fleas are 1.5 to 2.0 mm. in diameter and consist of a thin borosilicate glass sphere filled with ferrum reductum (Arthur H. Thomas Company 2464C).

Reagents. G. E. Dri-film 9987 for hydrophobic silicone coatings. Sulfuric acid (Mallinckrodt, low-nitrogen) diluted with an equal volume of redistilled water.

"Blue mixture" (*2*) containing 1 gram of copper sulfate pentahydrate, 10 grams of potassium sulfate, 5 ml. of concentrated sulfuric acid, water to 100 ml., and finally 0.2 gram of sucrose.

Hydrogen peroxide, 30% (Merck Superoxol, special reagent for microanalysis in wax-lined container, nitrogen content below 0.001%).

Ammonia receiving solution, 0.05 *M* potassium dihydrogen phosphate containing 0.103 mg. per ml. of bromo cresol green W.S. (Coleman and Bell).

Titration acid, 0.05 *M* hydrochloric acid containing 0.103 mg. per ml. of bromo cresol green W.S.

Titration end-point standard, 0.103 mg. per ml. of bromocresol green in 0.2 *M* acetate buffer, pH 4.5, used to approximate the end point for the first blank. The acetate standard is then discarded and first blank is used as matching standard for series.

PROCEDURE

The experimental samples were animal tissue sections 10 μ thick and 3 mm. in diameter (0.07-μl. volume), from which the paraffin was removed by placing the section in the destruction tube and washing with three changes of benzene. The method was checked for completeness of destruction from time to time against samples of casein of known macro-Kjeldahl nitrogen value. In each series of determinations, blanks and ammonium sulfate standards were included. For samples of approximately 1 microgram of nitrogen, twenty destruction tubes, including blanks, standards, and experimental material, were set up in the morning, permitting one person to complete the digestions and to make the transfers to distillation tubes by mid-afternoon.

DESTRUCTION

The destruction procedure was that of Bruel *et al.* (*2*), with the omission of selenium and the addition of the use of hydrogen peroxide and potassium persulfate.

To the 6 × 50 mm. destruction tubes containing the samples to be analyzed, 5 μl. of catalytic "blue mixture" are added, followed by 10 μl of 1 to 1 sulfuric acid. The tubes are placed in the first hot block at 90° C. or lower, and the temperature is raised slowly (about 2° per minute between 90° and 130°) to 130° to 170° C. to evaporate most of the water in 1 hour. When the upper portion of each tube is free of condensed water, the tubes are transferred to the destruction block at 245° ± 5° C. for 2 hours. The temperature of the destruction block is adjusted so that a ring of condensing sulfuric acid is established in the tube about 5 to 10 mm. above the surface of the block. After 2 hours these digests are removed to a cool block, cleared by addition of 5 μl. of 30% hydrogen peroxide, and reheated, peroxide is eliminated by dilution and heating, and finally 10 μl. of saturated potassium persulfate are added. After each addition of aqueous solution the tubes are transferred to the 90° block, and the water is eliminated as described above and then transferred to the destruction block where it is allowed to remain for 30 minutes.

Many investigators will have individual preferences with respect to destruction mixtures, catalysts, and time schedules for particular materials. Such variants may require changes in the temperature of the destruction block in order to maintain the position of the condensing ring of sulfuric acid at a suitable level. If appreciably higher destruction temperatures are desirable, it is advisable to use destruction blocks with holes only 10 mm. deep instead of the 15 mm. recommended here.

TRANSFER AND DISTILLATION

The digest is transferred to the coated distillation tube as described by Bruel *et al.* (*2*), with the substitution of a Teflon surface for their paraffin one. A 50-μl. pipet of redistilled water is discharged onto a clean hydrophobic Teflon surface to give three rounded drops of slightly unequal size. The same 50-μl. pipet is inserted into the destruction tube and the acid digest is sucked up as completely as possible and transferred to the bottom of the distillation tube. The smallest of the three drops is sucked up entirely from the Teflon surface and discharged from the pipet onto the wall of the destruction tube to rinse it down. After allowing drainage to the bottom, this portion is transferred as completely as possible to the bottom of the distillation tube. The second and finally the third and largest of the drops are similarly taken up, discharged to rinse the destruction tube, and transferred to the distillation tube. Because the transfer pipet must never touch the wall of the destruction tube except at the tip, the use of 6-mm. destruction tubes is technically less exacting than the 3-mm. Bruel *et al.* tubes. As directed by Bruel *et al.*, the transfer pipet must never touch the wall of the distillation tube above the level of the diluted digest.

To the transferred diluted digest (ca. 55 μl.) which is at the bottom of the tube, 20 μl. of 13 *N* carbonate-free sodium hydroxide are added and immediately thereafter a liquid seal of 100 μl. of ammonia receiving solution is set across the tube about 5 mm. above the alkalinized digest. The digest is mixed by rotating the tube, closed with a capillary cap, and distilled for 8 to 16 hours at 25° C. The distillation may be accelerated by half submerging vessels in 40° C. bath as described by Bruel *et al.*

TITRATION

A flea is dropped into the ammonia receiving solution and the solution is titrated with 0.05 *M* hydrochloric acid containing bromocresol green directly into the liquid seal to an end point at pH 4.5 to 4.6. With moderate care the liquid seal is stable and does not fall down into the alkaline digest unless severely jarred. Alternatively, the ammonia may be received in standard acid and Bruel's procedure followed for titration, or the ring of acid plus ammonia may be transferred to a third tube, nesslerized, and measured in a colorimeter. The authors have found that the errors introduced by the second transfer are of about the same order as the subjective errors of the titration.

VARIATIONS OF RANGE

As pointed out by Carlsberg workers, it is optimal to use approximately 1 μl. of concentrated sulfuric acid per microgram of organic material to be analyzed. The 6-mm. destruction tubes require 5 μl. of concentrated sulfuric acid to reflux properly and they handle as much as 30 μl. The volume of hydroxide should be scaled in proportion to the amount of sulfuric acid used. The authors employed 13 *N* hydroxide because it can be pipetted more precisely than 18 *N*. The strength of the receiving buffer may be modified to suit the expected amount of ammonia, the more dilute buffers yielding more precise titrations.

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Kjeldahl Ultramicrodetermination of Nitrogen

Applications in the Industrial Laboratory

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PROCEDURES for the Kjeldahl ultramicrodetermination of nitrogen have been described by Linderstrøm-Lang and his co-workers (*3*, *13*), Kirk (*14*), and others (*2*, *5*), and have been used in biochemical research for some time. In spite of the usefulness of its technique, however, the Kjeldahl ultramicromethod has not been tested to any great extent by those working in industrial laboratories. An important consideration here may be a reluctance on the part of busy analysts to devote time to learning what appears to be a difficult technique. In this article several examples are given of successful applications of Kjeldahl ultramicroprocedures to the solution of typical routine problems where very small amounts of nitrogen have to be determined. In view of experience acquired in this laboratory, the Kjeldahl ultramicromethod has been established on a permanent basis and other useful applications are anticipated. Three problems are described, which differ in their background and each may suggest further applications of the method.

NITROGEN IN ORGANIC NITRATES PRESENT IN ATMOSPHERE

It was of interest to secure information concerning the concentration of nitric acid esters in the atmosphere at locations where nitroglycerin and glycol dinitrate were being handled. Components in the air might be vapors of the corresponding nitric acid esters (toxic), inorganic nitrate dust (nontoxic), and traces of nitrate esters adsorbed on inert dust particles (toxic). It was recognized that the mass spectrograph could

The Kjeldahl ultramicrodetermination has useful applications in the industrial research laboratory. Examples are given of three types of problems where the method has proved useful in industrial practice, and suitable procedures are described. The Carlsberg technique is satisfactory for the analysis of research samples where the quantity of material is small and the percentage of nitrogen low, provided that the nitrogen is present in reduced form.

be used to ascertain the trace concentration of toxic nitrate vapor. A microchemical method was desired, however, for determining the total combined nitrogen whether present in the atmosphere as vapor or as dust. Deduction of the nitrogen figures obtained by the mass spectrograph from the total nitrogen values furnished by the microchemical method should provide data on the ratio of toxic to nontoxic nitrogen present.

Table I. Kjeldahl Microanalyses of Potassium Nitrate Solutions Reduced by Devarda's Alloy

	Nitrogen, Mg./Ml.
Calculated for KNO_3	0.3500
Found	0.3502
	0.3509

Table II. Kjeldahl Microanalyses of Dilute Nitroglycerin Solution Reduced by Devarda's Alloy

Sample Solution	Sample, Ml.	Nitrogen, Mg./Ml.		Nitrogen, %	
		Theory	Found	Theory	Found
KNO_3	0.972	0.3500	0.3548	13.86	14.04
NG[a]	2.000	0.1028	0.1025	18.50	18.45
			0.1046		18.83
			0.1018		18.32
				Mean	18.53

[a] 0.5 gram of nitroglycerin in 900 ml. of water at 20°.

Accordingly, atmospheric samplings were taken at various plant locations by aspirating metered quantities of atmosphere through different volumes of pure water. Such solutions were then forwarded to the microanalytical laboratory for study. Chloroform was later substituted for water as a collection medium. Accuracy of procedure was controlled by analysis of standard solutions made up from pure nitroglycerin or ethylene glycol dinitrate samples. Standard solutions of potassium nitrate were also employed. The method was first worked out on a micro basis and then shifted into the ultramicro range. Only analyses on the control solutions are reported here.

Because the Kjeldahl method is inapplicable to compounds with nitrogen bound to oxygen, solutions of nitrate in their extreme dilution have to be quantitatively reduced before kjeldahlization. Catalytic reduction of dilute nitrate solutions by Adams catalyst was found to be nonquantitative, only a 50% nitrogen recovery being obtained when the reduced solution was analyzed according to the conventional microprocedure. Reduction by Devarda's alloy (copper, aluminum, zinc) (*7*, *9*), on the other hand, was satisfactory and good nitrogen figures for nitroglycerin as well as for potassium nitrate were obtained by Kjeldahl microanalysis when their solutions were reduced by this method (Tables I and II).

For the Kjeldahl ultramicroprocedure the following important experimental techniques were employed at the start of this study: absorption of diffused ammonia by sodium dihydrogen phosphate solution contained in a platinum wire helix; electrometric titration; and use of a simple gravity microburet. Other techniques might have been chosen instead. Typical results are shown in Table III. In later work with research compounds containing nitrogen already in a reduced state, the techniques mentioned above were abandoned in favor of those embodied in the Carlsberg procedure.

Subsequent work on the nitroglycerin problem involved the analysis of chloroform solutions for traces of nitric acid esters. Here the ordinary Kjeldahl microprocedure in a modified Parnas-Wagner distillation flask was found sufficiently accurate for the quantities of sample received. Satisfactory results were obtained when the volatile solvent was first distilled from a chloroform–sodium hydroxide mixture in contact with the sample before the reducing alloy was added. A simple indicator titration was used to determine the ammonia. Nitrogen figures by the Kjeldahl micromethod on standard chloroform solutions of nitric acid esters were satisfactory for concentrations as low as 6×10^{-3} mg. of nitrogen per ml.

ORGANIC NITROGEN PRESENT AS AROMATIC NITRO COMPOUNDS IN ATMOSPHERE

Information was desired concerning the concentration of *o*- and *p*-nitrophenol in the atmosphere during a manufacturing operation where these substances were being produced. Atmospheric samplings were taken in this instance at various locations by aspirating metered quantities of atmosphere through a measured volume of isopropyl alcohol. In order to convert the nitro compound to the amino compound, so that it would be suitable for the Kjeldahl ultramicroprocedure, catalytic hydrogenation with Adams catalyst was employed. Reduction under these conditions was found to be quantitative for standard solutions of *p*-nitrochlorobenzene in isopropyl alcohol even in extremely high dilutions. Satisfactory analyses on prepared standards by means of the same ultramicrotechnique used for nitrogen in organic nitrates along with a necessary digestion are shown in Table IV. On the basis of such control experiments, analyses were run on atmospheric samples.

Table III. Kjeldahl Ultramicroanalyses of Potassium Nitrate and Nitroglycerin Solutions Reduced by Devarda's Alloy

Sample	Sample, Ml.	N in Sample, Mg.	0.02 *N* HCl, Theory, Ml.	0.02 *N* HCl Consumed, Ml.	N Found, Mg.
KNO_3	0.05	0.01752	0.0603	0.0600	0.01742
				0.0608	0.01766
				0.0632	0.01835
				Mean	0.01781
NG[a]	0.20	0.02055	0.0708	0.0631	0.01832
				0.0708	0.02056
				0.0704	0.02044
				0.0751	0.02198
				0.0694	0.02015
				0.0706	0.02050
				0.0709	0.02059
				0.0642	0.01804
				0.0683	0.01975
				Mean	0.02003
NG	0.05	0.00513	0.0182	0.0256	0.007237
				0.0215	0.006080
				0.0177	0.005004
				0.0128	0.003619
				0.0156	0.004410
				0.0208	0.005880
				Mean	0.00537
EGDN-NG[b]	0.05	0.00514	0.0182	0.0192	0.005428
				0.0176	0.004976
				0.0177	0.005004
				0.0177	0.005004
				Mean	0.00510

[a] NG, 0.5 gram of nitroglycerin/900 ml. of water at 20° C.
[b] EGDN-NG, 0.5 gram (75% nitroglycerin–25% ethylene glycol dinitrate) per 900 ml. of water at 21° C.

Table IV. Kjeldahl Ultramicroanalyses of *p*-Nitrochlorobenzene in Isopropyl Alcohol after Reduction by Catalytic Hydrogenation

Sample, Ml.	N in Sample, Mg.	0.01 *N* HCl, Theory, Ml.	Total Titer Less Blank	N Found, Mg.
1.007	10.6×10^{-3}	0.0729	0.0751	10.9×10^{-3}
			0.0692	10.1×10^{-3}
			0.0711	10.3×10^{-3}
			0.0676	9.8×10^{-3}
			0.0676	9.8×10^{-3}
			Mean	10.2×10^{-3}

NITROGEN IN RESEARCH PREPARATIONS

The need for the Kjeldahl ultramicromethod appears in situations where the amount of sample available is too small for an ordinary microdetermination of nitrogen or where the nitrogen percentage of a given microsample is unusually low. In such instances the Carlsberg method has been used to advantage in this laboratory and seems to yield more precision than the ultramicrotechnique described above.

It was decided to convert to this procedure for several reasons: Analyses can be done on a very fine scale; less surface of liquid is exposed to possible contamination from the atmosphere during the titration; beginners do better with the indicator titration than with an electrometric one; and stirring with the "electric flea" is analytically safer than with a rotating mechanical stirrer. Like the other Kjeldahl ultramicroprocedures, this one is adaptable to serial analysis, and there is the possibility of digesting many samples at one time or of performing numerous ammonia diffusions in one operation. Final titrations can then be run in succession.

Table V. Kjeldahl Ultramicroanalyses of National Bureau of Standards Acetanilide

Set	Sample	Sample, μl.	N, γ	0.01 *N* HCl Found,[a] μl.	0.01 *N* HCl Blank, μl.	Normality Found	N Theory, %	N Found, %
20	Ammonium oxalate	10.42	1.030	6.85	1.59	0.01073	...	...
				6.77	1.59	0.01086	...	...
	C_8H_9NO	10.42	1.150	7.71	2.28	...	10.37	10.51
				7.51	2.28	...	10.37	10.24
				7.43	2.28	...	10.37	10.13
21	Ammonium oxalate	10.42	1.030	6.90	0.85	0.01066	...	...
				6.85	0.85	0.01073	...	...
	C_8H_9NO	10.42	1.147	7.36	1.68	...	10.37	9.98
				7.69	1.68	...	10.37	10.42
				7.65	1.68	...	10.37	10.37
				7.68	1.68	...	10.37	10.41

[a] After deducting blank.

Before attempting to use the Carlsberg procedure on valuable research preparations, practice analyses were run on National Bureau of Standards acetanilide. As in previous work with the Kjeldahl ultramicromethod, dilute hydrochloric acid standardized against ammonia distilled from aliquots of ammonium oxalate of known strength was used in this titration. Carefully measured volumes of oxalate solution were carried along with the samples through the ammonia-diffusion operation as a control for completeness of diffusion. Typical precision in the standardization of acid and analysis of acetanilide is shown in Table V. Analyses for nitrogen in research samples are shown in Table VI.

DETERMINATION OF NITROGEN IN ORGANIC NITRATE SOLUTIONS

Micromethod. Apparatus (Figures 1 and 2). The reaction and distilling flask, *A*, was a modification of the Parnas-Wagner Kjeldahl microapparatus. The usual vacuum jacket was omitted so that the flask could be more readily heated, and a small reflux condenser, *B*, was added to the system. The silver tube condenser, *C*, leads to a receiver, *D*. An automatic 10-ml. reservoir buret graduated in 0.05 ml. was used in the titration. A silver tube condenser on the Kjeldahl microapparatus was found necessary.

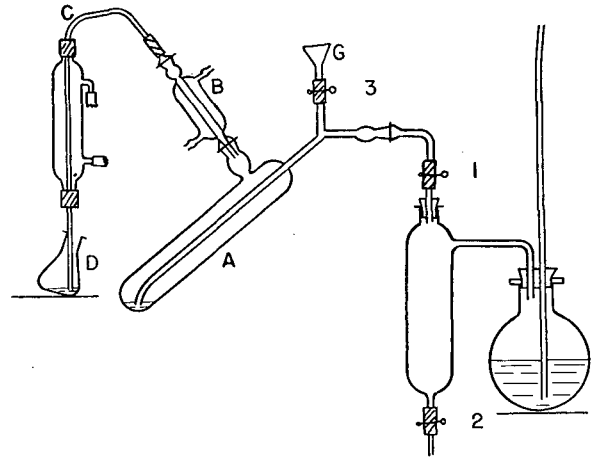

Figure 1. Modified Distillation Apparatus

Reagents. The following reagents were used: nitrate-free absolute alcohol; c.p. potassium hydroxide pellets; silicone oil (antifoam reagent, G. E. 9981 LTNV-70); boric acid (2%); bromocresol green–methyl red indicator (1 to 1 mixture dissolved in alcohol); Devarda's alloy (50% copper, 45% aluminum, 5% zinc) (100 mesh, washed and dried); conductivity water (nitrate- and ammonia-free); and hydrochloric acid (0.01 *N*, standardized against ammonia distilled into boric acid from measured volumes of ammonium oxalate solution made up from weighed out salt).

Procedure. The distillation apparatus is first steamed out until 30 ml. of water collect in receiver *D* (Figure 1). Five milliliters of 2% boric acid and 5 drops of 0.2% indicator are placed in the receiver (tip of silver condenser 1 cm. above surface of liquid), and the measured aliquot of sample is run in through *G*, followed by 2 drops of silicone oil. The funnel is rinsed with 0.5 ml. of ethyl alcohol and closed by pinchclamp 3. Four pellets of potassium hydroxide are placed in the funnel and dissolved in 1 ml. of water. The potassium hydroxide is then run in and clamp 3 is closed again. (The condenser tip is now put beneath the liquid in *D*.)

Two hundred milligrams of Devarda's alloy (measured by scoop) are placed in the funnel and washed down by two 0.5-ml. portions of water, clamp 3 being closed at once.

The distillation flask is heated by a boiling water bath. When boiling in the reaction flask begins, steam is admitted by opening clamp 1 and closing 2. The steam distillation is continued for 2 minutes after the appearance of green color in the indicator.

From here on the usual Kjeldahl technique applies. The microtitration with 0.01 *N* hydrochloric acid is carried to an end point where one additional drop produces a pink color.

When only microgram quantities of nitrogen are present in the aliquot taken for analysis, the contents of the receiver are quantitatively transferred to a 50-ml. beaker and brought to the same volume each time with water. Such solution is titrated electrometrically by means of the calomel and quinhydrone electrodes of Hawes and Skavinski (*5*), using a Fisher "senior titrimeter." A titration of ammonia from a known sample of ammonium oxalate and a blank titration will establish a reference end point in millivolts on the titrimeter to which all future titrations may be carried.

Calculation.

$$\% \text{ N} = \frac{\text{ml. of HCl (less blank)} \times \text{normality} \times 14.008 \times 100}{\text{mg. of sample}}$$

Ultramicroprocedure. The ultramicroprocedure described here for nitrate nitrogen is an adaptation of the Kjeldahl ultramicro-

procedure of Hawes and Skavinski (*5*) and requires much of their apparatus and technique. Samples equivalent to from 4 × 10^{-3} to 30 × 10^{-3} mg. of nitrogen in volumes of solution up to 1.0 ml. were taken for analysis.

APPARATUS (Figure 3). Test tube diffusion cell, platinum wire helix of 5 turns of No. 22 (British gage) wire, coil diameter 2.4 mm.; handle 15 mm., capacity 0.04 ml.

Calomel and quinhydrone electrodes.

Titration vessel (capacity 1.5 ml.) and No. 10 platinum wire corkscrew stirrer.

Gravity microburet. A 0.2-ml. serological pipet graduated in 0.001 ml. with a new tip drawn at an angle of 60° from the axis. This tip is in turn drawn down to a hair capillary and is adjusted by successive snippings to a delivery flow of 9 × 10^{-3} ml. per minute; the measurement is made with the buret horizontal and the tip below the surface of water. The buret is mounted on a pivoted stand.

Fisher titrimeter, the usual electrometric titration apparatus equipped with "magic eye" and dial to read potential in millivolts.

REAGENTS (in addition to those mentioned for microprocedure). Sodium dihydrogen phosphate monohydrate (0.2 *M* in water); 0.02 *N* standard hydrochloric acid; quinhydrone; and C.P. sodium hydroxide pellets.

PROCEDURE. Four milligrams of Devarda's alloy are placed at the bottom of a clean, dry, static-free test tube (tube held horizontal). The sample solution (equivalent to from 5 × 10^{-3} to 30 × 10^{-3} mg.) is next pipetted in (the tube now held vertical) and 1 drop of silicone oil is added.

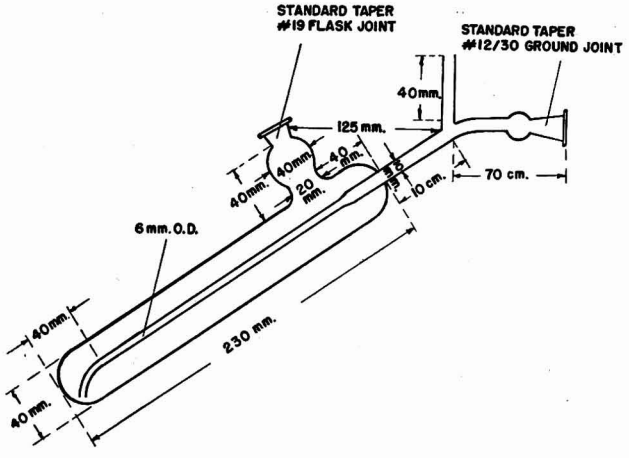

Figure 2. Modified Distilling Flask

Table VI. Kjeldahl Ultramicroanalyses on Research Samples

Set	Sample	Sample Solution, μl.	0.01 *N* HCl Found[a], μl.	N Theory, γ	N Found, γ	N Theory, %	N Found, %
22	Acetanilide	10.42	7.57	1.147	1.169	10.37	10.57
		10.42	7.60	1.147	1.173	10.37	10.61
		10.42	7.72	1.147	1.192	10.37	10.78
	$C_{24}H_{41}NO$,	10.42	6.60	1.015	1.018	3.90	3.91
	(Sample 1)	10.42	7.03	1.015	1.085	3.90	4.16
		10.42	6.81	1.015	1.051	3.90	4.02
		10.42	6.78	1.015	1.047	3.90	4.02
23	Acetanilide	10.42	7.46	1.147	1.144	10.37	10.35
		10.42	7.39	1.147	1.134	10.37	10.25
		10.42	7.13	1.147	1.094	10.37	9.89
		10.42	7.37	1.147	1.130	10.37	10.22
	$C_{24}H_{41}NO$,	10.42	6.47	1.015	0.992	3.90	3.85
	(Sample 2)	10.42	6.75	1.015	1.035	3.90	4.01
		10.42	6.59	1.015	1.011	3.90	3.92
24	Acetanilide	10.42	7.63	1.147	1.162	10.37	10.51
		10.42	7.43	1.147	1.131	10.37	10.48
		10.42	7.32	1.147	1.115	10.37	10.28
	$C_{14}H_{22}N_2O_2S$	10.42	6.67	0.997	1.016	9.92	10.11
		10.42	6.25	0.997	0.952	9.92	9.47[b]
		10.42	6.63	0.997	1.010	9.92	10.05
25	$C_{13}H_{20}N_2O_2S$	10.42	6.65	1.050	1.027	10.44	10.21
		10.42	6.59	1.050	1.017	10.44	10.12
		10.42	6.56	1.050	1.013	10.44	10.07

[a] After deducting blank.
[b] Incomplete digestion. Digest was brown.

The rubber stopper and platinum wire helix are rinsed with distilled water and the helix is dried on clean gauze. A trace of glycerol is smeared around the rubber stopper and the helix is dipped into a portion of the sodium dihydrogen phosphate hydrate solution. With the stopper held in hand, two pellets of sodium hydroxide are carefully let slide down the wall of the inclined test tube.

The helix and stopper are now quickly inserted and the tube and contents are rocked gently (behind a safety screen) for 10 minutes until evolution of hydrogen subsides. From 5 to 5.5 hours are allowed for complete diffusion with the test tube maintained in a slightly inclined position.

One milliliter of conductivity water is placed in the titration cup. The stopper of the test tube is carefully worked loose and the helix withdrawn. The helix is next dipped in the 1 ml. of water within the cup and after removal from the liquid is carefully rinsed off into the solution with 0.3 ml. of water.

A small scoop of quinhydrone is now sprinkled on the surface of the liquid and the cell is raised into position for titration. Stirring is maintained for 10 minutes before starting the electrometric titration, and points for a smooth curve are obtained by making readings at frequent intervals.

DETERMINATION OF NITROGEN IN NITRO COMPOUNDS

Ultramicromethod. APPARATUS. The apparatus used here is the same as that described above for the ultramicroprocedure. In addition, a conventional shaking machine for low pressure hydrogenation is required.

Centrifuge tubes of 30-ml. capacity with a bulge on one side were substituted for the borosilicate glass test tubes used with the platinum wire helix.

REAGENTS (in addition to several reagents used in ultramicroprocedure). Acid digestion mixture containing 0.1 gram of selenium dioxide, 0.15 gram of copper sulfate pentahydrate, 50 ml. of concentrated sulfuric acid, and 50 ml. of conductivity water; 30% hydrogen peroxide; freshly prepared Adams platinum oxide catalyst; and nitrogen-free isopropyl alcohol.

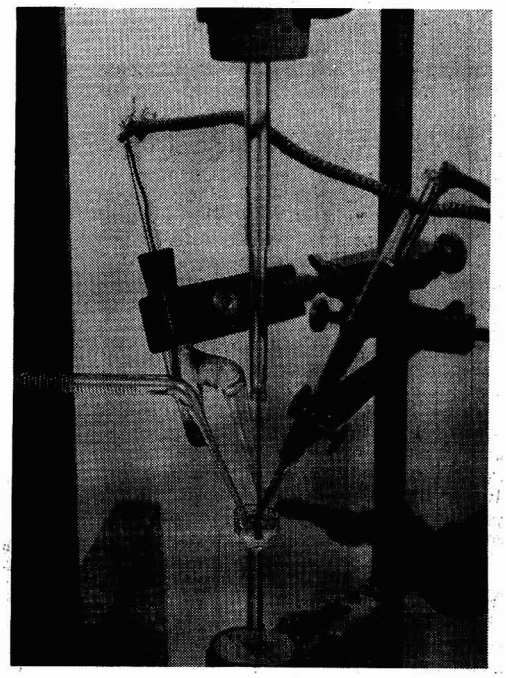

Figure 3. Ultramicro-Kjeldahl Titration

PROCEDURE. Ten milliliters of isopropyl alcohol solution of sample equivalent to 10.06 × 10^{-2} mg. of nitrogen per milliliter are diluted tenfold with more of the same solvent. The dilute solution is hydrogenated overnight in the conventional manner at 35 pounds (15.9 kg.) pressure of hydrogen in the presence of 10 mg. of Adams catalyst. The calculated amount of hydrogen uptake is negligible.

After hydrogenation a 1-ml. sample (1.007 by the authors' calibrated pipet) is withdrawn and is transferred to the bottom of a 30-ml. centrifuge tube with bulge on one side. A 0.20-ml. volume of acid digestion mixture is next added.

The centrifuge tube with its contents is placed in an upright position in a vacuum desiccator over phosphoric anhydride and concentrated at a vacuum of 150 mm. to a volume of 0.4 to 0.5 ml. The vacuum is then increased to 50 mm. and maintained until the volume is 0.3 ml. The solution is finally concentrated to less than 0.2 ml. under a 3-mm. vacuum. The centrifuge tube is then removed, 8 drops of 30% hydrogen peroxide are added, and the tube is placed in a sand bath for digestion according to the procedure of Hawes and Skavinski (*5*). After heating for 5.5 hours it is removed and cooled. If color remains, 1 or 2 drops more of 30% hydrogen peroxide are added and heating is resumed for 0.75 hour.

Then 0.80 ml. of conductivity water is added to the cold centrifuge tube. With the tube held in a nearly horizontal position 0.30 ml. of 50% sodium hydroxide is carefully placed in the bulge. Then the rubber stopper with its spiral containing 0.04 ml. of 0.2 *M* sodium dihydrogen phosphate hydrate solution is lubricated with glycerol and inserted without mixing the other two solutions in the centrifuge tube. After the end of the tube has been chilled in an ice bath, the alkali and sulfuric acid are thoroughly mixed and 5.5 hours are allowed for completion of diffusion. The rest of the procedure is carried out as described above. Blank runs were made on the isopropyl alcohol solvent carrying them through the digestion procedure.

DETERMINATION OF NITROGEN IN RESEARCH PREPARATIONS

Carlsberg Ultramicromethod. APPARATUS. With the exception of certain modifications developed in this laboratory, apparatus used in this work has been described (*1*, *3*, *6*, *10–12*). Because portions of this literature are not easily accessible to some who may be interested in the method, details of basic equipment are summarized here.

PERMANENT PIPET RACK. A permanent pipet rack, constructed of Flexaframe connectors and 0.5-inch stainless steel rod, is useful for protecting ultramicropipets in a crowded laboratory (Figure 4). It also furnishes support for the air pressure regulator which consists of a vertical glass cylinder 44 mm. in outside diameter and 620 mm. high, provided with a lower side arm and connected by means of rubber tubing to a leveling bulb. A glass inlet tube 4 mm. in outside diameter extends almost to the bottom of the cylinder and water is the confining liquid.

STAINLESS STEEL HEATING BLOCK. A heavy block with seven vertical borings 14 mm. in diameter and 18 mm. deep is used to contain glass vials for the acid baths. The authors' block is a hexagonal prism of stainless steel which happened to be on hand in the laboratory. It is 100 mm. high and measures 52 mm. on edge.

ILLUMINATION ASSEMBLY FOR TRANSFER OF DIGEST. A microscope with draw tube removed, but condenser retained, can be used with a simple source of diffused light to facilitate transfer of the digest drop (Figure 5).

ADJUSTABLE SUPPORT STAND. An adjustable stand of the rack and pinion type (Arthur H. Thomas Company, No. 9361-B) is useful for lowering and raising upright digestion or diffusion tubes in pipetting operations.

TITRATION STAND FOR MAGNETIC STIRRING. A conventional rack and pinion titration stand of the Carlsberg type equipped for magnetic stirring (Arthur H. Thomas Company, No. 2463-F) is employed (Figure 6). Stirring is accomplished with the usual glass spheres filled with iron (Arthur H. Thomas Company, No. 2464-C).

ULTRAMICROBURET. The inclined Kirk ultramicroburet (*4*) (Microchemical Specialties Company, No. 110) has a capacity of 35 μl. and its smallest scale units are in 0.1 μl. (Figure 6). Hundredths are estimated.

STAINLESS STEEL TEST TUBE RACK. A special test tube rack of stainless steel has been found useful for supporting 32 diffusion tubes at one time in a constant temperature water bath (Figure 4). Two thin, perforated sheets of steel, 254 × 60 mm. and Nos. 20 and 24 gage in thickness, respectively, maintained 10 mm. apart, one above the other, by separating blocks, are mounted on a base plate 10 mm. thick. The thinner sheet is the upper one. Two parallel bars 5 × 5 mm. in cross section extend lengthwise underneath the edges of each sheet and constitute a rigid support frame for the thin metal. The upper sheet contains 32 holes arranged in two parallel rows which are 14 mm. apart. These holes are 6 mm. in diameter and each is 6 mm. distant from its neighbor in line. The lower sheet has holes 5 mm. in diameter centered directly beneath the upper ones. The successive layers of separating block, support frame, perforated sheet, and covering block, located at each end of the rack, are tightly fastened to the base plate by pairs of countersunk screws extending upward from beneath. Each end of the rack is provided with an eyelet hook for suspending the rack in the water bath.

CONSTANT TEMPERATURE WATER BATH. A Warburg tank equipped with automatic heating and refrigerating units can be conveniently used for maintaining a constant temperature water bath at 40° C.

PIPETS. *Semiautomatic Pipets.* For use with the air pressure regulator, pipets of the following capacities are required: 10, 7, 4, and 18 μl. These pipets are either originals obtained from H. Holter in Copenhagen or copies prepared in this laboratory in the following steps:

1. Borosilicate glass capillary tubing (6 mm. in outside diameter, 1-mm. bore) is drawn down to a uniform 3 mm. in outside diameter by pulling in a brush flame from the blast lamp.
2. A sharp capillary constriction is next made at a point about 3 cm. from where the tapering down of the big capillary begins. Here the tubing is 4 mm. wide. The constriction is produced by heating a spot in the 4-mm. portion with a hot needle-point flame from the oxy-gas hand torch which is clamped in a ring stand. The capillary, held a little above the flame, is rotated slowly while the walls of the inner bore at the heated point contract to a thread. Inspection of the capillary thread should be made with a jeweler's loupe to make sure that a definite channel still remains. Too fine a bore requires too much pressure to expel liquid from the pipet; too coarse a one will not support a column of liquid.
3. By heating at a point 3.5 cm. below the constriction the 3-mm. capillary is drawn down to a 1-mm. outside diameter over a Bunsen flame. The taper thus starts about 2 cm. from the constriction.
4. A cut is now made with the tungsten carbide blade in the

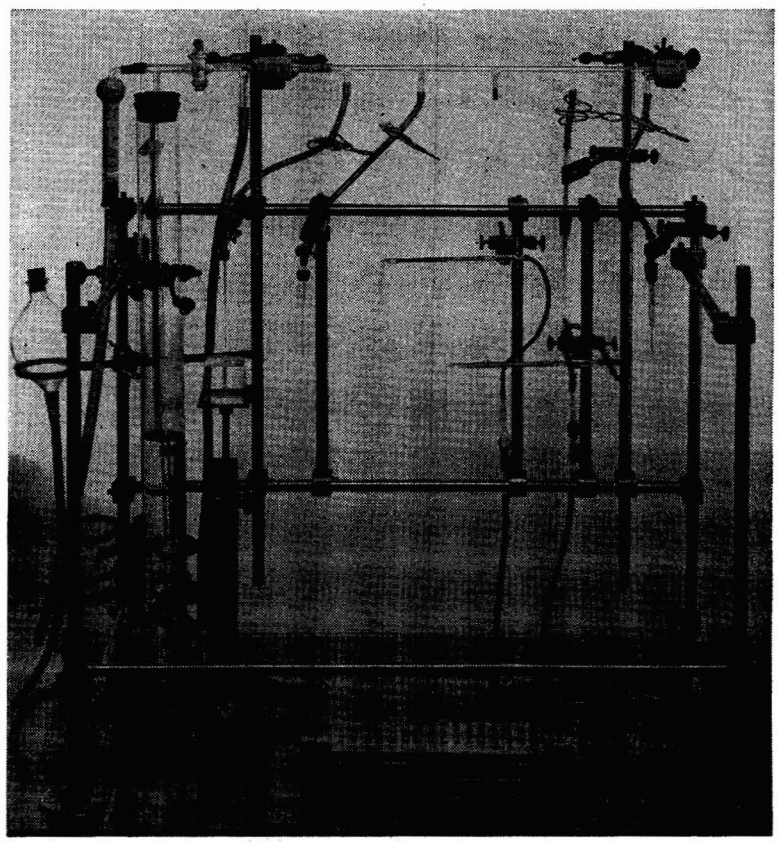

Figure 4. Permanent Pipet Rack for Linderstrøm-Lang Kjeldahl Ultramicrodetermination

Stainless steel test tube rack in foreground

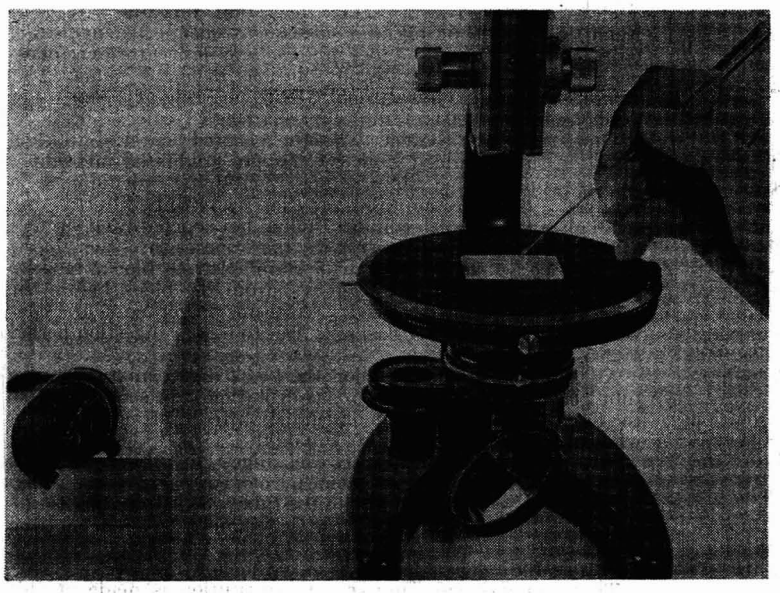

Figure 5. Illuminating Assembly for Transfer of Digest

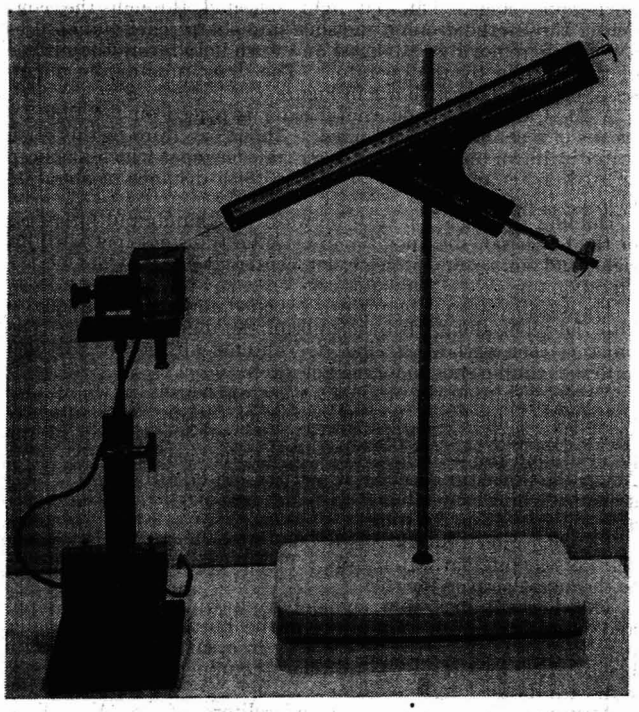

Figure 6. Carlsberg Ultramicro-Kjeldahl Titration with Kirk Ultramicroburet

1-mm. portion at a point 6 cm. from the taper and the end is ground to a bevel on a fine silicon carbide whetstone.

5. The pipet can be calibrated by weighing with water or by titration. For the former method the pipet is filled, allowed to drain to the constriction, and weighed. The water is discharged in the usual manner for these pipets and the weight of the empty pipet is determined.

Graduated Pipets. Pipets to deliver 1 and 9 μl. are made from 5.5-mm. capillary tubing with a 0.5-mm. bore.

1. The capillary bore is blown to an enlargement about three times as wide as itself in two places located about 10 cm. apart.

2. The tubing is then cut off at a point about 3 mm. away from one enlargement, which is then blown to a small heavy-walled bulb at the end of the capillary tubing.

3. The end of the bulb is next blown out and a piece of heavy-walled tubing is sealed to the open end of the bulb for a handle. The half of the bulb next to the handle is now heated in the lamp to redness and the glass pulled straight away. A slight enlargement of the capillary thus remains in the 5-mm. diameter tubing just before the beginning of the taper.

The capillary tubing tapers down within a distance of 1 cm. to a 1.3-mm. outside diameter from its original diameter of 5.5 mm. and continues almost unchanged in external diameter for about 8 cm. The wall is thin and uniform.

4. The needle is now provided with a sharp tip by pulling over a microburner at a point 6 cm. from the beginning of the 1.3-mm. portion. A faint scratch is next made just below this new taper by means of a tungsten carbide blade and the hair is broken off. The tip is gently buffed, holding it vertically against a fine silicon carbide whetstone until trial and error show an orifice sufficient to deliver a jet of water.

5. A right-angled bend is now made in the needle at a point 6 cm. back from the tip by bending over a soft microflame. The bend is just at the base of the heavy taper.

6. The pipet is calibrated at two marks by weighing with water. These marks are exactly 9 cm. apart and correspond to 90 units of ordinary millimeter graph paper, a piece of which is pasted on one side of the capillary after the weighing data have been obtained.

Transfer Pipet. The pipet used for transferring the acid digest is made in the same manner as the graduated pipet, but with no right-angled bend. The stem and first bulb hold about 50 μl.

Hand Delivery Pipets. Calibrated pipets for delivering 50 and 20 μl. (Microchemical Specialties Company No. 28 A-50 lambda and No. 280 A-20 lambda) are also needed.

DIGESTION TUBES. Narrow digestion tubes of the Carlsberg type are used, 40 mm. in length, 2.4 mm. in outside diameter, and 1.8 mm. in inside diameter.

DIFFUSION TUBES. Tubes used for diffusion are 25 mm. long, 6 mm. in outside diameter, and 4 mm. in inside diameter.

SPECIAL DISTILLED WATER RESERVOIR. To furnish a microjet of distilled water with sufficient force to rinse out digestion tubes, a reservoir located 2 meters above the bench is necessary. This reservoir carries a siphon delivery tube extending 2 meters downward and ending in a capillary tip drawn out long and fine enough to reach the bottom of a digestion tube.

GLASS SUCTION CAPILLARY. For withdrawing rinse water from digestion tubes, another glass capillary tip similar to the one above is also necessary. This is connected by suction tubing to a vacuum line.

HOLDERS FOR DIGESTION AND DIFFUSION TUBES. Instead of Carlsberg holders consisting of three vertical bronze pins in a piece of wood, suitably bored Lucite blocks can be used for supporting digestion and diffusion tubes. Such blocks offer the advantage of more security for centering and yet permit visibility of the tube within. Digestion tube holders take one tube; diffusion tube holders, two.

GLASS CONTAINERS FOR SULFURIC ACID BATHS. Small glass vials of the Carlsberg type serve as containers for the sulfuric acid used as a bath during digestion. These are flat-bottomed borosilicate glass cylinders 65 mm. high and 14 mm. in outside diameter. An 11-mm. outside diameter constriction is located at a point 30 mm. up from the base, and the neck is similarly constricted to form a beaded rim.

CAPS FOR DIFFUSION TUBES. For protecting diffusion tubes while in the water bath, caps consisting of gum rubber connectors and glass capillary tips are required.

Reagents. SPECIAL DISTILLED WATER. Conductivity water distilled in a ground-glass apparatus over alkaline permanganate is used in preparing all aqueous solutions. Fifty milliliters of solution, prepared by dissolving 0.4 gram of potassium permanganate and 15 grams of potassium hydroxide in 50 ml. of water, are added to 2.5 liters of distilled water. After the mixture is boiled for 0.5 hour with no water in the condenser jacket, distillation is begun and the first 300 ml. of distillate are discarded. Only two thirds of the original volume are distilled off.

BLUE MIXTURE. In a 100-ml. volumetric flask are placed 1 gram copper sulfate pentahydrate, 10 grams of potassium sulfate, and 0.2 gram of sucrose. Seventy-five milliliters of conductivity water are added to dissolve the solid materials and 5 ml. of concentrated sulfuric acid are pipetted in. The cool solution is finally diluted to the mark.

SULFURIC ACID–SELENIUM MIXTURE. A solution is prepared by adding 50 mg. of powdered selenium to 5 ml. of concentrated sulfuric acid and heating until clear.

SULFURIC ACID–POTASSIUM SULFATE BATH. A stock solution is prepared by dissolving 10 grams of potassium sulfate in 25 ml. of concentrated sulfuric acid.

PARAFFIN. Paraffin taken from the interior of a clear block is used (Socony Vacuum Company, Tavern Paraseal wax).

MISCELLANEOUS CHEMICALS. Acetone, toluene, and 18 *N* hydroxide.

DILUTE SULFURIC ACID. A 0.015 *N* acid is prepared by diluting an aliquot of 0.15 *N* acid which has been standardized against standard 0.100 *N* sodium hydroxide laboratory solution.

BROMOCRESOL GREEN INDICATOR (0.4 mg. of dye per ml., pH 4.6). A 100-mg. portion of dye is dissolved in 2.9 of 0.05 *N* sodium hydroxide with warming (*8*). This solution is quantitatively transferred to a 250-ml. volumetric flask and diluted to the mark with special distilled water. The pH is adjusted to 4.6 by the addition of a few drops of 0.05 *N* sodium hydroxide, the value being measured on the Beckman pH meter. The 0.05 *N* alkali is obtained by diluting an aliquot of 0.100 *N* sodium hydroxide with conductivity water.

SPECIAL PHOSPHATE SOLUTION. A special phosphate solution is freshly prepared for use with each series of titrations. It contains 0.125 ml. of 0.067 *M* disodium hydrogen phosphate, 0.5 ml. of bromocresol green (0.4 mg. of dye per ml., pH 4.6), and 0.625 ml. of conductivity water.

STANDARD 0.01 *N* HYDROCHLORIC ACID. A 50-ml. portion of standard 0.100 *N* hydrochloric acid laboratory solution is added to 50 ml. of bromocresol green (0.4 mg. of dye per ml., pH 4.6) and diluted to 500 ml. with conductivity water.

COLOR STANDARD. A solution to reproduce the proper end point in the titration can be prepared by diluting 0.2 ml. of bromocresol green (0.4 mg. of dye per ml., pH 4.6) to 2.0 ml. with a suitable buffer of pH 4.6. A phosphate buffer for pH 4.6 consisting of 21.30 ml. of 0.1 *M* citric acid and 18.70 ml. of 0.2 *M* disodium hydrogen phosphate may be used for this purpose.

DRI-FILM. General Electric Dri-Film 9987 has been found useful as a hydrophobic coating for the outer surface of pipet tips.

Procedure. The following laboratory directions are a condensation of the detailed description as given in Brüel's article (*3*). A few modifications of the authors are included.

PREPARATION OF GLASSWARE. Sufficient digestion tubes are successively treated with hot chromic-sulfuric acid cleaning solution, cold distilled water, and conductivity water, and are dried in the oven. They are first boiled in the acid in a beaker and upon cooling are transferred to a suction flask. Complete rinsing is accomplished by alternate evacuation and filling under distilled water. Each tube is finally rinsed on the inside with conductivity water from the reservoir, and its final contents are withdrawn by means of the suction capillary. The clean tubes are stored after drying in a wide-mouthed weighing bottle.

Diffusion tubes are successively treated with boiling distilled water, cold acetone, hot toluene, and cold acetone, and are finally boiled in two portions of distilled water. They are then dried in the oven and stored under a glass cover.

Diffusion tubes are internally coated with paraffin by filling with melt and rotating between the palms of the hands until solidification begins on the inner walls. Excess melt is quickly shaken out and each tube is rotated until the paraffin has set.

PREPARATION OF SAMPLE. After calculation of the dilution of sample equivalent to about 1 microgram of nitrogen in the volume of solution delivered by the calibrated sample pipet, the calculated weight of sample is placed in a 1-ml. Krumholz volumetric flask and dissolved, and the solution is diluted to the mark.

INTRODUCING SAMPLE SOLUTION. A volume of 10.42 μl. of the sample solution (the capacity of the authors' pipet) is delivered to the bottom of the digestion tube. (Two or three controls of a standard test sample are set up at the same time along with several solvent blanks.) Occasionally the outside of the pipet tip is treated with silicone oil, Dri-Film 9987, to prevent liquid from adhering to it.

The sample pipet is filled with sample solution by means of a gentle suction on the proper rubber tubing when the stopcock to the permanent air pressure regulator is closed off. After the meniscus has risen above the capillary construction of the pipet, the suction is broken. Then the meniscus falls back to the constriction, where surface tension prevents any further drainage. At this moment the volumetric flask is lowered from the pipet tip and the upright digestion tube in its Lucite block is substituted in its place and raised into position.

When the stopcock is opened, air from the calibrated pressure regulator gently expels the contents of the pipet at the bottom of the digestion tube.

By a similar procedure 4 μl. of Carlsberg "blue mixture" is added from another semiautomatic pipet to the sample at the bottom of the digestion tube.

DEHYDRATING THE SAMPLE. Digestion mixtures are subjected to vacuum drying and subsequent chemical dehydration by placing the digestion tubes in a vacuum desiccator over phosphoric anhydride. (For water solutions drying is achieved at 150 mm. of mercury for 24 hours; with charring at 4 mm. For alcohol solutions 300 mm. suffice for charring.)

DIGESTING THE SAMPLE. To the charred material in each digestion tube is added from a Carlsberg graduated micropipet 1μl. of concentrated sulfuric acid containing selenium as a catalyst. The digestion tubes are then ready to be inserted into small glass flasks which contain 1 ml. of hot concentrated sulfuric acid and potassium sulfate for the digestion bath. Such baths are first heated to 295° C. in a stainless steel block, but are allowed to cool slightly by removal from the block before the tubes are actually immersed. (Asbestos finger cots are convenient for handling hot flasks.) A 5- to 6-hour digestion period at 295° is observed.

At the onset of the digestion the black digest mixture in the tube generally rises because of gas evolution. In such instances the flask and its tubes are momentarily lifted up from the block, whereupon the liquid seals break and fall.

When the digestion is over, each digestion tube is removed from its slightly cooled bath by means of a conical glass rod which is gently pressed into the neck of the tube. Acid adhering to the outside of the tube is rinsed off with conductivity water and the tube is wiped with a clean, lint-free towel. It is then placed in a beaker and stored in a desiccator until time for transfer.

TRANSFERRING THE DIGEST. A substitution is made at this step for the Carlsberg paraffin block, by using a microscope slide coated with paraffin on its upper surface. In this way it is possible to secure optical illumination of the transfer drop by use of the microscope stage. Diffused light reflected through the condenser throws the drop on the slide into sharp relief and ensures a complete removal of all digest and wash liquid from the surface of the paraffin by the operator. The draw tube of the microscope is removed as is shown in Figure 5.

A 20-μl. drop of conductivity water is placed on the slide by means of a calibrated hand pipet. About one third of this wash water is drawn up into a Carlsberg transfer pipet which has been treated on the outside with Dri-Film for a distance of about 45 mm. up from the tip.

Holding the digestion tube between the thumb and forefinger of the left hand, the operator inserts the transfer pipet with his right and guides it to the exact center at the bottom of the digestion tube.

The wash water in the pipet is expelled and is drawn back up into the pipet along with the bulk of the digest solution. The pipet is then withdrawn and its contents are gently expelled onto the paraffin slide to form a new drop.

A second third of the original water drop is next drawn up into the pipet. This time the inner walls of the digestion tube are rinsed by gently expelling water while moving the tip of the pipet around the walls as it approaches the bottom of the tube. Again the pipet tip is centered and the liquid withdrawn. This second washing is combined with the first portion of the digest solution already on the slide.

The digestion tube is rinsed once more with the remaining third of the original water drop. This portion is likewise added to the digest drop on the slide.

The digest drop is now completely drawn up into the pipet and is quantitatively deposited at the bottom of an upright, paraffin-lined diffusion tube standing in a suitably bored Lucite block. It is important not to touch the upper part of the inner wall with the acid digest solution.

AMMONIA DIFFUSION. Nine microliters of 18 *N* sodium hydroxide solution are injected into the digest liquid at the bottom of the diffusion tube by means of a Carlsberg graduated pipet. A coating of Dri-Film on the outer surface of this pipet prevents adherence of liquid upon withdrawal. The diffusion tube is maintained in a vertical position during this operation by supporting it within a Lucite block.

After the sodium hydroxide pipet has been withdrawn, the diffusion tube is sealed with 50 μl. of conductivity water which is placed at a point about 5 mm. below the rim of the tube. A 50-μl. calibrated Misco hand pipet is used.

Now 7 μl. of 0.015 *N* sulfuric acid are injected into the seal by means of another Carlsberg semiautomatic pipet and the diffusion tube is capped with a glass capillary tip held in place by a rubber connection.

The diffusion tube is placed in a stainless steel rack which is then immersed in a constant temperature water bath set at 40 °C. The rack should be submerged to a depth sufficient to cover only the lower drop of liquid in the diffusion tube. A period of 1.5 hours is allowed for complete diffusion, after which time the rack is withdrawn from the water bath and the diffusion tubes are put under cover.

TITRATION. The titration is carried out using the Kirk ultramicroburet and the conventional Carlsberg stand with magnetic stirring. The inclined buret is provided with an auxiliary capillary tip which is bent downward to an exact vertical position and attached by a rubber tubing connection ligatured with fine wire.

The diffusion tube is uncapped and placed in a double-bore Lucite block beside a similar tube containing a seal of color standard. Eighteen microliters of freshly prepared phosphate solution are injected by means of a Carlsberg semiautomatic pipet into the liquid seal which is to be titrated. A stirring bead (flea) previously cleaned with 1 to 1 hydrochloric acid and carefully washed with conductivity water is dropped into the seal.

The titration is carried to an end point of pH 4.6 using 0.01 *N* hydrochloric acid containing bromocresol green. The end point is assumed to be reached when the color matches that of the standard.

STANDARDIZATION OF HYDROCHLORIC ACID. Hydrochloric acid used in the titration is restandardized each time that a series of samples is analyzed. A volume of ammonium oxalate solution equivalent to 1 microgram of nitrogen is placed at the bottom of a paraffin-lined diffusion tube by means of the semiautomatic pipet used for delivering all liquid samples. Identical volumes of the conductivity water used as a solvent for the ammonium oxalate are also measured out into diffusion tubes for the determination of the blank.

The oxalate samples and blanks are then set up for the ammonia diffusion in the same manner as the digested samples. The regular procedure is followed, beginning at the point where 9 μl. of 18 *N* sodium hydroxide are added to the liquid at the bottom of the diffusion tube.

COORDINATION OF STANDARD, SAMPLE, AND BLANK RUNS. Complete data are available when a typical series includes analyses of the following: standard test samples, analytical samples, blanks on solvent used for both standard and samples, ammonium oxalate samples for standardization of hydrochloric acid, and blanks on water used to dissolve ammonium oxalate.

$$\text{Normality} = \frac{(\gamma \text{ of N in oxalate sample})}{14.008 \times (\mu\text{l. of HCl total} - \mu\text{l. of HCl for water blank})}$$

$$\%\,N = \frac{\text{normality} \times 14.008 \times (\mu\text{l. of HCl total} - \mu\text{l. of HCl for sample solvent blank})}{\gamma \text{ of sample}} \times 100$$

ACKNOWLEDGMENT

The authors wish to acknowledge the helpful encouragement of R. P. Chapman, director of the Analytical and Testing Division of the Stamford Research Laboratories, under whose supervision this work was performed. Acknowledgment is also made to L. V. Clark, J. H. Steele, and F. H. Bailey at the New Castle Laboratory in the Explosives Division of the American Cyanamid Company for the preparation of the standard nitroglycerin and ethylene glycol dinitrate solutions used in this work.

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NOTES ON ANALYTICAL PROCEDURES . . .

Distillation-Duffusion Unit

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WITH the introduction by Conway and Byrne (*3*) of a simple diffusion or isothermal distillation unit, a new and profitable field of microanalysis was initiated which has been well summarized by Conway (*2*). The adaptation to the microgram scale has been made by numerous investigators, including Gibbs and Kirk (*4*), Borsook and Dubnoff (*1*), Needham and Boell (*6*), Tompkins and Kirk (*7*), and Winnick (*8*). The same principle has been used for very fine scale analyses by Linderstrøm-Lang and co-workers (*5*).

The chief objections to the application of diffusion units have been the comparative slowness of the diffusion, which requires, depending on the type of unit and the technique, from 1.5 to 12 or more hours; and the fact that certain materials which have a relatively low vapor pressure, or for which there does not exist a good chemical absorbent, are difficult to diffuse isothermally. With iodine particularly, the vapor pressure, although reasonably high, does not allow rapid diffusion. The determination of the halogens, chlorine and bromine, which are collected in potassium iodide solution, suffers from the back-diffusion of the iodine that is released.

It would appear desirable to develop a unit in which the isothermal distillation principle is extended to include a distillation from one phase at a higher to a second phase at a lower temperature and to combine with this principle the short distances and easy access to the absorption chamber which make the transfer more rapid. If the central compartment of the Conway cell, containing the absorbing solution, could be maintained at a low temperature while the outside chamber from which the volatile material is distilled was kept at a raised temperature, the rapidity of the transfer should be markedly enhanced. At the same time constituents for which there is no good chemical absorbent, such as alcohol, might well be transferred quantitatively because of the temperature differential.

With this idea in mind, the glass unit shown in Figure 1 was developed (obtainable from the Microchemical Specialties Company, Berkeley, Calif.). It consists of a top portion in

which a liquid phase is allowed to spread in a thin layer around the entire periphery without spilling into the extended tube below. Bulbous protuberances blown on the side allow the sample and any reagent which is to be mixed with the sample to be kept separated until the cell is sealed and evacuated. The receiver compartment is attached to the top compartment by means of a ground-glass joint which is arranged to allow evacuation of the interior. This is necessary to prevent pressure development by heating during the distillation, which can blow the seal open. The unit is held on a sheet of wood or metal having holes drilled in it, so that the receiver can extend downward into an ice-water bath. The top portion containing the samples and added reagents is exposed to heat from an infrared heat lamp, which maintains the temperature of the contents just below boiling and allows rapid evaporation of the liquids and volatilization of any dissolved gases. Although the distances in the cell are less favorable than in the Conway diffusion unit, the transfer is very rapid because of the lack of intervening long lengths of relatively small tubing, traps, and other obstructions to free molecular diffusion.

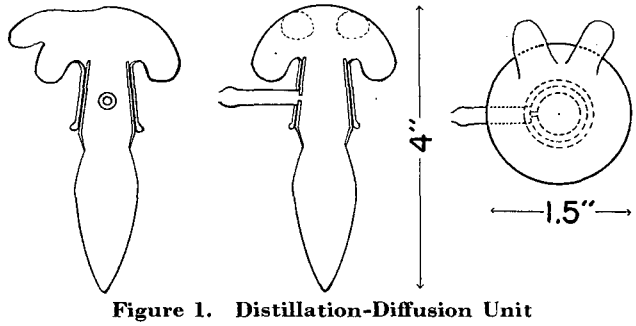

Figure 1. Distillation-Diffusion Unit

Cross-section and top views

The apparatus has been tested with ammonia in order to correlate it with the well established techniques for that constituent; 10 to 15 minutes are adequate for complete transfer of ammonia from an alkalinized solution in the upper portion of the unit to the receiver acid in the bottom. This is a marked saving of time, but the main advantages of the unit are not realized for constituents such as ammonia, which are readily diffusible and are normally titrated. Preliminary tests with distillation of arsenic trichloride and of alcohol indicate that 15 minutes are sufficient for complete transfer of these materials.

The shape and configuration of the unit are such that titration is possible but not convenient without transfer of the receiver material. It is therefore adapted better to those determinations which are finally colorimetric in nature than to those which are volumetric. Among these may be mentioned the catalytic determination of iodine, which is performed in the photoelectric photometer or spectrophotometer, and arsenic which may be determined by means of the arsenomolybdate reaction. In the case of alcohol, both colorimetric and volumetric procedures are available. All these methods are at present under test and will be the subject of forthcoming communications.

There is reason to believe that the apparatus may be more readily adapted to distillation of certain other constituents, such as chlorine and bromine, than is the present Conway unit. The unit described is not considered as a replacement or substitute for the Conway unit, because the advantages are primarily realized only in certain types of determinations to which the Conway unit is not readily adapted. The general simplicity of the latter will continue to recommend it for diffusions of ammonia and nitrogen fractions readily transformed to ammonia and for determinations involving transfer of carbon dioxide and other volatile constituents.

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Chloroform Solutions of Dithiocyanatodipyridine Copper (II)

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PRECIPITATION of copper (II) by means of pyridine (py) and thiocyanate as a green, complex, nonelectrolyte of composition $[Cu(py)_2(SCN)_2]$ has been recommended by Spacu (*10–12*) for the quantitative gravimetric estimation of the element on both micro and macro scales. The solubility of the compound in solvents such as chloroform has been used by Biazzo (*3*) and others (*1, 2, 4–9*) as a basis for the colorimetric estimation of copper. In all colorimetric procedures which have been discussed, however, direct comparisons between solutions of the complex and similar solutions containing known quantities of copper (II) have been suggested. The absence of absorption spectra data for such systems prompted a brief spectrophotometric study.

EXPERIMENTAL

A stock solution, 0.003 *M* in copper (II) ion, was prepared by dissolving the calculated weight of pure copper shot in nitric acid, evaporating to dryness on a steam bath, taking up the residue in water, and diluting to 1 liter. Two hundred milliliters of this solution and 200 ml. of chloroform were placed together in a separatory funnel. Sufficient pyridine (ca. 10 ml.) to turn the aqueous layer azure blue was added and then the calculated quantity of ammonium thiocyanate. The resulting green suspension was shaken vigorously, all of the color being transferred to the chloroform layer. The clear green chloroform solution (0.003 *M* in the complex) was removed and used for the preparation of solutions of other concentrations, either by dilution or by evaporation of portions of the solvent. Because extraction was not effective in preparing solutions of concentrations above 0.003 *M*, the evaporation technique was essential. By this means, concentrations up to 0.012 *M* were obtained.

The absorption spectra of these solutions were measured with a Cenco-Sheard spectrophotolometer over the range 400 to 700 mμ, using 1-cm. Corex cells and a nominal entrance band of 5 mμ. Measurements were made at 5- to 10-mμ intervals.

All chemicals employed were of analytical reagent quality. The completeness of extraction and the effects of the presence of excess reagents were studied.

DISCUSSION

As shown in Figure 1, the absorption spectrum of dithiocyanatodipyridine copper (II) in chloroform is characterized, in the visible range, by a single comparatively sharp and intense band centering at 415 mμ. At concentrations above 0.001 *M*, the intensity of this band is sufficient to render its measurement impractical. Absorption at 415 mμ is in strict accord with Beer's law up to concentrations of at least 0.001 *M*. Maximum trans-

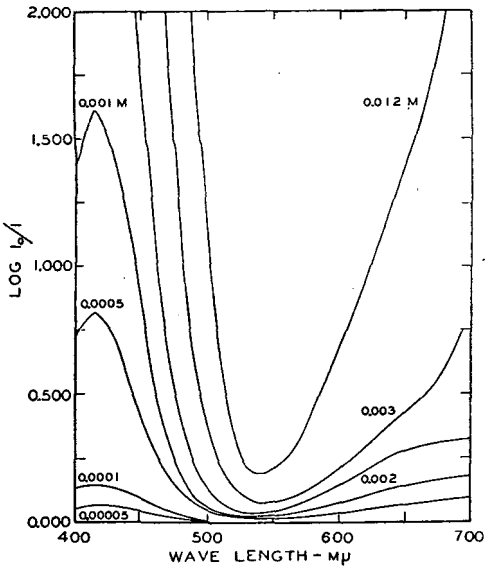

Figure 1. Absorption Spectrum of Dithiocyanatodipyridine Copper (II) in Chloroform

mittance is apparent at 540 mμ. The spectrophotometric characteristics of the solution remained unaltered over periods of many days.

It is suggested, in the light of these results, that existent colorimetric methods employing this compound would be improved by substitution of absolute measurements at 415 mμ for indirect color comparison. It has been the authors' observation that chloroform has a greater solvent effect and gives more stable solutions than bromoform, chlorobenzene, bromobenzene, carbon tetrachloride, benzene, and hexane. Excess thiocyanate appeared to be without effect in producing the color system. Excess pyridine beyond that necessary to give a deep blue aqueous layer was likewise without effect. Extraction of the compound into chloroform was complete under any conditions where the reactants were present in at least stoichiometric quantities.

Use of the filter characteristics of chloroform solutions of dithiocyanatodipyridine copper (II) apparent in Figure 1 may also be profitable.

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Determination of Sulfur by Elementary Isotopic Analysis

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THE authors have recently described an isotopic method for the determination of oxygen (*2*), carbon (*3*), and nitrogen (*4*) in organic compounds by using their respective heavy isotopes (*1*). They have now extended the method to sulfur, using $S^{34}O_2$ as the tracer.

A known weight, a, of the sample analyzed containing $X\%$ of sulfur is burned with an excess of oxygen and simultaneously equilibrated with a known weight, b of heavy sulfur dioxide, $S^{34}O_2$, for 60 minutes at 700° to 800° C. in a quartz vessel. The per cent sulfur is then calculated from the formula

$$X\ \%\ \mathrm{S} = 100\ \frac{b\,(m-n)}{a \times n}$$

where m and n are, respectively, the initial and final—i.e., after equilibration—atomic per cent excess of S^{34} in the sulfur dioxide. The weight of the enriched sulfur dioxide used is calulated using the normal atomic weight of the element (32.06).

The enriched sulfur dioxide was obtained by decomposing some enriched $Na_2S^{34}O_3$ with concentrated phosphoric acid. The enriched, as well as the ordinary sulfur dioxide, was analyzed by the Consolidated Engineering Company (Pasadena) mass spectrometer. The results were as follows:

	Enriched Sample, Atom %	Ordinary Sample, Atom %
$S^{32}O_2$	81.18 ± 0.04	94.67 ± 0.03
$S^{33}O_2$	1.553 ± 0.010	0.764 ± 0.019
$S^{34}O_2$	17.05 ± 0.03	4.58 ± 0.02
$S^{36}O_2$	0.209 ± 0.005	0.00 ± 0.005

These results are based on two scannings each of several samples. The consistency and accuracy of the measurements are illustrated in Table I.

The sample is burned with excess oxygen and equilibrated in a heated quartz vessel with $S^{34}O_2$. In order to concentrate the sulfur dioxide for measurement, the reaction gases are frozen in liquid nitrogen, the excess oxygen is pumped off, and the condensed gases (sulfur dioxide, carbon dioxide, and water; if a trace of sulfur trioxide is present, it is converted into sulfuric acid) are passed back and forth several times over dried calcium

Table I. Analysis of Enriched and Normal Sulfur Dioxide

	Enriched SO_2, Atom %					Normal SO_2, Atom %				
Sample No.	Scan No.	$S^{32}O_2$	$S^{33}O_2$	$S^{34}O_2$	$S^{36}O_2$	Sample No.	Scan No.	$S^{32}O_2$	$S^{33}O_2$	$S^{34}O_2$	$S^{36}O_2$
1	1	81.26	1.535	17.00	0.210	1	1	94.64	0.803	4.56	0.00
	2	81.16	1.565	17.06	0.213		2	94.59	0.787	4.62	0.00
2	1	81.19	1.555	17.04	0.217	2	1	94.65	0.752	4.60	0.00
	2	81.09	1.544	17.12	0.200		2	94.64	0.777	4.58	0.00
3	1	81.20	1.550	17.05	0.202	3	1	94.68	0.722	4.60	0.00
	2	81.20	1.570	17.02	0.209		2	94.66	0.758	4.58	0.00
						4	1	94.70	0.757	4.54	0.00
							2	94.66	0.753	4.59	0.00
Av.		81.18 ±0.04	1.553 ±0.010	17.05 ±0.03	0.209 ±0.005			94.67 ±0.03	0.764 ±0.019	4.58 ±0.02	0.00 ±0.00

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Table II. Results of Sulfur Analyses

Substance	Carbon Disulfide	Thiophene		Dimethyl Sulfate	
n_D^{20} of Sample	1.6273	1.5285		1.3872	
Best literature value	1.6276	1.5287		1.3874	
Boiling point at 760 mm., ° C.	46.2	84.0-84.3			
Best literature value	46.3	84.0			
Analysis No.	1	2		3	
Determination	1	1	2	1	2
a, mg. substance	30.40	27.02	23.98	34.08	15.14
b, mg. S added as SO_2 (using at. wt. of S = 32.08)	21.57	12.27	10.54	10.51	8.85
m, % excess of S^{34} above normal (−4.58) in *b*	12.47	12.47	12.47	12.47	12.47
$S^{34}O_2$ content of equilibrium mixture (3 scannings each)					
Sample 1	10.32	11.47	11.16	11.35	13.26
2	10.28	11.27	11.31	11.52	13.28
3	10.29	11.45	11.28	11.36	13.26
4	...	11.36	...	11.56	13.23
Av.	10.30 ± 0.02	11.38 ± 0.07	11.25 ± 0.06	11.45 ± 0.09	13.26 ± 0.012
n, average % excess of S^{34} in equilibration mixture	5.72	6.80	6.67	6.87	8.68
m − *n*	6.75	5.67	5.80	5.60	3.79
S in substance, % Experimental	83.69	37.85	38.21	25.14	25.52
Average	83.69	38.03		25.33	
Theoretical	84.22	38.10		25.42	
Deviation, theoretical experimental	+0.53	+0.07		+0.09	
Deviation, % of sulfur content	0.60	0.18		0.35	

chloride in order to remove the water formed in the burning. The gases are then frozen in liquid nitrogen and allowed to warm up in a dry ice bath. The carbon dioxide liberated is pumped off and the remaining sulfur dioxide is warmed up to room temperature, sampled, and analyzed.

For each determination three to four samples were taken and each sample, in turn, was scanned three times. The average of the three scannings is given in Table II.

Various types of sulfur compounds were selected for analysis—namely, thiophene, dimethyl sulfate, and carbon disulfide. The divalent sulfur of thiophene and carbon disulfide equilibrated as readily as the hexavalent sulfur of dimethyl sulfate with the tetravalent sulfur of sulfur dioxide.

One determination was made on *freshly* distilled and dried carbon disulfide and two check determinations each were made on carefully fractionated thiophene and a middle fraction of vacuum-distilled dimethyl sulfate. The results of these three analyses are shown in Table II.

A comparison of the theoretical and experimental sulfur contents shows good agreement. The average probable deviation from theoretical equals 0.3% of the sulfur content in the usual analytical range.

ACKNOWLEDGMENT

The authors are greatly indebted to Harry Thode of McMaster University, Hamilton, Ontario, Canada, for the loan of the $Na_2S^{34}O_3$, which made this investigation possible.

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Cell for Routine Polarographic Analyses

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IN CONNECTION with routine polarographic analyses of copper solutions the author had occasion to use a cell (Figure 1) designed for conservation of the anode pool of mercury.

The cell is a development of the Maassen (*5*) cell; the porous diaphragm in the wall of the Maassen dropping electrode compartment has been replaced by a viscose membrane at the bottom of the dropping electrode compartment.

The dropping mercury chamber consists of a piece of 30-mm. glass tubing, 80 mm. long and fire-polished at both ends. One end is covered with viscose sheeting, previously soaked for several days in distilled water, and held in place with a rubber band. The other end carries a 3-hole rubber stopper bearing the dropping capillary and inlet and outlet tubes for nitrogen. The anode chamber consists of a 200-ml. beaker, at the bottom of which is placed a layer of mercury. The dimensions can be varied to suit the analysis at hand.

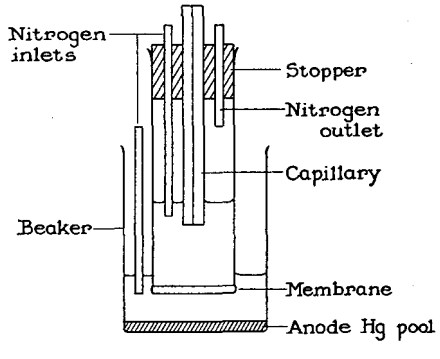

Figure 1. Diagram of Cell

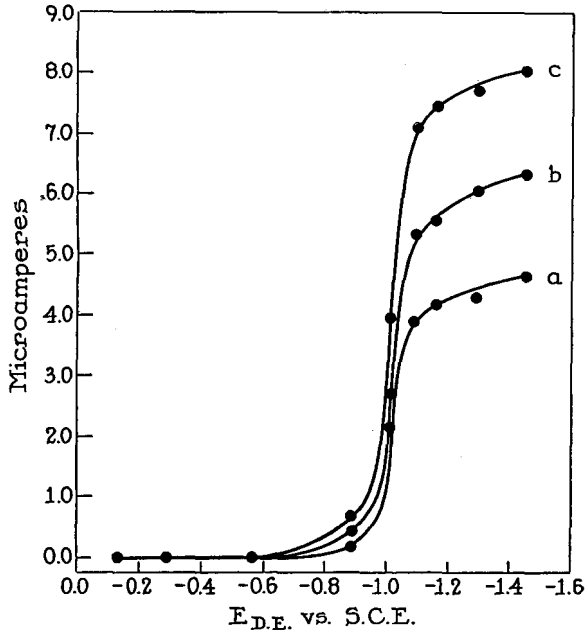

Figure 2. Polarograms of Zinc Chloride in 1 *N* Potassium Chloride Containing Small Amount of Methyl Red

a. 0.412 millimolar
b. 0.618 millimolar
c. 0.824 millimolar

Diffusion currents corrected for residual current. Capillary characteristics: drop time 2.60 seconds, 3.78 mg. of mercury per second. T = 26°

In use, the anode chamber is filled to a convenient level with the solution of the supporting electrolyte and to the cathode chamber is added the solution of the supporting electrolyte containing the unknown. After deaeration in the usual fashion, the cathode chamber is lowered until the membrane end is immersed to a depth of several millimeters below the level of the anode liquid; the chamber is kept in place by a suitably placed clamp. The polarogram is then determined in the usual manner (the inlet tubes being adjusted to allow passage of a slow current of nitrogen over the anode and cathode surfaces). At the conclusion of the analysis the cathode chamber is rinsed out with some of the next unknown and is then ready for the next analysis.

If desired, the solution of the supporting electrolyte in the anode chamber may be replaced by a potassium chloride solution saturated with calomel to give a reference electrode of constant and known potential, or a permanent saturated calomel electrode may be connected by means of a salt bridge to the anode chamber for determining the potential of the anode during the course of the polarogram.

Figure 2 presents the results of several polarograms obtained with zinc solutions of varying concentrations in 1 *N* potassium chloride containing a small amount of methyl red as a maximum suppressor. The polarograms were obtained with a manually operated instrument similar in design to that described by Kolthoff and Lingane (*1*). Step heights are proportional to concentration and $E_{1/2}$ values do not vary with concentration. The average $E_{1/2}$ value, determined graphically, is 1.021 ± 0.005 volt and is in good agreement with the reported value (*3*), 1.022, for zinc in 1 *N* potassium chloride solutions. From these observations it is to be inferred that the internal resistance offered by the membrane is not sufficient to affect the $E_{1/2}$ value noticeably, for it has been shown (*2*, *4*) that $E_{1/2}$ values shift with appreciable changes in internal resistance.

In working with the cell, it was noted that deaeration of the anode solution could be dispensed with, if the time involved in obtaining the polarogram was in the neighborhood of 5 minutes. The diffusion of oxygen from the anode compartment to the cathode compartment apparently was negligible during this period. To elaborate on this point, Figure 3 presents polarograms obtained at various intervals with the anode solution saturated with air, and the cathode solution previously deaerated and then sealed with a water seal. In 15 minutes there is but slight effect on the polarogram from diffusion of oxygen or diffusion of products of the reaction of oxygen with the anode materials.

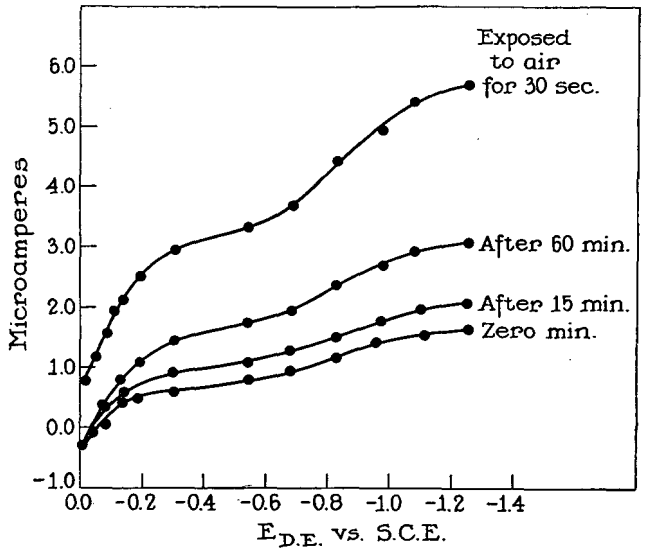

Figure 3. Polarograms Representing Diffusion of Oxygen

Diffusion at various intervals after immersion at zero time of a previously deaerated cathode solution into anode solution saturated with air. Anode solution exposed to air. Cathode chamber sealed with liquid seal. 1 *N* potassium chloride solution plus trace of methyl red in both anode and cathode compartments. T = 26°. Capillary characteristics as in Figure 2

If sufficient mercury to cover the membrane at the bottom of the cathode compartment is allowed to accumulate, diffusion currents drop considerably, owing to resistance of the mercury to the passage of ions.

ACKNOWLEDGMENT

The author is indebted to Gerald Hansen of these laboratories and to W. Langerman of the Fisher Scientific Company for suggestions regarding details of the circuit.

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RECEIVED April 20, 1949.

Training in Industrial Hygiene and Human Relations

The School of Public Health, University of Michigan, Ann Arbor, Mich., is offering an inservice training course in industrial hygiene and human relations for safety personnel, June 19 to 21, 1950. This is the second course that has been given in industrial hygiene for safety personnel, but the first to feature human relations in connection with accident prevention. Emphasis will be placed on recognition rather than correction of health exposures for which the advice of industrial hygienists should be utilized.

Colorimetric Method for Determining a Surface-Active Agent

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UNTIL Jones (*3*) developed his methylene blue method, there was no easy way to determine surface-active agents. Basic fuchsin is a better reagent, however, because its insolubility in chloroform simplifies the extraction and makes it possible to use plain chloroform as a blank, with a consequent saving in time. Basic fuchsin reacts with a variety of sulfated and sulfonated materials, such as alkyl aryl sulfonates, the dioctyl ester of sodium sulfosuccinic acid, and sulfonated petroleums, forming a chloroform-soluble, fluorescent, magenta-colored complex.

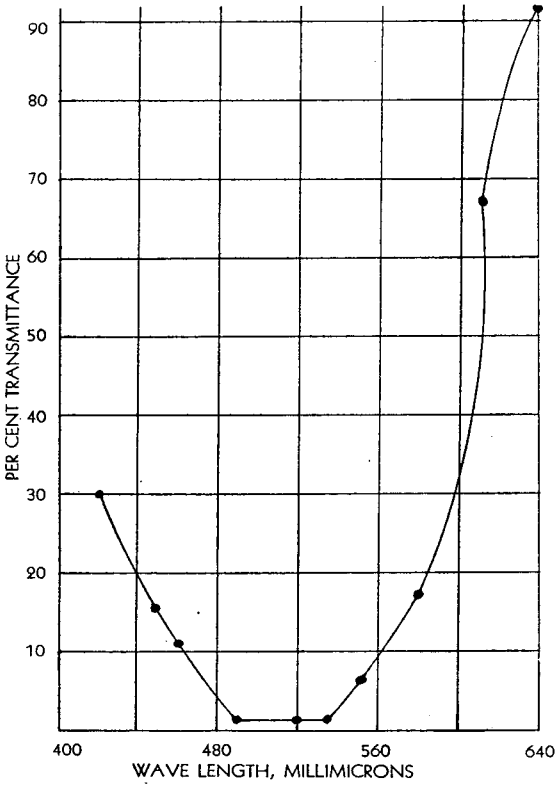

Figure 1. Absorption of Colored Extract

Basic fuchsin has been used as an analytical reagent by others, but not for surface-active groups. It has been used in Schiff's reagent (*5*) and for determining bromine (*2*). Other uses of basic fuchsin are described by Mellan (*4*).

EXPERIMENTAL

The reaction appears to be $RSO_3 + BF \rightarrow RSO_3BF$, where RSO_3 is the anion of a sulfonated compound and BF is the cation of basic fuchsin. The RSO_3 group seems to react with a component of basic fuchsin, as a blue component is noted in the water layer if an excessive amount of wetting agent is added. Basic fuchsin is composed of rosaniline and pararosaniline. It is not believed that both components take part in the reaction, but this has not been definitely established. Basic fuchsin also reacts with alkalies, to form a brown fluorescent chloroform-soluble complex which turns red upon being filtered through cotton. The brown color is probably due to the formation of a pseudo-base. The acid groups of cotton are able to convert the base of the magenta-colored state. The nitrates of alkali metals react with basic fuchsin to produce a magenta-colored chloroform-soluble complex on the acid side, as do the surface-active agents. Potassium iodide, iodine, potassium bromide, and calcium chloride also form magenta-colored chloroform-soluble complexes with basic fuchsin. Basic fuchsin also reacts with sodium pentachlorophenate quantitatively to produce a red chloroform-soluble compound, preferably at an alkaline pH. All these reactions will occur with methylene blue; however, with methylene blue, alkalies produce a red chloroform-soluble complex which turns blue upon being filtered through cotton.

It is generally believed that the addition of electrolytes to a colloid electrolyte (basic fuchsin) causes a salting out of the colloidal electrolyte. The fact that nitrates and calcium and sodium chloride form chloroform-soluble "complexes" with basic fuchsin would seem to contradict the salting out mechanism. As basic fuchsin is insoluble in chloroform, the aggregated fuchsin should also be insoluble.

No information other than an abridged spectrophotometric curve has been obtained with regard to the chloroform-soluble complex formed by basic fuchsin with dodecylbenzene sodium sulfate.

An abridged spectrophotometric curve obtained with a Leitz-Rouy photometer is shown in Figure 1. This curve was prepared from the extract resulting from the reaction between dodecylbenzene sodium sulfate, manufactured by the Monsanto Chemical Company, which is approximately 40% active material; the balance is sodium sulfate (*4*). This curve shows an absorption band from 480 to 535 mμ which is the green region of the spectrum; therefore, for colorimetric determinations a filter covering this region is necessary. Basic fuchsin has an absorption band at 520 to 550 mμ.

A calibration curve was prepared with a Klett-Summerson colorimeter, using a green filter with a mean transmittance of 520 mμ. A spectrophotometric curve was also prepared with the compound used above. In this instance Beer's law holds good up to 1 mg.

PROCEDURE

Reagents. Reagents used are 0.1% basic fuchsin, concentrated hydrochloric acid, and chloroform, U.S.P.

Analysis of Solutions. Place a sample containing approximately 0.5 mg. of active agent in a 125-ml. separatory funnel and dilute to 20 ml. with distilled water. Add sufficient concentrated hydrochloric acid to obtain a pH of 1.2 as determined by a meter or other suitable means. Add 2 ml. of 0.1% basic fuchsin, mix, extract with 20 ml. of chloroform, and allow to separate. Draw off the chloroform layer into a 100-ml. volumetric flask through a funnel nearly full of absorbent cotton. The cotton removes water-soluble dye. Repeat the extraction until clear,

Table I. Recoveries

Amount in Solution, Mg.	Amount Recovered, Mg.	Recovery, %
1.0	1.05	105
1.0	1.05	105
0.5	0.50	100
0.5	0.51	102
Amount on Material, Mg.		
1.0	0.99	99
1.0	0.99	99
0.5	0.50	100
0.5	0.52	104

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generally three times. Wash the cotton filter with chloroform, and make up to volume with chloroform. Transfer the solution to a photoelectric colorimeter and read, having previously set the instrument to zero with chloroform.

Analysis of Textile Material. Take a piece of material that is expected to have no more than 0.5 mg. of surface-active material present and place in a 125-ml. separatory funnel. Extract with 100 ml. of hot isopropyl alcohol which has been heated on a steam bath. Extract with 20 ml. of boiling water to free absorbed alcohol, and compress material with a stirring rod as much as possible. Place the extract in a dye beaker in a steam bath and drive off all alcohol, as determined by odor and cessation of bubbling, but do not allow the extract to go to dryness. The residue should be 20 ml. or less. Transfer to a separatory funnel and proceed as with solutions.

SUMMARY

At an acid pH basic fuchsin will react quantitatively with dodecylbenzene sodium sulfate, giving a chloroform-soluble magenta-colored extract which may be measured in a photoelectric colorimeter. The method is accurate and simple. The method is nonspecific, as side reactions with groups other than the sulfite group can occur; however, there is no interference from sodium sulfate, which does not precipitate basic fuchsin or form a chloroform-soluble complex with basic fuchsin. Sodium sulfate does not react with methylene blue.

The fact that basic fuchsin is not a specific reagent for surface-active agents is not believed to hinder its use. Although this method was actually calibrated for only one compound, the author has made numerous calibrations with the methylene blue method, and found that side reactions did not interfere other than to produce a deviation from Beer's law, making it necessary to plot a curve.

Maximum accuracy cannot be achieved with readings that are either very high or very low. With instruments giving a reading in per cent transmittancy, the minimum error will occur at 36.8% transmittancy (*6*). Ayres shows that greatest accuracy is obtainable over the transmittancy range of 20 to 60% for photometric analysis (*1*). A small experimental error is magnified more on a percentage basis in the lower concentration ranges than in the higher ones.

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Kelly Tube for Sedimentation Analysis

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PAPERS (*1–3, 5, 6, 9, 10*) dealing with improvements in the technique of sedimentation analysis with the Kelly tube include elaborate calculations of the correction factor to be included in the original Kelly equation (*4*) to account for the progressive increase in the liquid level in the settling tube due to the recession of the liquid from the capillary side arm. The present paper describes a practical device for maintaining the liquid level in the settling tube constant so as to retain the validity of the original equation. The uncertain errors caused by ordinary methods of measuring the angle of inclination of the capillary side arm of the Kelly tube in the working position of the apparatus after it is placed in a thermostatic bath have been one of the major drawbacks of Kelly's apparatus (*7, 8*). Because the sign of the angle of inclination is directly utilized in calculating the distribution of the particle size, the need for a precision determination of the angle cannot be overemphasized. The constant-level device is further useful in the precision determination of the angle of inclination of the capillary side arm.

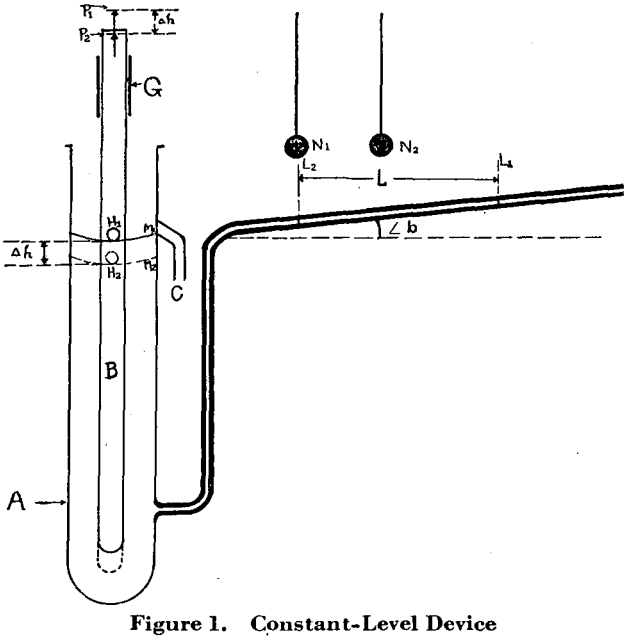

Figure 1. Constant-Level Device

CONSTANT-LEVEL DEVICE

In Figure 1, test tube B with a side hole, H, at M is firmly clamped at a predetermined height to receive the overflow and hence to function as a self-operating constant-level arrangement. The amount of overflow and the consequent loss of solid particles from the suspension (which is usually dilute) are very insignificant; a recession of 10 cm. in the capillary (using Kelly's dimensions for the apparatus) is equivalent to 0.3 ml., which may correspond to the total recession at the end of an experiment.

At the commencement of the experiment, a little excess of the suspension is poured into the settling tube, to ensure that M has been reached. Because the suspension is turbid, it is not possible to observe whether or not the excess has entered B, but this can be ascertained by inserting a narrow glass tube and emptying B by applying suction. The volume displaced by the immersed portion of B must be taken into consideration, while calculating the volume of the suspension under investigation.

The self-adjusting constant-level device eliminates the personal error of the observer in noting the initial level, particularly with turbid suspensions. The extreme importance of maintaining the level constant is appreciated if it is realized that a difference of 0.1 mm. in the level at M will cause a difference of $0.1/\sin b = 3.82$ mm. in the horizontal portion of the capillary, if $\angle b$ is 1.5°.

Alternative arrangement can be made to maintain the liquid level constant—e.g., a side tube, C (shown in Figure 1), may be joined at M to permit the overflow. Such devices demand very accurate glass blowing for joining the tube in a required position. The device suggested in Figure 1 using test tube B can be easily constructed and readily assembled.

PRECISION DETERMINATION OF ANGLE OF INCLINATION OF CAPILLARY SIDE ARM

If the settling tube, A, is filled with water up to any convenient levels, M_1 and M_2, corresponding positions of water in the capillary side arm will be L_1 and L_2, respectively. Designating the vertical difference between M_1 and M_2 as Δh and the linear recession from L_1 to L_2 as L, we have $\sin b = \Delta h/L$. Although L can be measured with reasonable accuracy on a linear scale, Δh cannot be directly measured with precision owing to parallax errors when reading the meniscus in A. The degree of accuracy desired in measuring Δh will be evident from the following calculations. Using Kelly's dimensions for the apparatus, for a maximum possible value of $L = 20$ cm. with $\angle b = 1.5°$, $\sin b = 0.0262$ giving $\Delta h = 0.524$ cm. To obtain $\sin b$ with an error not exceeding $\pm 1\%$, it is necessary to read $\Delta h = 0.524 \pm 0.006$ cm. In view of this difficulty, the device described below is used to estimate indirectly the value of Δh to the desired degree of precision.

In Figure 1, a pin is attached along the inner side of B at its mouth with molten wax so that its point, P_1, protruding above the mouth of B well above the thermostatic bath level, serves as a point of observation through a vernier microscope traveling vertically. G is a close-fitting tube of glass or metal such as a cork borer, firmly clamped, serving as a guide sleeve. The true vertical movement of the microscope can be tested by observing the path of movement of the microscope cross wire along a plumb line suspended in front of the microscope objective. By bringing P_1 always at the intersection of the cross wires in the microscope eyepiece, the vertical movement of B in the plane of the optical axis of the microscope can be ensured. N_1 and N_2 are two plumb lines forming a vertical plane nearly at right angles to the optical axis of the microscope. If P_1 is also brought in plane with N_1 and N_2 which can be inspected visually, a really vertical movement of B through G can be guaranteed.

B is slowly lowered into A filled with water and clamped so that some water enters B through the side hole in position H_1, the meniscus in A being at M_1. The readings for P_1 on the microscope scale and for L_1 on the linear scale are noted. A small quantity of water from A is removed by means of a pipet, so that level L_2 is nearly approached. Then B is further lowered until more water from A enters B through the side hole in position H_2 and B is again clamped. Thus, M_1 is altered to M_2 and L_1 recedes to L_2. The readings of P_2 and L_2 are again noted. The difference between M_1 and M_2 is obviously equal to that between H_1 and H_2 and therefore equal to that between P_1 and P_2. Hence, Δh corresponds to the vertical movement of the pin point from P_1 to P_2 which is accurately recorded by the microscope. In this method, levels M_1 and M_2 are automatically adjusted by the positions of H_1 and H_2, provided water is caused to flow into B at the time of adjustment; this step is absolutely essential. Parallax errors are eliminated, as the direct observation of the liquid meniscus is avoided.

The precision of this method depends upon the least count of the vernier scale of the microscope. This method has given constant and reproducible results for a given setting of the apparatus in its working position. A cathetometer can be substituted for the microscope. This method is independent of the bore dimensions of tube A and the capillary side arm.

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Adjustable Constant Flow Regulators for Corrosive Gases

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THE apparatus described were designed specifically for obtaining a continuously adjustable constant flow rate of chlorine, but, by suitable modification of the experimental arrangement, regulator liquid, and trap solution, it may be used either as a constant flow regulator or as a manostat for any gas. Furthermore, two regulators may be used to obtain a constant flow of gas through a system at constant pressure.

In the simple regulator shown in Figure 1 the lower chamber is about four fifths filled with concentrated sulfuric acid. Tube A is connected directly to the chlorine supply. Tube B is attached to a capillary flowmeter, F, which in turn is connected to the system. Tube C is connected through a trap containing concentrated sodium carbonate solution to a water-jet air pump. Tube D is open to the atmosphere. A rubber aspirator bulb is attached to tube E.

The regulator is placed in operation by first forcing about half of the acid into the upper chamber. After the air pump is turned on, the chlorine supply is adjusted to give a bubble rate of from 1 to 10 per second. The flow rate is adjusted by raising or lowering the liquid level in the upper chamber.

If the bubble rate is excessive, chlorine will be forced out of tube D, the flow rate will vary erratically, and the greater part of the chlorine will be wasted. The regulator will not give a rigorously constant flow rate until the acid has become saturated with chlorine. Small cyclic rate variations corresponding to bubble formation may be largely eliminated by placing a 2-liter reservoir between the regulator and the flowmeter.

The dimensions of the regulator are not critical, with the following exceptions: The diameter of tube D must be large enough (~10 mm.) so that the pressure drop through it is very small; otherwise the flow rate will vary as a function of the pumping velocity. The annular distance in the upper chamber should be at least 1 cm., in order that the liquid head vary as little as possible. The diameter of the bubble outlet should be about 10 mm. In the regulators in use in this laboratory, the

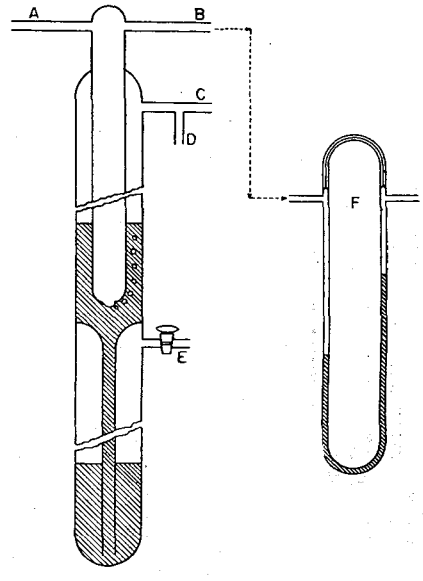


Figure 1. Flow Regulator

diameter of the outer tube is 45 mm., that of the upper inner tube is 22 mm., and all other tubing is 11 mm. The over-all length is 85 cm.

In using this apparatus as a manostat for pressures greater than atmospheric, the flowmeter is replaced by a manometer in parallel with the system. For pressures less than atmospheric, a vacuum pump is connected as usual to C while the system is attached at D. A and B are open to the atmosphere.

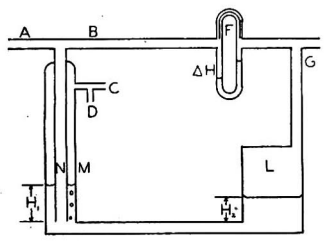


Figure 2. Modified Flow Regulator

With the regulator described above, any variation of the flow resistance of the process into which the flowmeter delivers necessitates a manual resetting of the regulator to maintain constant flow. A modified regulator has been developed to feed back the back pressure due to the resistance and use it to adjust the height of the liquid column and hence the fore pressure to the flowmeter.

The modification, called an Isofluxor, is shown diagrammatically in Figure 2 and the actual construction of one model is shown in Figure 3. The back pressure of the process is tapped at G and led to L. Because the annular space, M, is at atmospheric pressure (through D), the head of liquid ($H_1 - H_2$) is a measure of the back pressure at G. The head of liquid, H_1, is a measure of the fore pressure at B. The difference, $H_1 - (H_1 - H_2) = H_2$, is therefore a measure of the pressure differential across the capillary of the flowmeter. If H_2 is maintained constant with changes in back pressure, the ΔH across the flowmeter will be constant, and the volume flow will be constant.

However, in order to compensate for an increase in back pressure, the liquid level in L (H_2) must go down as that in M (H_1) rises to increase the fore pressure. Because an increase in back pressure, Δp, must appear as an increase in $H_1 - H_2$, and $H_1A_M + H_2A_2 +$ constant = total volume of regulator liquid at any one setting = constant, we may write $\Delta H_1 - \Delta H_2 = \Delta P$ and $\Delta H_1 = \frac{A_L}{A_M}\Delta H_2$.

$$\text{Hence} \quad \Delta H_2 = \Delta P\left(\frac{1}{\frac{A_L}{A_M} - 1}\right) = \Delta P\left(\frac{A_M}{A_L - A_M}\right)$$

The effect therefore can be minimized by making L of large cross section with respect to M.

If the pressure on both ends of the capillary is increased by the same amount, although the volume flow will remain essentially constant, the mass flow will increase, because unit volume will contain greater mass at greater pressure. From $PV = nRT$ we have $n/V = P \times 1/RT$. Mass per unit time will thus be directly proportional to pressure, at constant volume per unit time $\bar{n} = P \times \bar{V}/RT$.

Because, within limits, volume flow is directly proportional to ΔH in a capillary flowmeter, the effect of the change in H_2 may be made equal to the pressure-mass effect, giving constant mass flow, usually of most interest in gaseous reactions.

Consider a case where the normal back pressure is 5600 mm. of sulfuric acid (760 mm. of mercury) and the flow is $\bar{V}$ ml./minute = $\bar{n}$ mole/minute at ΔH mm. of sulfuric acid differential. Fore pressure is then 5600 + ΔH. Assume an increase of h mm. in back pressure. Fore pressure will increase to 5600 + ΔH + $h(A_L - A_M)/A_L$ mm. and the back pressure will be 5600 + h mm. The flowmeter differential will become $\Delta H - hA_M/A_L$ and the volume flow will change to $\bar{V}(\Delta H - hA_M/A_L)/\Delta H$ ml./minute. The delivery pressure has changed to 5600 + h, so only $\bar{V}\left(\frac{5600}{5600 + h}\right)\frac{\text{ml.}}{\text{minute}}$ are needed to deliver $\bar{n}$ mole/minute.

$$\text{Then set} \quad \bar{V}\left(\frac{\Delta H - h\frac{A_M}{A_L}}{\Delta H}\right) = \bar{V}\left(\frac{5600}{5600 + h}\right)$$

$$\frac{A_M}{A_L} = \frac{\Delta H}{5600 + h}$$

Assuming A_M to be constant and h to be small compared to 5600, because $\Delta H = H_2$ we can shape chamber L so that $A_L = (5600\ A_M)/H_2$. If L has a surface of revolution we may write $D_L = 2\sqrt{\frac{5600\ A_M}{\pi H_2}}$. If H_2 = 100 mm. and A_M = 6.3 sq. cm., then D_L = 22.6 cm. At lower values of H_2 the chamber becomes of unwieldy and uneconomical size except for precise applications.

The construction of one model shown in Figure 2 gives A_M/A_L = 0.037, so a 27-mm. increase in back pressure causes H_2 to drop 1 mm. and n/V to increase 0.5%. If the capillary is chosen so that normal flow is at 200 mm. = ΔH, these will cancel for this particular flow rate. At half this rate, with the same capillary, the error will be only −0.5% for a similar change in back pressure.

TIME OF RESPONSE

The liquid displacement compensating for an increase in back pressure takes gas from the main stream to the system until equilibrium is established, so the flow rate to the system follows an exponential time curve after a disturbance.

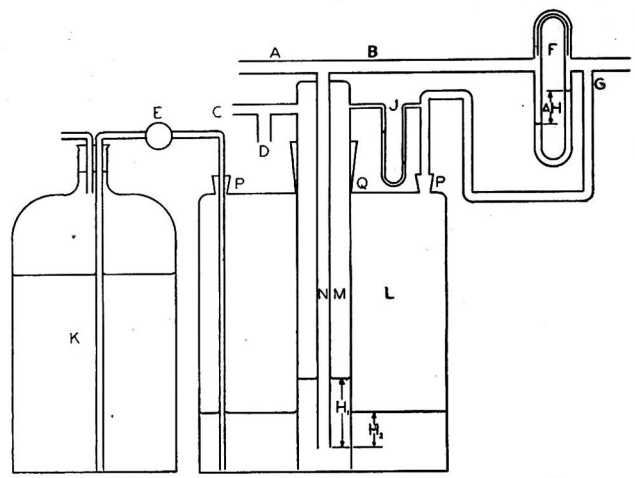


Figure 3. Construction of One Model of Flow Regulator

Consider a case where the constant flow, F_1, from the flowmeter is delivered into a flow resistance R_1, the back pressure being $H_1 - H_2 = h_1$ and the delivered flow, F_2. At the initial stable condition $F_1 = F_2 = h_1/R_1$. An instantaneous change of R to R_2 will make $F_1 > F_2 = h/R_2$, or $F_1 - F_2 = A_M \times dh/dt$. Because $h = F_2R_2$, then $dh/dt = (dF_2/dt) \times R_2$, and $F_1 - F_2 = A_MR_2 \times (dF_2/dt)$.

Solving for t

$$\frac{dF_2}{dt} = \left(\frac{F_1}{A_MR_2} - \frac{F_2}{A_MR_2}\right)$$

$$t = -A_MR_2\ln\left(\frac{F_1}{A_MR_2} - \frac{F_2}{A_MR_2}\right) + C$$

When $t = 0$, $F_2 = F_1 \times (R_1/R_2)$

$$\text{So} \qquad C = A_M R_2 \ln \left(\frac{F_1}{A_M R_2} - \frac{F_1}{A_M R_2} \times \frac{R_1}{R_2} \right)$$

$$\text{and } t = -A_M R_2 \left\{ \ln \left[\frac{1}{A_M R_2} (F_1 - F_2) \right] - \ln \left[\frac{F_1}{A_M R_2} \left(1 - \frac{R_1}{R_2} \right) \right] \right\}$$

$$\text{Exponentially } e^{\frac{-t}{A_M R_2}} = \frac{1}{F_1} (F_1 - F_2) \left(\frac{R_2}{R_2 - R_1} \right)$$

$$F_1 - F_2 = e^{\frac{-t}{A_M R_2}} F_1 \left(\frac{R_2 - R_1}{R_2} \right)$$

$$F_2 = F_1 - F_1 \left(\frac{R_2 - R_1}{R_2} \right) e^{\frac{-t}{A_M R_2}}$$

For example, let $F_1 = 78 \frac{\text{ml.}}{\text{min.}}$; $A_M = 396 \frac{\text{ml.}}{\text{min.}}$; $R_1 = \frac{36 \text{ mm.}}{78 \text{ ml./min.}}$

Let the resistance be suddenly changed to $R_2 = \frac{59 \text{ mm.}}{78 \text{ ml./min.}}$

$$\text{Then } F_2 = 78 - 78 \times \frac{59 - 36}{59} e^{\frac{-t \times 78}{0.396 \times 59}}$$

$$F_2 = 78 - 30.4\, e^{-3.34t} \text{ min.}$$

Using as a measure of response the time required for half of the correction to take place, we find $t_{1/2} = 0.432$ minute. An experimental test run with the same constants gave $t_{1/2} = 0.584$ minute, 35% longer. This is attributed to fluid friction hindering the liquid transfer.

CONSTRUCTIONAL DETAILS (FIGURE 3)

A, *B*, *C*, *D*, and *G* are of 9-mm. tubing, *N* is of 10-mm., and *M* is of 28-mm. tubing. *L* is a standard 4-liter bottle (inside diameter 150 mm.). *K* is a reservoir of regulator liquid, so that the flow rate may be set to the required value. *PP* are 14/35 joints and *Q* is a 35/45 joint. *J* is a safety manometer preventing the liquid from rising through *M* and out *C* in cases of extreme back pressure. *J* may also be used to indicate the back pressure above atmospheric.

OTHER USES

The regulator may also be used from the low pressure side of a system to provide constant pressure at a point in a system, regardless of flow resistance between the point and the regulator.

In this service *G* is connected to the point to be held constant, while *C* goes to a vacuum aspirator and trap, *D* being connected to the downstream end of the system. *A* and *B* are open to the atmosphere. H_2 is set to the required pressure (above or below atmospheric). A tendency for the pressure to increase owing to an increase in flow resistance between the regulator and the point causes H_1 to rise, lowering the pressure at *D*, up to the capacity of the vacuum system or the limit of liquid rise (H_1) (determined by *J*).

Because the apparatus is made entirely of glass, nearly all corrosive gases may be handled with a proper choice of regulator liquid—e.g., for chlorine the liquid may be sulfuric acid.

RECEIVED February 24, 1950.

CRYSTALLOGRAPHIC DATA

29. Antabuse (Tetraethyl Thiuram Disulfide)

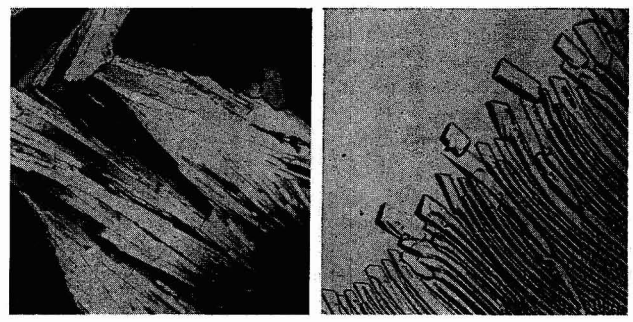
Contributed by D. G. GRABAR AND W. C. MCCRONE, Armour Research Foundation, Illinois Institute of Technology, Chicago 16, Ill.

A RESTATEMENT of the objectives of this crystal series seems desirable at this time. The project was first undertaken because optical crystallography is neglected as an analytical tool because too few compounds have been described. An analyst now may determine the optical properties of an unknown material, but there is little chance of finding those properties tabulated so that the compound can be identified.

We hope by publication in ANALYTICAL CHEMISTRY to initiate a process which will enable a group of crystallographers to complete the tabulation of crystal data for most of the common everyday compounds. This would make optical crystallography a useful analytical technique, justify its study in the academic curriculum, and produce more crystallographers further to speed the process of accumulating data. We realize that this is the first step in a very long program and that a great deal of help will be required.

Crystallographers can help by submitting data for inclusion in this program. Most crystallographers, however, apparently feel that only complete data will be accepted for a given compound. One of the principal purposes of this statement is to correct this impression; quite incomplete and even fragmentary data will be gladly accepted. We would like to receive any part of the following:

1. Solubility data on the compound with information as to best solvents for good crystals.
2. Any information on hydrates or other solvates, polymorphs, decomposition, etc.
3. Goniometric data (complete or incomplete).
4. Optical properties (complete or incomplete).
5. X-ray data (powder data and/or single crystal data).
6. A pure sample preferably of well-formed crystals suitable



A *B*

Figure 1. Antabuse Crystals

A. **Grown from melt**
B. **Grown from a thymol mixed fusion**

for single crystal x-ray work (about 0.1 to 0.5 mm. in longest dimension). The size of the sample desired depends on availability of the compound (1 mg. of B_{12} up to not more than 2.5 grams of the more common compounds).

The emphasis throughout this project is, of course, on data for the common and important compounds. Data for unusual, uncommon, or rare compounds will not be completed or published, at least at this time. All data submitted will, however, be added to a general crystal file which already contains many unpublished data. This file is now being completed with respect to the published literature on optical and x-ray data. We would like very much to extend the coverage of this file to include even unpublished data, so that it would furnish as complete as possible a source of crystallographic data. We are already in a position to invite inquiry from anyone desiring such information and hope gradually to improve the coverage offered.

Finally, publication of each monthly description is now recognized by crediting the contributor with authorship. Each publication is so noted in ANALYTICAL CHEMISTRY and is indexed by author and title in the abstract journals. If a description is published in which this laboratory had only the job of minor checking, photomicrographs, crystal drawing, and fusion data, the outside contributor will be listed as sole author. If, however, it is necessary to complete the fundamental data, x-ray, optical, etc., a junior author from the foundation will be added. If a minor part of the data was submitted and our laboratory has to do a major part of the determinative work, a major author from the foundation will be named. In every case, we will try to be very fair, even to the extent of sacrificing our position in cases of doubt.

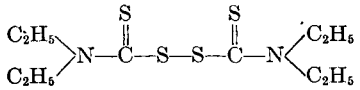
The procedure for each compound will, in every case, be as follows:

1. Literature search.
2. Checking of data submitted. (This does not necessarily mean repeating work; a, b, and c could be checked against goniometric data and by the relationship between density, molecular weight, number of molecules per cell, and cell volume. If all these data were consistent, the cell dimensions would be accepted.
3. Completion of data to include crystallization, goniometric, optical, x-ray, and fusion data.
4. Photomicrography, crystal drawing, and writing up of data in standard form for publication in ANALYTICAL CHEMISTRY.

The foundation sincerely hopes that this project can develop information of great usefulness to the analytical chemist and to those starting out on structure determinations on one of the compounds that happens to have been covered. Comments, criticisms, or suggestions on any phase of this program will be greatly appreciated.

CRYSTALLOGRAPHIC DATA FOR ANTABUSE

Antabuse is the drug recently discovered to be of value in the treatment of alcoholism. It is extremely soluble in most organic solvents and good crystals can be obtained from ethyl alcohol, benzene, and dioxane. No polymorphism was observed during this study.



Structural formula of antabuse

CRYSTAL MORPHOLOGY

Crystal System. Monoclinic.

Form and Habit. Crystallizes from ethyl alcohol in needles elongated parallel to c, and in tablets lying on 010 showing clinopinacoid {010}, orthopinacoid {100}, and clinodome {011}. A variety of other dome, prism, and bipyramid forms usually also appears. The simple form show in Figure 2 is obtained by recrystallization from thymol on a microscope slide.

Axial Ratio. $a:b:c = 0.870:1:0.545$.

Interfacial Angles (Polar). $011 \wedge \bar{0}11 = 47.5°$.

Profile Angle. $011 \wedge \bar{0}11$ in 100 plane $= 123°$.

Beta Angle. 126°.

X-RAY DIFFRACTION DATA

Cell Dimensions. $a = 13.84$ A.; $b = 15.90$ A.; $c = 8.66$ A.

Formula Weights per Cell. 4.

Formula Weight. 296.52.

Density. 1.292 (pycnometer); 1.302 (x-ray).

Principal Lines

d	I/I_1	d	I/I_1
9.11	0.16	3.07	0.05
7.97	Very weak	2.98	0.13
7.58	0.40	2.91	0.11
6.38	1.00	2.82	Very weak
6.09	0.38	2.77	0.09
5.53	0.18	2.70	0.04
5.29	Very weak	2.64	0.04
5.09	0.40	2.60	Very weak
4.76	0.07	2.52	0.16
4.54	0.26	2.47	0.15
4.31	0.12	2.43	0.09
4.16	0.69	2.38	Very weak
4.07	Very weak	2.33	Very weak
3.94	0.13	2.28	0.07
3.77	0.09	2.25	0.06
3.60	0.33	2.22	0.13
3.45	0.20	2.19	Very weak
3.38	0.19	2.15	0.09
3.34	Very weak	1.87	0.10
3.25	0.08	1.71	0.11
3.17	0.28		

OPTICAL PROPERTIES

Refractive Indexes (5893 A.; 25° C.). $\alpha = 1.590 \pm 0.005$; $\beta = 1.67 \pm 0.01$; $\gamma = 1.740 \pm 0.005$.

Optic Axial Angle (5893 A.; 25° C.). $2V = 84° \pm 5°$.

Dispersion. $v > r$

Optic Axial Plane. 010.

Sign of Double Refraction. Negative.

Acute Bisectrix. $BX_a \wedge a = 3°$ in obtuse β.

Extinction. $\gamma \wedge c = 33°$ in obtuse β.

Molecular Refraction (R) (5893 A.; 25° C.). $\sqrt[3]{\alpha\beta\gamma} = 1.67$. R (calcd.) = 84.2. R (obsd.) = 85.0.

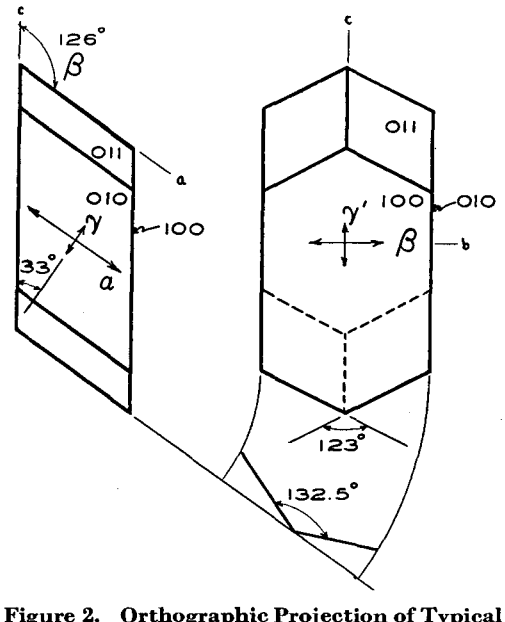


Figure 2. Orthographic Projection of Typical Crystal of Antabuse

FUSION DATA

Antabuse melts at 69–70° C. without sublimation or decomposition. The melt supercools and crystallization usually must be initiated by seeding. The crystals grow rapidly parallel to c and the crystal front in a thymol mixed fusion shows characteristic well-shaped rhombs lying on pinacoid or dome faces. Some crystals may show the characteristic optic axis interference figure.

It is a pleasure to acknowledge the assistance of Irene Corvin and Anne Humphreys in obtaining the powder diffraction data.

CORRESPONDENCE

Silica Refractories

SIR: Since the article on "Silica Refractories" [Herdle, A. J., and Wolthorn, H. J., ANAL. CHEM., 21, 705 (1949)] was published it has come to our attention that when varying amounts of the calcium oxide are present as such, high results will be obtained by the method as described. In most cases, this has been overcome by using the following excitation conditions:

Capacitance, mfd.	60
Prespark period, sec.	10
Exposure period, sec.	20
Filter	Screen

Other parameters are the same as for the original method. This modification is less reproducible than the original, so that determinations are made in triplicate.

Table I compares results obtained by the two methods with those obtained by a chemical method. Calibration curves were based on the same standards.

Table I. Supplementary Determinations

	Per Cent Calcium Oxide		
No.	Chemical method	Original method	Revised method
1	2.49	2.63	2.31
2	2.39	2.29	2.42
3	2.14	2.31	2.14
4	2.40	2.67	2.46
5	2.09	1.99	2.04
6	2.50	2.71	2.47
7	2.24	2.24	2.12
8	1.68	1.80	1.69
9	1.73	1.80	1.83
10	2.48	4.18	2.85
Average deviation (excluding 10)		0.13	0.06

A. J. HERDLE
H. J. WOLTHORN

Carnegie-Illinois Steel Corporation
Youngstown 9, Ohio

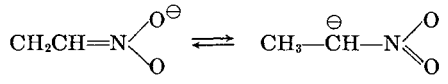
BOOK REVIEWS

Electronic Interpretations of Organic Chemistry. *A. Edward Remick.* 2nd edition. vii + 600 pages. John Wiley & Sons, Inc., 440 Fourth Ave., New York, N. Y., 1949. Price, $6.00.

The second edition of this well-known book has been awaited with interest by all those concerned with electronic interpretations of organic chemistry. There are many good features in this book, especially in the sections on contributions from chemical physics and in the new chapter on stereochemistry. This reviewer strongly feels, however, that a rather confusing picture would be considerably clarified if the author abandoned the attempt to follow the English school terminology with its large number of special effects. Inasmuch as the theory is only roughly qualitative, albeit extremely serviceable, it seems rather pointless to devote much time to terminology of *Is, Id, +E −E* type, to say nothing of proposals (page 62) that "heteroelectromeric" and "homoelectromeric" might be useful additions to the list. The uninitiated may well be bewildered by the fact that although it is clearly stated on page 58 that mesomerism is not to be thought of as a kind of tautomerism, the author quotes on page 79 an interpretation of 1,4 addition through an ion "which may tautomerize."

Some interpretations given of well-known organic reactions are misleading—for instance, the discussion of the Diels-Alder reaction (page 447) in which it is stated that pyridine and quinoline have been successfully substituted for alkadienes; that there is no known catalyst for the reaction (disregarding the work of Wasserman); that the reaction of maleic anhydride with unconjugated olefins involves primary dissociation of the diene to form a carbanion (no evidence whatever). Furthermore, steric factors which provide a ready interpretation of, for instance, the diallyl case (page 449) are ignored.

There may well be some evidence that free radicals are involved in the Grignard reaction, but it is hard to accept the statement (page 501) that the "reaction products [ethane and ethylene] could have been formed only by disproportionation of free radicals." It is difficult to consider seriously that Hantzsch's results on the acidification of the sodium salt of nitroethane find an "evident interpretation" in the assumption that the following process is a slow one (page 241):



A number of topics which are absent from the book could have been profitably included—although there is a discussion of Raman spectra, nothing is said of infrared spectra. We might further wish that in a book on electronic interpretation there would be some discussion of a number of reactions of considerable interest, such as Wagner-Meerwein, benzilic, Bechmann, or Claisen rearrangements. The last-mentioned rearrangement is, it is true, considered on page 509, but is immediately dismissed with the statement that there can "no longer be much doubt as to [its] mechanism," implied to be free radical in type.

GILBERT STORK

Chemie für Bauingenieure und Architekten. *Richard Grun.* viii + 212 pages. Springer Verlag, 1 Jebensstrasse, Charlottenburg 2, Berlin, Germany, 1949. Price (paper), 16.50 marks.

This book deals with the chemistry of most structural materials. It should be of interest to all who would like to know about the chemical properties of concrete, steel, wood, cements, asphalt, and plastics, to name a few of the materials described. The subject matter is described in an interesting manner but suffers from both superficiality and inaccuracy. All metals other than steel are discussed in three pages, paint and protective coatings in one. While the chemistry in the text is mainly de-

scriptive, a more thorough introduction is needed to the terminology and principles involved. The many inaccuracies (or possibly typographical errors) also detract from the book. References to German architectural and engineering periodicals are liberally sprinkled throughout the text.

HENRY FREISER

Analytical Chemistry of Industrial Poisons, Hazards, and Solvents. *Morris B. Jacobs.* xviii + 768 pages. Second edition, revised and enlarged. Interscience Publishers, Inc., 215 Fourth Ave., New York 3, N. Y., 1949. Price, $8.50.

This revised and enlarged second edition contains about 100 additional pages of new material developed since the last revision in 1944. Recent progress in the field of analytical chemistry applicable to industrial hygiene appears to have been well covered. New industrial poisons are discussed, including recently developed analytical procedures pertaining thereto.

The book contains 18 chapters dealing with such subjects as the sampling and measurement of gases, vapors, mists, and dusts; absorbers and absorbents; chemical and microscopic examination of various dusts; lead, arsenic, mercury, and metallic materials; sulfur, phosphorus, nitrogen, oxygen, ozone, halogens, carbon monoxide, carbon dioxide, cyanides, nitriles, paraffin and unsaturated aliphatic hydrocarbons, alcohols, glycols, ethers, acids, esters, aldehydes, ketones, aniline, and other organic nitrogen compounds known to possess harmful properties.

The appendixes comprise tables relative to such subjects as limits of flammability of gases and vapors, toxicity and probable safe concentration limits of exposure for toxic gases, vapors, dusts, fumes, and mists, and conversion tables for gases and vapors.

An excellent review of the literature has been made in the preparation of this revised edition; however, the author has made no particular effort to appraise the relative importance of accuracy of the numerous analytical methods described.

The 132 figures accompanying the text enhance its value. The size and style of type used and the general arrangement of the material presented are good. A few errors were found in the references.

This book should be found useful in many fields of analytical chemistry, and especially to those interested in problems pertaining to the general subject of industrial hygiene.

G. W. JONES

Optical Society of America

THE winter meeting of the Optical Society of America was held in New York, N. Y., March 9 to 11, 1950. Abstracts of the papers that are believed to be of special interest to analytical chemists are reproduced here.

The Infrared Spectrum of CH_2ClF. EARLE K. PLYLER AND MARY A. LAMB, National Bureau of Standards.

The infrared spectrum of CH_2ClF has been measured in the gaseous state from 2 to 30 μ. The longest wave-length band was observed at 26 μ. Twenty-five bands have been observed with cells 5, 60, and 100 cm. in length and with gas pressures up to 60 cm. of mercury. Nine of the observed bands have been classified as fundamentals, and the remaining bands are attributed to harmonics and combinations. Several bands in the region from 1.5 to 2.5 μ were measured on a high-resolution grating instrument, and it was possible to resolve seven bands in a series of lines in this region. These bands are located at 1.672, 1.686, 1.699, 1.735, 2.229, 2.285, and 2.430 μ. From these results some of the constants of the molecule have been determined.

Raman Spectra of *cis*- and *trans*-2-Butene and 1,3-Butadiene in the Gaseous and Liquid States. CHARLES M. RICHARDS AND J. RUD NIELSEN, University of Oklahoma.

The Raman spectra of *cis*-2-butene, *trans*-2-butene, and 1,3-butadiene in the gaseous and liquid states have been obtained with a Lane-Wells spectrograph and internally water-cooled mercury lamps. Polarization measurements have been made on these compounds in the liquid state. The Raman frequencies in the 3000-cm.$^{-1}$ region are generally about 10 cm.$^{-1}$ higher, the gaseous state, those between 1200 and 1700 cm.$^{-1}$, are from 3 to 10 cm.$^{-1}$ higher, while the lower frequencies are about equal in the two states of aggregation. For each of the 2-butenes the observed spectrum has been interpreted in detail, several new fundamentals have been determined, and a couple of changes have been made in previous assignments. The spectrum of 1,3-butadiene has been interpreted on the assumption that the molecule has the symmetry C_{2h} (trans- form), two new fundamentals have been determined, and one change has been made in previous assignments. The fact that seven faint bands could not be interpreted indicates that a small fraction of the molecules have a cis- configuration.

Apparatus for Low Temperature Study of the Raman Effect. R. C. LORD AND E. NIELSEN, Spectroscopy Laboratory, Massachusetts Institute of Technology.

A simple modification of a conventional excitation unit (*1*) enables the study of the Raman effect in liquids at any temperature down to about −160° C. The chief feature of the arrangement consists of a Dewar-jacketed sleeve that fits around the Raman tube and enables the cooling of the tube by a flow of cold nitrogen gas. By adjustment of the temperature of the gas and its rate of flow, easy and precise control of the temperature of the Raman tube can be obtained. It is also possible to use elevated temperatures (up to 150° C.) by heating the nitrogen. The advantages of the system are its simplicity, ease of operation, quick change from low temperatures to normal operation and vice versa, and the same intensity of illumination as that afforded by room-temperature operation. The setup has most recently been used to obtain Raman spectra of liquid diborane and heavy diborane, including qualitative depolarization factors, at a temperature near −120° C.

(1) Harrison, Lord, and Loofbourow, "Practical Spectroscopy," pp. 511–13, New York, Prentice-Hall Publishing Corp., 1949.

The Resolving Power of Infrared Prism Spectrometers. ROBERT J. MELTZER, The Johns Hopkins University.

The equation for the resolving power of a spectrometer under conditions of fixed wave number band pass, in instances where available source brightness or available detector sensitivity, and not diffraction, sets the limitation, has been given by Strong (*2*). The energy-limited and diffraction-limited resolving powers have been computed for four prism materials, LiF, NaCl, KBr, and KRS_5, as a function of apex angle under two conditions: (1) The aperture is limited by the size of the prisms which may be cut from crystals now available. (2) The aperture of the spectrometer is limited by the opacity of the prism material at the base of the prism. In the first instance the resolving power is a maximum for some apex angle: LiF, 60°; NaCl, 52°; KBr, 47°; KRS_5, 32°. In the second instance the apex angle should be as large as is consistent with the critical angle of the material. These computations lead to a comparison of double dispersion with zero dispersion systems, such as the recent system proposed by Shurcliff (*1*). The former provide at least twice the detector response at constant wave number band pass, when absorption losses are negligible, and even higher response when such absorption losses cannot be ignored. A design of a multiple-prism polarizing spectrometer was mentioned.

(1) Shurcliff, W. A., *J. Optical Soc. Am.*, **39**, 1048 (1949).
(2) Strong, John, *Ibid.*, **39**, 320 (1949).

A Rapid Scanning Spectrometer for Oscillographic Presentation in the Near-Infrared. B. W. BULLOCK AND S. SILVERMAN, Applied Physics Laboratory, The Johns Hopkins University.

A rapid scanning spectrometer (*1–5*) for oscillographic presentation has been built for use in the "photoconductive" infrared

region. It is designed to produce spectra from 0.36 mμ to better than 5 mμ using a PbTe cell. The carbon dioxide doublet at 4.2 mμ is resolved with a scanning rate of 120 cycles per second and a scanned interval of better than 1.5 mμ with fluorite optics. A wave-length calibrating device has been incorporated into the instrument; this presents a fiduciary scale, synchronized with the spectrum, on the second beam of the twin-beam C.R.O. Adequate solutions have been found for the problems of synchronizing oscilloscope sweep and scanning drive, and for the problems of amplifier design for the sensitive cells.

(1) Bullock, B. W., and Silverman, S., *J. Optical Soc. Am.*, 39, 200 (1949).
(2) Daly, F. F., and Sutherland, G. B. B. M., *Proc. Phys. Soc. (London)*, 59, 77 (1946).
(3) Deal, Bradshaw, and Matsen, *J. Chem. Phys.*, 38, 209 (1948).
(4) Feldt and Berkley, National Electronics Conference, Chicago, 1946.
(5) Silverman, S., *J. Optical Soc. Am.*, 38, 664A (1948).

Improved Diffraction Gratings and Echelles (*2*). DAVID RICHARDSON, R. S. WILEY, AND G. J. SHELDON, Bausch & Lomb Optical Company.

The efficiency of both gratings and echelles depends upon the flatness and angle of the active groove face. A microscope interferometer equipped with oil immersion objectives is used for observing test rulings and controlling the setting of the grating ruling diamond. A similar instrument with 32-mm. objectives is suitable for the work with echelles. Extreme equality of spacing is required for an approach to theoretical resolving power. This property of a ruling can be observed through the use of a refinement of the Gale (*1*) interferometer test method. A plano-interferometer equipped with an Hg 198 lamp permits observation of random or periodic spacing errors that reduce resolving power and produce Rowland ghosts. Some examples of the relation between interferometer tests and the actual performance of experimental plane gratings and echelles were given.

(1) Gale, H. G., *Astrophys. J.*, 86, 437 (1937).
(2) Harrison, G. R., *J. Optical Soc. Am.*, 39, 522 (1949).

Simultaneous Recording of Two Wave-Length Ranges with the Littrow Spectrograph. ROBERT W. MURPHY AND HAROLD K. HUGHES, Socony-Vacuum Laboratories, Brooklyn, N. Y.

This paper reported another phase of the program being followed by Socony-Vacuum laboratories, Technical Service Department, designed to reduce the size of sample and improve the efficiency of spectroscopic analyses (*1*). Two wave-length ranges are recorded from a single exposure by the use of an auxiliary mirror system in a Littrow-type prism spectrograph. Radiation passing into the spectrograph is divided into two parts. The portion incident on the upper half of the prism-lens aperture receives the dispersion and collimation to produce the normal ultraviolet spectrum on the photographic plate. A system of two mirrors, interposed before the lower-half aperture, provides an additional angular deviation and increase in path length to produce a visible spectrum adjacent to the ultraviolet spectrum. The instrument described was designed for use with the Bausch & Lomb large Littrow spectrograph. Its purpose is to record, in one exposure, a spectral range sufficient for the detection and estimation of all the elements, except boron, which can be excited in the arc. Through the use of the auxiliary unit, the ranges 2530 to 3500 A. and 3540 to 10,000 A. are covered, including, for example, the phosphorus lines and the potassium lines at 7665 and 7699 A. The elimination of an extra exposure results in substantial reductions in analytical time and in sample requirements.

(1) Hughes, H. K., and Murphy, R. W., *J. Optical Soc. Am.*, 39, 501 (1949).

A Recording Grating Monochromator for the Range 180 to 4000 Millimicrons. WALTER S. BAIRD, Baird Associates, Inc.

A grating monochromator has been built for use over a spectral range extending from the ultraviolet through the lead sulfide cell region to 4 microns. A flat grating is used with a spherical mirror 4 inches in diameter and of 1-meter focal length, serving as both collimator and telescope. Two gratings are provided: one of 15,000 lines per inch to cover the range from 180 to 2000 mμ with a first-order theoretical resolving power of 60,000 and a second of 7500 lines per inch to cover the range from 180 to 4000 mμ with a first-order theoretical resolving power of 30,000. Provision has been made for automatic recording of a spectrum on a scale linear in wave length with the aid of either a photocell or a sulfide cell and a Leeds & Northrup Speedomax recorder. Sample curves were shown illustrating the application of the instrument to the recording of narrow band filter characteristics and absorption spectra in the ultraviolet, visible, and near infrared regions.

Phase Contrast Microscopy for Opaque Specimens. JAMES R. BENFORD AND RICHARD L. SEIDENBERG, Bausch & Lomb Optical Company.

Phase contrast microscopy is by now a familiar subject in the field of transmitted light microscopy. Its application in reflected light is more recent (*1*, *3*). Early systems for reflected light phase contrast (*2*, *4*, *5*) either located the phase annulus directly in the objective focal plane, or else compromised on this desired location and placed it beyond the vertical illuminator, somewhere between aperture and field planes in the microscope. This paper described a different approach to the problem, resulting in an instrument design which obviates the elaborate equipments required by the above-mentioned systems, and requires only one phase annulus and one illuminating annulus for all objectives, and in which the phase annulus is located in the ideal aperture plane of the microscope.

(1) Cuckow, *Nature*, 159, 639 (May 10, 1947).
(2) Cuckow, "Phase Contrast Incident Light Microscope," Iron and Steel Inst. Papers, April 1949.
(3) Jupnik, Osterberg, and Pride, *J. Optical Soc. Am.*, 36, 710 (1946).
(4) Jupnik, Osterberg, and Pride, *Ibid.*, 38, 338 (1948).
(5) Taylor, *J. Roy. Microscop. Soc.*, 66, 49 (May 1949).

Absorption and Emission Spectra of Promethium. W. F. MEGGERS, B. F. SCRIBNER, AND W. R. BOZMAN, National Bureau of Standards.

A 5-mg. sample of promethium 61, prepared by the Oak Ridge National Laboratory, was loaned for spectroscopic research. This sample was put in solution and its absorption spectrum between 3000 and 9000 A. was plotted with the aid of a Beckman spectrophotometer. These results are practically identical with those reported by Parker and Lantz (*1*). The strongest absorption bands have wave lengths 494.5, 548.5, 568.0, 685.5, 702.5, and 735.5 mμ (±0.5 mμ). Small portions of the solution were dried on copper electrodes employed in photographing a.c. arc and spark spectra with a concave grating of 22-foot radius. Wave lengths and relative intensities were determined for more than 1000 lines between 2200 and 6900 A. Excepting samarium 62, no other rare earths could be detected in this promethium 61 sample, but common impurities from chemical ware and reagents were troublesome. Most of the 59 lines reported by Timma (*2*) have been confirmed. The strongest lines appear to be 3892.17 and 3998.97 A. (±0.02 A.). Hyperfine structure is suspected in many lines—e.g., 5868.79, 5875.32, 5927.17, and 5946.49 A.—indicating that the nuclei of $^{147}_{61}Pm$ atoms possess mechanical and magnetic moments.

(1) Parker, G. W., and Lantz, P. M., *J. Am. Chem. Soc.* (in press).
(2) Timma, D. L., *J. Optical Soc. Am.*, 39, 898 (1949).

Spectrographic Determination of High Hafnium in Hafnium-Zirconium Dioxide. ALFRED B. CHANDLER, Foote Mineral Company, Paoli, Pa.

A method was presented for the direct determination of hafnium in the concentration ranges of 2 to 50% hafnium in $(Hf–Zr)O_2$. It is based on the use of intensity ratios of a pair of weaker lines of these elements (*1*), Hf 2638.710 A. and Zr 2640.151 A. These lines were selected to give a log ratio of 1.0 at 10% hafnium. Hafnium analyses above 50% have been made using a 1 to 1 dilution with hafnium-free zirconium dioxide. Standards were prepared from hafnium-free zirconium dioxide obtained by a double fractionation of $3ZrCl_4–2POCl_3$ complex (*2*). HfO_2 was obtained from Phillips Eindhoven, Holland.

(1) Coulliette, J. H., IND. ENG. CHEM., ANAL. ED., 15, 732 (1943).
(2) Gruen, D. M., and Katz, J. J., Atomic Energy Commission U-498 (U.A.C.-123) (June 1949).

The Ultraviolet Dissociation Spectra of Nylons. GLADYS A. ANSLOW AND RUTH C. SHEA, Smith College.

The ultraviolet absorption spectra of nylon films, formed of polyhexamethylene adipamide and of polyhexamethylene sebac-

amide and of Nylon 6B in a 10^{-5} *M* 85/15 ethyl alcohol–water solution, were compared with the spectra of adipamide, malonamide, and pelargonamide in crystalline form or in water or alcohol solutions. The amide solutions had been heat-treated to impose the two types of association of amides through hydrogen bridges which result from fast or slow cooling and exhibit distinctive absorption spectra (*2*). The short wave-length continuum which appears in the spectra of these molecules has been attributed to the dissociation of the hydrogen-bridged bonds following electronic excitation (*1*). The spectra of the nylon films resemble those of slowly cooled amides, and that of the Nylon 6B solution the spectra of rapidly cooled amides, the former being long linear polymers, the latter dimers or polymers with only a few members, in which the hydrogen bridges between units are ruptured by the absorption.

(1) Anslow, Hsieh, and Shea, *J. Chem. Phys.*, 17, 426 (1949).
(2) Anslow, G. A., and Shea, R. C., *Phys. Rev.*, 75, 1318 (1949).

Spectrochemical Methods of Brass Analysis. M. F. Hasler and C. E. Harvey, Applied Research Laboratories.

Two analytical techniques were discussed: a point-to-plane procedure suitable for the rapid routine analysis of metal specimens, and a solution method that permits the validation of standards. The latter also offers an alternative method for control analysis under some circumstances. Certain fundamental problems were discussed from the standpoint of the above procedures: the interrelation of metallurgical variables and discharge conditions; other related variables; the synthesis of standards; quantitative calculations in varying two and three major constituent systems; comparison of photographic and quantometric recording.

A Curve Computer. W. E. Knowles Middleton, National Research Council of Canada.

An instrument has been designed and constructed for the purpose of multiplying, dividing, adding, or subtracting the ordinates of two Cartesian curves, and plotting the result. The principle is that of the Wheatstone net, balanced automatically by means of a servo system. Certain logarithmic operations can also be performed, and a planimeter attachment integrates the area under the curve representing the product, etc. The overall accuracy is about 0.3%. The curve computer has many applications in photometry and colorimetry, such as the conversion of filters from one thickness to another, and the computation of tristimulus values.

New Automatic Colorimeter for Cotton. Dorothy Nickerson, U. S. Department of Agriculture, and Richard S. Hunter and Marshall G. Powell, H. A. Gardner Laboratory, Inc.

This instrument is based on a satisfactory application of the Hunter color and color-difference meter (*1*) to problems of raw cotton measurement. For cotton colors Hunter's coordinates R_d and b provide, without conversion, a picture close to that of measurements in terms of Munsell value and chroma. Therefore an instrument was designed to be fully automatic and self-standardizing, and graphically to show on a two-dimensional scale simultaneous values for reflectance and yellowness. Furthermore, the instrument is self-contained in a movable cabinet about table height, with a minimum of exposed parts, and working parts in the horizontal plane of the table. Electrical measurements of photocell currents are converted to color as in the color-difference meter, except that Brown Electronik amplifiers replace the galvanometer, and reversible motors responding to the signals from these amplifiers replace the human operator, both in standardizing the instrument and in turning dials to obtain color settings. Although this particular instrument is limited to the range of cotton colors, the principles upon which it is designed are adaptable to other limited ranges of color, in either two or three dimensions.

(1) Hunter, R. S., *J. Optical Soc. Am.*, 38, 661A (1948).

Color Harmony Manual. Walter C. Granville, Container Corp. of America, Chicago, Ill., Carl E. Foss, Princeton, N. J., and I. H. Godlove, General Aniline & Film Corporation, Easton, Pa.

The third edition (*4*) of the "Color Harmony Manual" represents a complete revision of the earlier editions (*3*) and includes 263 colors in addition to the 680 in the regular abridgment of the Ostwald system of color organization. The new edition was shown and the basis for the revision discussed. Spectrophotometric measurements have been made for both the matte and glossy sides of all chips on a G.E. recording spectrophotometer. Tristimulus specifications or I.C.I. illuminant *C* were obtained at the same time from an automatic, continuous tristimulus integrator (*1*) attached to the spectrophotometer. Representative portions of these data were presented, and a comparison made with the corresponding data (*2*) of the earlier edition of chips.

(1) Davidson, H. R., and Imm, L. W., *J. Optical Soc. Am.*, 39, 633 (1949).
(2) Granville, W. C., and Jacobson, E., *Ibid.*, 34, No. 7 (1944).
(3) Jacobson, Egbert, "Color Harmony Manual," Container Corp of America, Chicago, 1942 and 1946.
(4) Jacobson, Granville, and Foss, *Ibid.*, 1948.

Application of the Hunter Color-Difference Meter to a Tomato Color Measurement Problem. S. G. Younkin, Campbell Soup Company.

In the present study, a Hunter color-difference meter was used to obtain color specifications of tomato purees, and for the first time it has been possible in our laboratories to make rapid, repeatable, small color-difference measurements. A porcelain-enamel reference standard having color specifications similar to tomato purees was used to obtain values of Hunter's L, a_L, and b_L by viewing 130 ml. of each puree through the base of a specially constructed glass cell. Values of a_L and b_L were plotted on a chromaticity diagram with L values designated numerically for each plotted point. Munsell renotation loci for hue and chroma were placed on these diagrams for orientation purposes. Visual examinations were made of purees contained in square glass bottles. Samples were viewed by daylight and scored on the basis of appearance. Altogether there were several thousand purees prepared from fruits grown at widely separated points, under different environmental conditions, and harvested at different degrees of maturity. Essentially a perfect correlation was obtained between color-difference meter specifications and visual scores regardless of the magnitude of color differences.

Officers of Division of Analytical Chemistry

The Nominations Committee of the Division of Analytical Chemistry requests the cooperation of the members of the division in suggesting names of members for nomination to the offices of chairman-elect, secretary-treasurer, councilor, and alternate councilor. The committee is to present two nominees for each office. The nominations are for offices to be filled for the year 1951, for which elections will be held at the fall 1950 meeting of the Society. Suggestions should be sent to the Chairman of the Nominations Committee, William Seaman, American Cyanamid Company, Calco Chemical Division, Bound Brook, N. J.

The Analyst's Calendar

Scientific Apparatus Makers of America. Chicago, Ill., May 18 to 20

Society for Applied Spectroscopy. New York, N. Y., May 26 and 27

Symposium on Molecular Structure and Spectroscopy. Mendenhall Laboratory of Physics, Ohio State University, Columbus, Ohio, June 12 to 17

Third Annual Summer Symposium. Ohio State University, Columbus, Ohio, June 16 to 17

International Microchemical Congress. Graz, Austria, July 2 to 6

Instrument Conference and Exhibit. Instrument Society of America, Buffalo, N. Y., September 18 to 22

AIDS FOR THE ANALYST . . . . .

Constant Rate Feed Device. Lester G. Lundsted, Arthur B. Ash, and Nathan L. Koslin (present address, Nalin Laboratories, Columbus, Ohio), Wyandotte Chemical Corporation, Wyandotte, Mich.

THE investigation of vapor phase reactions in the laboratory frequently requires suitable means of introducing a liquid feed at low, but constant, reproducible rates in order to permit evaluation of such variables as flow rate, temperature, and tube packing. A device that accomplishes this purpose and is particularly suitable for small amounts of material is described below. Previous workers have described various types of feed apparatus based on other principles [Zentner, IND. ENG. CHEM., ANAL. ED., **16,** 47 (1944), which makes use of the principle of the Mariotte bottle; Goldwasser and Taylor, *J. Am. Chem. Soc.*, **61,** 1260 (1939), which depends upon displacement of the feed liquid by mercury; and Burwell, IND. ENG. CHEM., ANAL. ED., **12,** 681 (1940), which depends upon gas liberated by electrolysis as the displacing medium].

Although this device is based on well known principles, it has not been described elsewhere and may prove useful to organic chemists and others confronted by small scale flow rate problems. It has been found capable of feeding a wide variety of liquids, including volatile and corrosive compounds, at flow rates on the order of 0.25 to 5.0 grams per minute with a reproducibility of approximately ±5%.

As illustrated in Figure 1, the device is made from parts available in nearly any laboratory, the other main requirement being a source of moderate gas pressure (air or nitrogen). In operation, a slow current of air or nitrogen is allowed to pass through the needle control valve, *A;* the pressure in the apparatus proper is read on the open-end manometer, *D,* and controlled by regulator *B. B* consists of a T-tube which can be slid up or down through one hole of a two-hole stopper fitted tightly in the mouth of a test tube containing mercury. The head of the T is connected to valve *A* and manometer *D* by means of rubber tubing of length sufficient to allow the tip, *C,* to be adjusted at any level between the bottom of the test tube and the top of the contained liquid.

The manometer is connected to the liquid reservoir, *F,* through the three-way stopcock, *E,* the third arm of which is open to the atmosphere. The outlet from flask *F* consists of a capillary tube, *G,* one tip, *J,* of which has been drawn out and constricted. One may, if desired, cut the capillary tube at *K* and attach any one of different tips by means of suitable flexible tubing, thus simplifying the replacement of one tip with another in order to extend the range of flow rates. The other tip of *G* may be covered with glass cloth or glass wool, in order to filter out sediment or dirt which might otherwise plug the constricted tip, *J. J* may serve as a drop counter; in any case, it should be above the liquid level in *F* to prevent possible siphoning.

If it is desired to add a fluid to a reactor which is not transparent, a separate glass sight tube above the apparatus will permit visual observation of the flow.

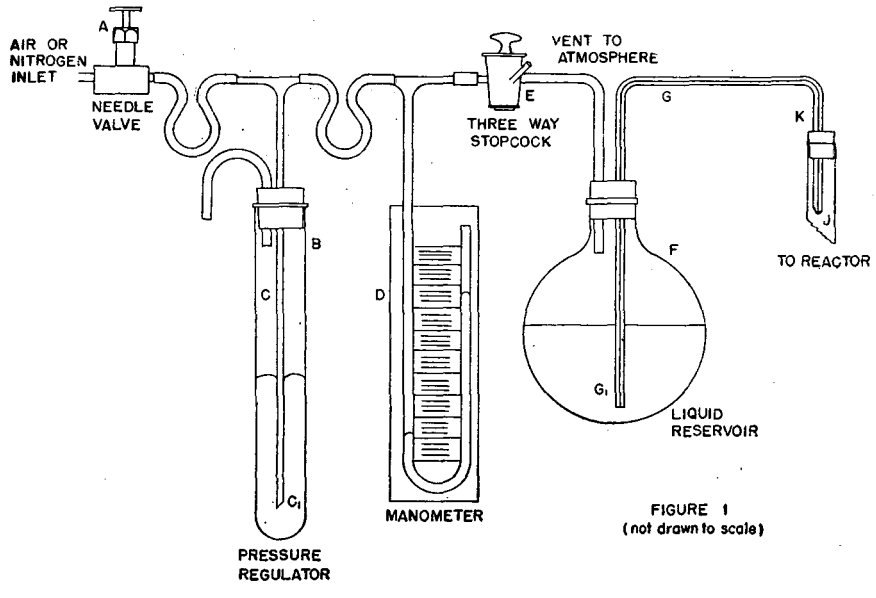
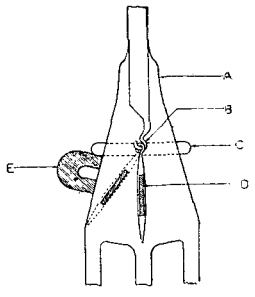


FIGURE 1
(not drawn to scale)

Calibration of the feed system to permit adjustment to a predetermined flow rate is accomplished by determining the weight or volume flow rates corresponding to several manometer readings. A plot of these flow rates *vs.* the corresponding manometer settings on log-log paper produces a nearly linear curve from which manometer settings to give any desired flow rate may be read.

Magnetic Distributing Adaptor for Fractional Distillation Columns. Elizabeth J. Rock and George J. Janz, The Cryogenic Laboratory, Pennsylvania State College, State College, Pa.



THE magnetic distributing adaptor described was designed to eliminate the possibility of contamination with stopcock grease in the fractionation of certain substances. Combined with a distillation column having the well known type of magnetic take-off control, an all-glass system can be assembled in which no ground-glass joints or stopcocks need be used.

The design of the adaptor is extremely simple. It consists of a flask, *A,* having the requisite number of take-off arms to which the receiving flasks are sealed. The distillate is conducted to the appropriate receiver by a "magnetic policeman," *D,* which consists of a glass rod of proper length with an iron core sealed in as shown. It is suspended from the tip of the inlet tube by a glass hook, *B,* which gives it freedom to swing to the side arms. The policeman is controlled by a small powerful permanent magnet, *E.* In practice, an Alnico magnet (1 ounce in weight, and having a 6-pound pull, Terry Sales Company, Toledo, Ohio) was found very satisfactory. The iron ring, *C,* around the outside of the adaptor flask provides a convenient means of holding the magnet against the flask wall, so that it remains in position controlling the policeman until the distillate fraction in question has been collected.

It has been found useful to seal a take-off arm directly below the top of the policeman when it hangs in its rest position—i.e., no magnetic force acting. This outlet may then be used to collect the forerun in the fractional distillation.

This magnetic distributing adaptor was developed in the course of work under Contract N6 ORN-269 of the Office of Naval Research under the direction of J. G. Aston. The apparatus was constructed by Fritz Malloy.