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Summaries of Papers in this Issue

A Flexible Program for Calculations in Emission-spectrographic Analysis

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B. L. TAYLOR and F. T. BIRKS

Analytical Sciences Division, Atomic Energy Research Establishment, Harwell, Didcot, Berks.

Analyst, 1971, **96**, 753–763.

The Determination of Alumina in Iron Ores, Slags and Refractory Materials by Atomic-absorption Spectroscopy

As chemical methods of determining alumina are time-consuming, the simpler, more rapid atomic-absorption technique was adapted to iron ores, slags and refractory materials.

The basic technique comprises fusion of the sample with a sodium tetraborate - sodium carbonate mixture, extraction with dilute nitric acid, appropriate dilution and spraying under recommended conditions for aluminium. As the flux materials enhance the aluminium absorption, sample and corresponding calibration solutions should contain equivalent amounts.

Interference tests on synthetic solutions of the other constituents showed that the inhibiting effect of silica was suppressed by lanthanum chloride. A standard addition of lanthanum chloride was therefore incorporated and calibration conditions were developed to cover the ranges 0 to 1 per cent., 0 to 5 per cent., 0 to 10 per cent. and 10 to 35 per cent. of aluminium.

Applications to miscellaneous B.C.S. materials showed good agreement with accepted values and reproducibilities of $\pm 0{\cdot}035$ per cent., $\pm 0{\cdot}12$ per cent., $\pm 0{\cdot}18$ per cent. and $\pm 0{\cdot}38$ per cent. of aluminium, respectively, at the above levels.

W. D. COBB and T. S. HARRISON

Group Chemical Laboratories, British Steel Corporation, Scunthorpe Group, P.O. Box No. 1, Scunthorpe, Lincolnshire.

Analyst, 1971, **96**, 764–770.

The Atomic-fluorescence Determination of Mercury by the Cold Vapour Technique

A method for the determination of low levels of mercury by using atomic fluorescence in conjunction with the cold vapour technique is described, and shows significant advantages over the corresponding absorption technique.

K. C. THOMPSON and G. D. REYNOLDS

Shandon Southern Instruments Ltd., Frimley Road, Camberley, Surrey.

Analyst, 1971, **96**, 771–775.

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X-ray Spectrometric Determination of Rare Earth Elements by Using a Fusion Technique

A general method for the determination of rare earth elements by X-ray fluorescence spectrometry is described. The sample is fused with sodium tetraborate, chromium is added to act as internal control-standard, and the resulting bead is analysed directly. This method overcomes variations in sample form and particle size. Individual rare earths can be determined at levels from 0·1 to 100 per cent., and by using the L spectra and a lithium fluoride 220 crystal, line overlap is kept to a minimum.

C. PLOWMAN

Central Electricity Generating Board, Scientific Services Department, Kirkstall, Leeds, LS4 2HB.

Analyst, 1971, **96**, 776–778.

The Use of a Shield for the Reduction of Fogging on Photographic Plates in Spark-source Mass Spectrography

In spark-source mass spectrography, secondary effects cause pronounced fogging of the photographic plate in the vicinity of the isotope lines of the major elements, and the limit of detection of elements whose lines fall within this area is considerably raised.

A shielding device has been designed to reduce the amount of ions produced by secondary effects and to prevent them from reaching the photographic plate. This reduces the background in the region of the major isotope lines and enables elements in this region to be determined with increased sensitivity and precision.

C. W. FULLER and J. WHITEHEAD

Tioxide International Limited, Billingham, Teesside.

Analyst, 1971, **96**, 779–784.

Automatic Radiofrequency Titration of Acids in Tertiary Butyl Alcohol - Acetone Medium

The mixed solvent t-butyl alcohol - acetone can be used as a differentiating medium for the titration of acids with a standard solution of tetra-n-butylammonium hydroxide dissolved in a mixture of toluene and methanol. Titration curves of various shapes can be obtained and the simultaneous determination of certain acids achieved. The differences in curve shapes obtained by radiofrequency titration can be used as the basis of separation. The low toxicity of t-butyl alcohol (compared with other solvents at present in widespread use for the titration of weak acids) combined with its low solvating power and good differentiating properties make it a suitable medium for the routine determination of such acids in admixture.

W. J. SCOTT and G. SVEHLA

Department of Analytical Chemistry, The Queen's University, Belfast.

Analyst, 1971, **96**, 785–797.

Improvements to the Nitrite - Diazo Dye (Blom's) Method of Determining Hydroxylamine as Used in the Determination of Residues of Aldicarb

The precision of determination of hydroxylamine, and hence of residues of aldicarb, by Blom's method has been improved by controlling the pH of the solutions at the diazotisation and coupling stages and by removing the excess of iodine, after oxidation of the hydroxylamine, by extraction into bromobenzene. The latter previously required chemical reduction to iodide.

D. F. LEE and J. A. ROUGHAN

Ministry of Agriculture, Fisheries and Food, Plant Pathology Laboratory, Hatching Green, Harpenden, Herts.

Analyst, 1971, **96**, 798–801.

NEWS

THE ANALYST

A Flexible Computer Program for Calculations in Emission-spectrographic Analysis

By B. L. TAYLOR and F. T. BIRKS

(*Analytical Sciences Division, Atomic Energy Research Establishment, Harwell, Didcot, Berks*)

A computer program has been written in FORTRAN IV to evaluate for spectrochemical analysis spectral information stored on photographic plates. With this program, ratios of line intensities are calculated from microphotometer readings; it includes the computation of the emulsion calibration function using either the two-step or seven-step method. A formatless data input technique is employed and use is made of descriptive headings and labels to facilitate the introduction of data. These headings and the codes used for labelling the readings are chosen so as to be readily understood by the spectrographer. The program is characterised by considerable flexibility with regard to the number of spectra and number of analytical and internal standard lines that can be used. The maximum number of spectra that can be evaluated is sixty and up to nineteen analytical lines can be present in each spectrum. The program contains many data checks, together with appropriate diagnostic messages, which are designed to avoid the presence of undetected errors in the results.

THE ratio of the light intensity of an analytical line to that of an internal reference line is a quantity of prime importance in analytical emission spectrography. In general, the calculation of this intensity ratio has to be carried out for several analytical lines in each of several spectra recorded on a photographic plate. Writing a computer program to calculate these ratios is not difficult when the type of analysis is fixed and the analytical and reference lines do not alter. However, if a versatile program is required that is to be applicable to any emission-spectrographic determination, the task becomes more difficult. This paper describes one method of writing such a program. It is written in FORTRAN IV for use with the Harwell IBM 360/75 computer. The mode of data input is punched card, punched paper tape or keyboard, but for simplicity the following description is given in terms of punched card input.

General considerations

The following standard procedure is used in this laboratory for photographically recording spectra and measuring them for the purposes of spectrochemical analysis. On each plate a two or seven-step iron-arc spectrum is recorded by using a step filter or a rotating step sector; this provides the intensity pattern used for the calibration of the photographic emulsion. The spectra for standards and analysis samples, with or without a two-step filter, are recorded on the remainder of the plate. The transmittances of lines and backgrounds are measured with a modified Hilger and Watts microphotometer which gives a reading proportional to the amount of light reaching the detector. In order to determine the relative transmittance* the ratio of the reading for the exposed portion of the emulsion to the reading for a clear portion is taken. (The latter is maintained at an arbitrary value of 50 during the measurements.)

The main problem in writing a versatile program to compute ratios of intensities is concerned with the input of data. Each microphotometer reading has to be introduced in a way that indicates the line and spectrum to which it refers. In addition, the data for the emulsion calibration and a list of the required intensity ratios have to be read in. The

* The nomenclature used throughout follows the recommendations given in (*a*), "Nomenclature, Symbols, Units and their Usage in Spectrochemical Analysis—I (Tentative)," I.U.P.A.C., 1969, and (*b*), "Methods for Emission Spectrochemical Analysis," 5th Edition, A.S.T.M., Philadelphia, 1968.

usual method used in the FORTRAN language for identifying data depends entirely on the sequence and column positioning of the data in the card deck. This method suffers from a number of drawbacks, especially when there are several types of input data and the amount of data varies from one computation to another. Under these circumstances failure of the user to satisfy the rigid requirements of a formatted data input technique is a frequent source of job failure.

One method of removing some of the restrictions was suggested by Franke and Poste.[1] They used a method in which each numerical value submitted was identified by a two-digit numerical code which preceded the number. This removed the necessity of submitting the data in a fixed sequence but exact column positioning was still necessary. In addition, numerical coding presents difficulties both in punching and checking the data which might well discourage potential users of the program. In our program an alternative approach has been used that is based on the use of easily understood key words and non-numerical codes for labelling the different types of data. These codes, which are chosen by the user, are used to associate each microphotometer reading with a particular line. They are also used when specifying the ratios required. The need for exact column positioning has been removed by using a formatless-data input routine that already exists in the Harwell Subroutine Library. This subroutine enables the data to be read, one word at a time, irrespective of the position of the word on the data card. A word is defined as a string of characters separated from any other string by at least one blank.

CARD TYPE		
1		TITLE RFB 89 29/8/69 A1542
2		EMULSION CALIBRATION 44·13 33·25 23·56 12·22 6·08 2·88 1·45
3		RATIO INTERNAL STD CO LINES MN CR NI AL MO CU W
4	A	DATA SPECTRUM 1 LINE SI 8·78 48·96 19·99 49·04 12·51 49·46
	B	DATA SPECTRUM 2 LINE MN * * * * * * 2·59 44·35
5		XXXXXXXXX

Fig. 1. Examples of types of data card

DESCRIPTION OF THE PROGRAM

There are five types of card used for data input, each defined by a key word, which is the first word on the card. Some typical examples are shown in Fig. 1. The key words specifying the type of data, and the other words on the cards, are designed to aid both in punching and checking the data. There is no restriction concerning the column positioning of any of the information other than that both words and numbers must be separated by at least one blank. The five types of card must be submitted in a fixed order but the order of the cards within any one class is irrelevant. As an additional aid in presenting the input data, sets of cards can be made available with the labels pre-punched on them, each class on a different coloured card. The five types of card are as follows.

Title—This contains the title of the job. With the IBM 360/75 system, in addition to the characters 0 to 9 and A to Z, there are twenty-four special characters, such as *, /, %,) and -, that can be used in the title.

Emulsion calibration—The program is designed to use either the two-step or seven-step emulsion calibration procedure.[2] If more than seven microphotometer readings are punched, the program assumes that the two-step method is being used and carries out the appropriate function-fitting procedure. For the two-step method the microphotometer readings are punched in pairs of strong and weak steps, *e.g.*, 4·1 8·9 2·1 4·7 11·3 23·2 etc. For the seven-step calibration, the readings are punched in descending order, that is, weak step first. The transmission ratio of the calibration device is treated as a local constant and is not read in as data. If the word COEFFICIENTS is punched after EMULSION CALIBRATION, the two previously determined coefficients of the emulsion calibration function can be read in from this card (see APPENDIX).

If the wavelength range of the analytical lines is such that a single emulsion calibration does not adequately cover it, the data are divided into wavelength sets and each set, *plus* the corresponding emulsion calibration data, is submitted for a separate cycle of the program (see section on *End card*).

Intensity ratios—The cards of this type serve both to introduce the codes used to label the microphotometer readings and to specify the intensity ratios required. The way in which each microphotometer reading for a line is processed is determined solely by the label given it and the ratios listed on the RATIO cards. Each internal reference line code is punched on to a separate card and the analytical lines to be compared with it follow on the same card. The line codes are chosen by the user, subject to the limitations that: no more than eight characters are used; there are no embedded blanks; the first character is a letter from A to Z; and only letters and numbers are used (*i.e.*, no decimal points are allowed). For the microphotometer readings for the copper line at 324·75 nm, valid codes would be CU32475, LINE2, CU, CU2, CUW (where W could be used to indicate a weak step reading of a spectral line), etc.

This is a very versatile method of data input. For example, it is possible, by introducing the same data more than once with a different label each time, to obtain the ratios of a particular line against a number of different internal reference lines. This procedure may be useful when developing an analytical method. Again, if it is considered necessary to measure a particular reference line more than once, in order to compensate for drift in the microphotometer, each reading can be given a different code and the analytical lines to be compared with that reading are listed on the appropriate RATIO card. In the most general instance every reading could be given a different code, thus allowing it to be processed independently of all the other readings. More usually, however, the spectra to be evaluated are related and the same analytical and reference lines are used for each spectrum. In these circumstances, the same line codes can be used in each spectrum.

Microphotometer readings—The microphotometer readings for the analytical and reference lines are punched on to the cards together with the line codes and the spectrum number. The spectrum number is of the form IS.IR where IS and IR are integers and the maximum value of IR is 4. The numbering sequence is therefore 1.1, 1.2, 1.3, 1.4, 2.1, 2.2, etc. This method of numbering the spectra is designed to cope with the situation when replicate spectra are taken for each sample. The number IR can then be used as the replicate number. If necessary, the average ratio of intensities for up to four replicates can be calculated and printed with the results. Only the IS portion of the spectrum number is punched on to the card and the pairs of readings, up to four in number, in the order line followed by background, are automatically numbered IS.1 to IS.4. It should be emphasised that the way in which the spectrum number is used is left to the user and spectra numbered 2.1, 2.2, 2.3, 2.4 can be completely independent spectra or four replicates from a single sample. The maximum value of IS is fifteen so that data for sixty spectra can be evaluated. When less than four pairs of readings are available for a card the gaps in the data are indicated by punching a single asterisk (*e.g.*, card 4B, Fig. 1), except when the gap is at the end of the card in which case the space is left blank (*e.g.*, card 4A, Fig. 1). A single asterisk can be used in place of a background reading when no correction for background is required. If, for a particular line, there are no data for any of the four spectra, no card is submitted.

With this method of presentation of the microphotometer readings, no distinction is made between data for the analytical and reference lines. This contrasts with a possible alternative technique in which the reference line reading is identified by being punched immediately after that for the analytical line. This last method suffers from several disadvantages, among which is that it generally involves considerably more data punching.

End card—A card with at least eight x symbols is used to indicate the end of the data. If instead a second title card is placed at this point, the calculation will be repeated with a second set of data.

Originally the mode of data input was punched cards, but more recently the microphotometer has been modified so that the readings are transferred directly to paper tape. The key words, line codes, etc., are added from a keyboard. However, these paper tape data are still in card image form.

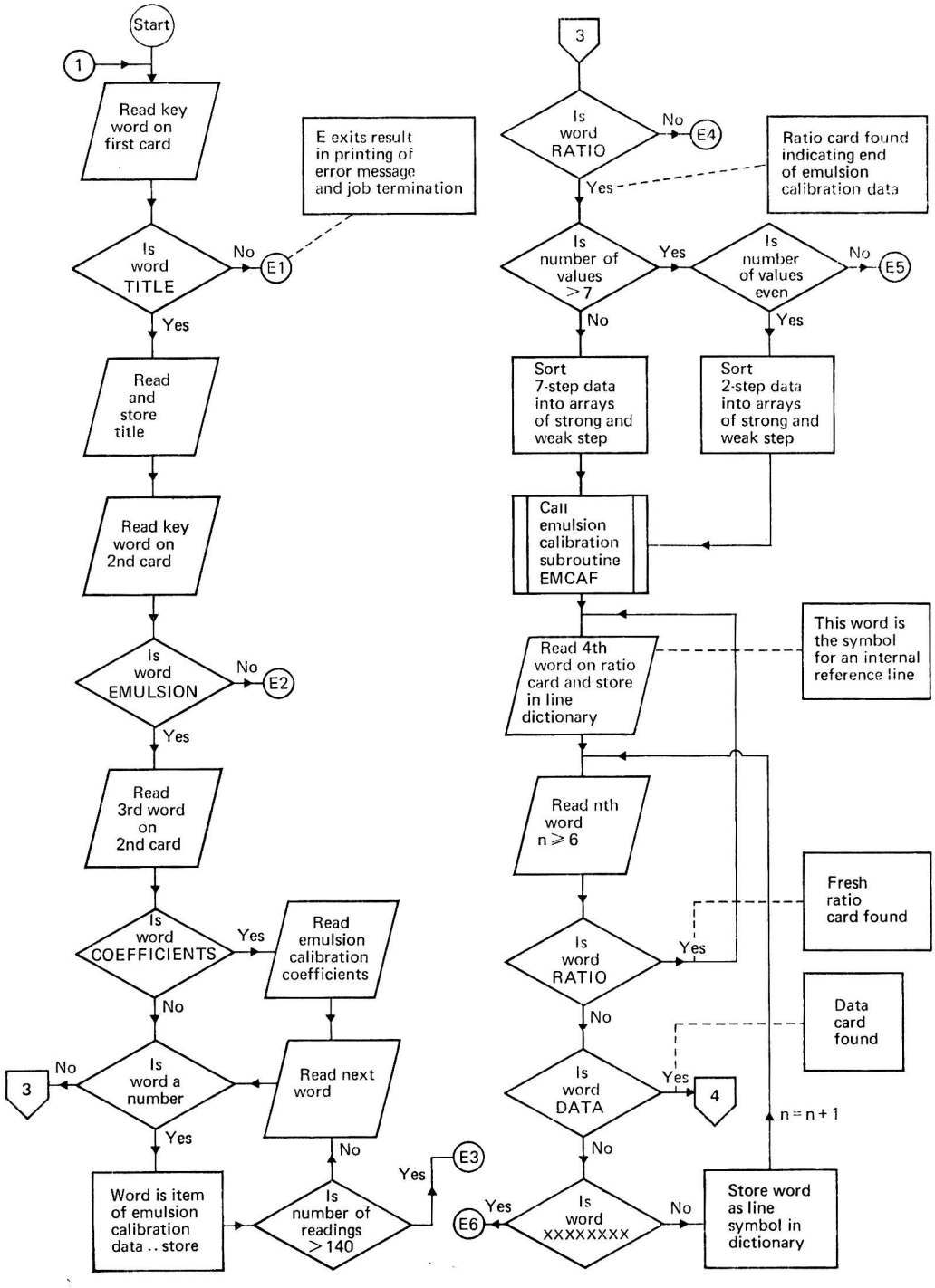

Fig. 2(*a*). Flow diagram of main program

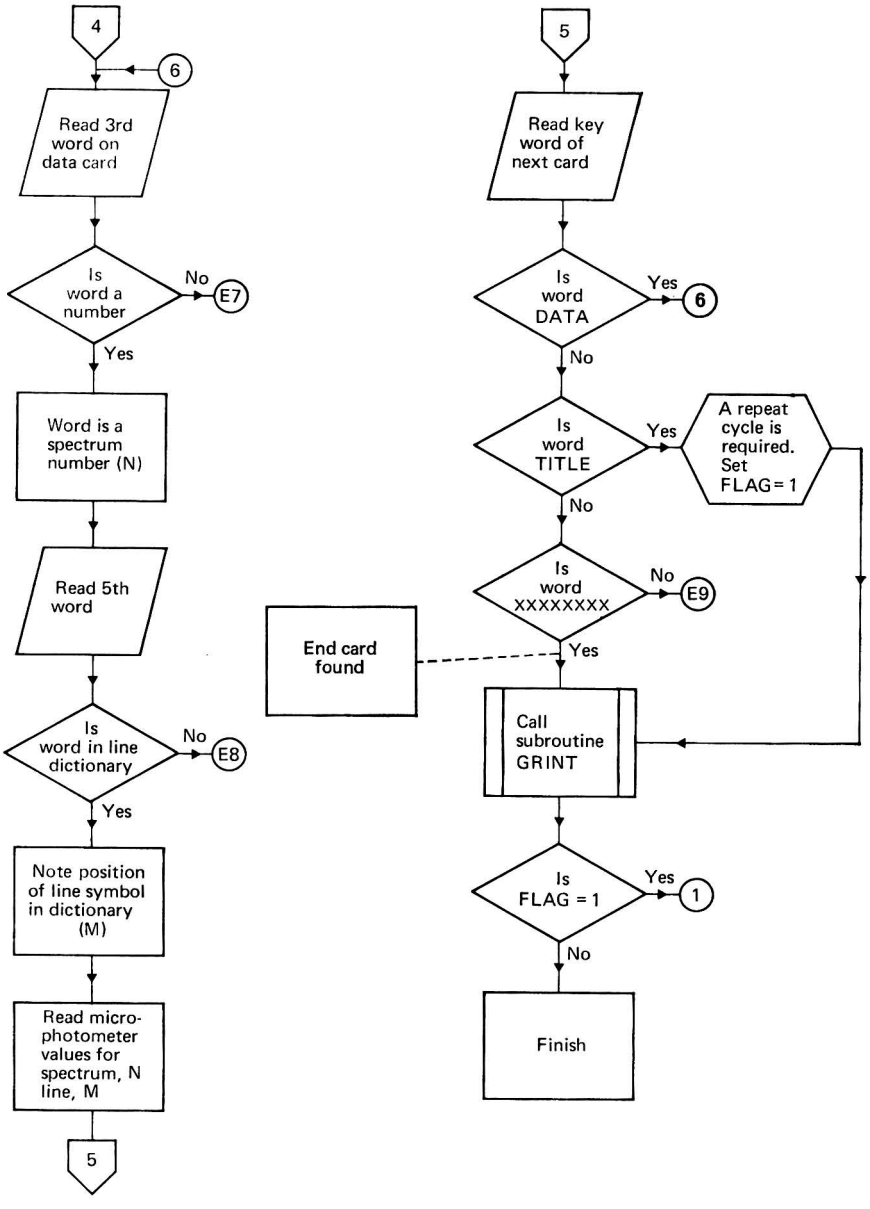

Fig. 2(*a*)—*continued*

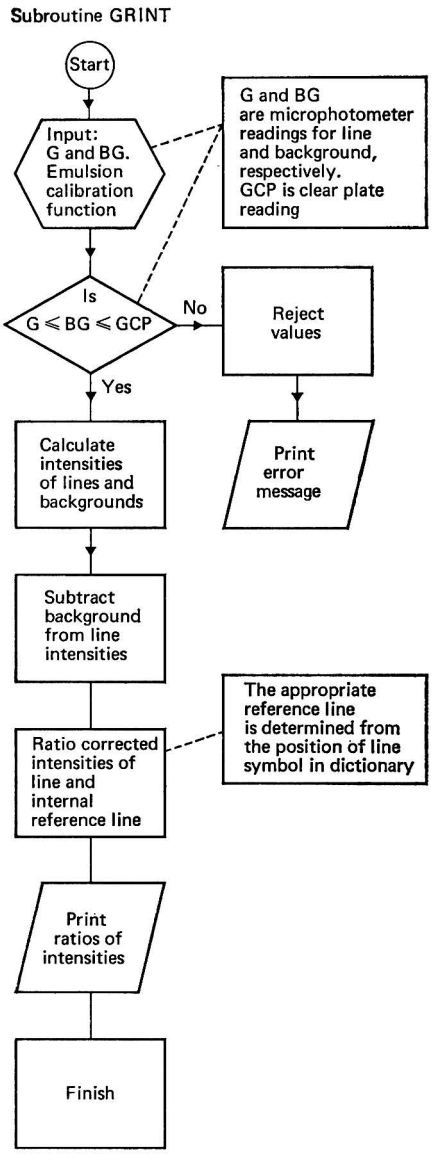

Fig. 2 (*b*). Flow diagram of subroutine GRINT

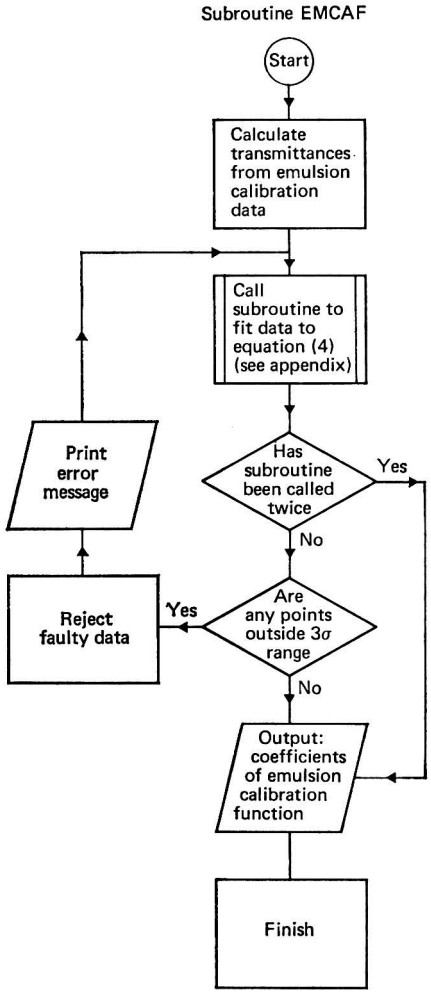

Fig. 2 (*c*). Flow diagram of subroutine EMCAF

METHOD OF CALCULATING INTENSITY RATIOS

With the input data correctly read in the program calculates the intensity ratios in a conventional manner.[2] The steps in the calculation are as follows: firstly, the emulsion calibration data (two or seven-step) are used to derive the emulsion calibration function (see Appendix); secondly, the microphotometer readings for the analytical lines, reference lines and their backgrounds are converted to transmittances and the intensities calculated using the emulsion calibration function; and thirdly, background corrections are made for the analytical and reference lines and the ratios of the corrected intensities are calculated.

Simplified flow diagrams of the main parts of the program are shown in Fig. 2 (*a*), (*b*) and (*c*). With standard samples, having determined the intensity ratios, the construction

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INPUT DATA

SPECTRUM NUMBER

	1.1		1.2		1.3		1.4	
CØ	1.82	48.34	4.45	48.86	2.50	48.87	—	—
SI	8.78	48.96	19.99	49.04	12.51	49.46	—	—
FE	1.62	48.12	6.43	47.88	2.26	48.29	—	—
MG	0.89	40.99	3.62	44.99	1.28	44.74	—	—
GA	4.86	46.48	5.13	46.79	4.02	46.77	—	—
B	33.87	46.49	39.98	47.13	34.97	46.07	—	—
PB	7.55	40.30	4.56	43.44	4.70	42.80	—	—
SN	31.53	37.26	33.77	40.78	32.92	40.23	—	—
AGW	24.42	42.43	13.75	43.92	12.46	45.06	—	—
CØ1	1.75	47.53	4.30	48.03	2.46	48.16	—	—
MN	5.37	40.22	16.17	43.91	6.69	44.50	—	—
CR	6.02	39.42	22.70	42.90	9.74	43.74	—	—
NI	7.21	27.27	17.96	33.92	8.98	34.87	—	—
AL	7.23	24.01	23.86	32.14	13.00	32.18	—	—
MØ	11.63	20.42	13.20	23.92	10.47	26.93	—	—
CUW	9.32	40.88	8.16	41.71	4.84	43.13	—	—

	2.1		2.2		2.3		2.4	
CØ	2.99	48.33	2.56	49.85	2.95	49.38	2.51	49.56
SI	5.88	47.97	3.78	49.98	6.15	49.10	7.56	49.65
FE	3.64	47.94	2.08	48.52	4.74	49.48	29.75	49.55
MG	1.82	44.76	1.00	44.07	2.11	46.26	1.24	45.01
GA	4.55	44.82	3.98	45.27	4.96	46.33	4.40	46.12
B	33.81	46.73	34.11	46.77	34.99	47.99	1.72	45.58
PB	5.57	44.49	5.59	44.89	6.03	46.90	7.08	42.58
SN	34.74	40.70	34.18	39.45	38.68	44.38	3.55	41.92
AGW	17.53	44.52	18.70	45.23	20.05	47.85	1.55	46.31
CØ1	2.88	47.19	2.44	49.12	2.82	48.65	2.50	48.51
MN	—	—	—	—	—	—	2.59	44.35
CR	23.74	43.30	16.64	44.09	27.81	45.42	21.48	44.86
NI	11.68	35.40	9.30	35.74	16.83	41.99	11.23	39.19
AL	14.04	31.35	8.67	31.17	17.63	39.26	6.23	34.25
MØ	8.03	25.40	6.71	26.54	10.60	33.25	3.95	29.09
CUW	7.22	42.61	6.90	43.84	10.68	45.44	1.83	43.57

	3.1		3.2		3.3		3.4	
CØ	2.39	48.15	4.17	48.43	3.13	46.61	1.53	48.09
SI	4.64	48.33	3.72	48.19	1.28	46.73	26.64	49.04
FE	18.67	47.97	22.13	48.71	6.24	46.44	18.01	48.33
MG	0.49	39.10	0.37	40.29	0.12	33.36	9.95	42.57
GA	4.12	44.32	4.96	44.66	4.57	42.87	3.79	44.65
B	0.67	43.05	0.41	43.80	0.20	39.19	28.73	46.09
PB	2.62	34.24	1.08	32.39	0.35	19.56	33.97	42.54
SN	1.38	35.06	0.82	38.14	0.33	33.66	—	—
AGW	1.01	40.47	0.66	42.91	0.31	38.51	24.68	43.90
CØ1	2.28	47.01	4.10	47.43	3.16	46.01	1.48	47.21
MN	1.15	39.17	0.91	40.17	0.46	34.33	—	—
CR	11.98	39.07	12.80	42.25	3.92	38.64	—	—
NI	3.13	25.74	5.71	34.29	1.69	28.43	21.80	31.52
AL	3.49	21.90	4.63	29.09	2.19	24.88	13.61	25.35
MØ	2.01	17.82	1.58	22.69	0.50	18.07	—	—
CUW	0.71	38.39	0.56	41.54	0.30	38.61	2.97	41.43

Fig. 3(*a*). Microphotometer readings

of the analytical curve is carried out manually. The computer is not used at this stage as it is considered desirable to use the ability of an experienced spectrographer to recognise and reject faulty data. Once the ratios have been obtained the effort required to produce the analytical curve is relatively small.

The total execution time on the IBM 360/75, with the data shown in Fig. 1, was 9·3 s, consisting of 4·1 s of central processor time and 5·2 s wait time.

```
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INPUT DATA FOR EMULSION CALIBRATION
          44.13  35.25  23.56  12.22  6.08  2.88  1.45

**OUTPUT FROM MA14A**

NO. OF EQUALITY CONSTRAINTS    = 0
NO. OF EQUATIONS OF CONDITION  = 6
NO. OF VARIABLE PARAMETERS     = 2

******** SOLUTION ********
      1  0.174056E 01
      2  0.295192E 01

******** RESIDUALS ********
      1 -0.154729E-01
      2 -0.422842E-01
      3  0.111391E 00
      4  0.875895E-02
      5  0.110919E-01
      6 -0.976565E-01

*****END OF MA14A OUTPUT*****

SUM OF SQUARES OF RESIDUALS 0.24172E-01
NO. OF REJECTED POINTS 0

TWO-STEP KAISER COEFFICIENTS

D(1) = 0.52396E 00   D(2) = 0.88862E 00

RATIOS SPECIFIED
GROUP 1  INTERNAL STD CO      LINES S I   FE   MG
GROUP 2  INTERNAL STD GA      LINES B     PB   S N   AGW
GROUP 3  INTERNAL STD CO1     LINES MN    CR   N I   AL   MO   CUW
```

Fig. 3(*b*). Emulsion calibration information and list of requested ratios

Detection of errors in the data input

Although the method of data input has been designed to minimise, as far as possible, the occurrence of user errors, they can still occur. It is important that when they do they should be detected by the user's program and a message given stating clearly the nature of the error. If this precaution is not taken one of two things will happen; either the error will go undetected and the final intensity ratios will then contain hidden errors, or, less seriously, the computer supervisor program may detect the error and terminate the program. The latter situation is undesirable because the message given in these circumstances is not always easy to correlate with the user's data input error. The following tests are made on the data as they are read in: the order of the types of card is checked by means of the key words on each card; each microphotometer reading is tested to ensure that it is less than the clear plate reading and that the reading for a line is less than that for the corresponding background; the number of internal reference lines and the total number of line codes used are checked to make sure that they do not exceed 10 and 20, respectively; and, for the two-step method of calibration, the data are checked to ensure that they are in pairs of strong

and weak-step readings. Also, any numerical value that is written in a form not conforming with FORTRAN IV rules generates a message clearly indicating the error and the point at which it has occurred.

RESULTS

The printed output from the program for which the data in Fig. 1 were the input is shown in Fig. 3 (*a*), (*b*) and (*c*). The input data are printed for recording and checking purposes. Also printed are the coefficients of the emulsion calibration function, the sum of squares of the residuals and the standard error (σ), all obtained from the data-fitting routine. If, during the data fitting, any points are found to lie outside the 3σ range they are rejected and a second fitting is carried out. The intensity ratios are printed in an easily comprehended tabular form.

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INTENSITY RATIOS

SPECTRUM NUMBER

	1.1	1.2	1.3	1.4
SI	0.222	0.199	0.207	–
FE	1.112	0.692	1.095	–
MG	1.899	1.193	1.831	–
B	0.071	0.042	0.051	–
PB	0.608	1.102	0.841	–
SN	0.036	0.042	0.035	–
AGW	0.124	0.332	0.301	–
MN	0.331	0.224	0.372	–
CR	0.293	0.128	0.246	–
NI	0.210	0.144	0.244	–
AL	0.198	0.062	0.141	–
MØ	0.078	0.171	0.171	–
CUW	0.184	0.497	0.512	–

	2.1	2.2	2.3	2.4
SI	0.522	0.699	0.496	0.351
FE	0.829	1.201	0.641	0.065
MG	1.569	2.326	1.348	1.885
B	0.069	0.059	0.076	2.420
PB	0.816	0.714	0.827	0.604
SN	0.032	0.025	0.031	1.209
AGW	0.219	0.178	0.214	2.667
MN	–	–	–	0.954
CR	0.082	0.126	0.064	0.090
NI	0.204	0.234	0.136	0.199
AL	0.141	0.239	0.118	0.375
MØ	0.281	0.307	0.218	0.589
CUW	0.393	0.354	0.257	1.317

	3.1	3.2	3.3	3.4
SI	0.536	1.113	2.289	0.048
FE	0.117	0.161	0.511	0.083
MG	4.187	9.089	19.107	0.153
B	5.390	10.054	17.773	0.083
PB	1.494	4.123	10.602	0.038
SN	2.753	5.351	11.316	–
AGW	3.702	6.545	11.999	0.102
MN	1.853	3.988	5.788	–
CR	0.169	0.283	0.787	–
NI	0.677	0.661	1.722	0.029
AL	0.584	0.796	1.318	0.064
MØ	1.007	2.291	5.258	–
CUW	2.875	6.201	8.525	0.514

Fig. 3(*c*). Intensity ratios

CONCLUSIONS

The computer method of calculation has been used in the emission spectrography laboratory of the Actinide Analysis Group, A.E.R.E., for about 3 years and has been found versatile enough to deal with the wide variety of analyses encountered in this work. Also available in this laboratory is an alternative method of computation in the form of a RESPEKTRA calculating board.[3] Comparison of these two methods has led to the following observations.

Convenience—The computer technique has been proved to be simple to use by personnel not particularly familiar with computer programming, and failure of the computation caused by a user's error is very rare. The ease with which the required ratios are specified encourages the use of more internal reference lines than might otherwise be practical. By contrast the RESPEKTRA board is not found easy to use by untrained staff.

Reliability—For a period of several months after the introduction of the computer method, all data were evaluated by both methods. In general the agreement was good, and where significant differences did occur, the cause was traced in all cases to user errors on the RESPEKTRA board. Provided the input data have been correctly introduced the computer method has so far proved to be completely reliable.

Speed—Using a keyboard method for input and output of data, the turn-round period between the time the input data enter the computer and the time the results arrive back at the keyboard is about 10 to 20 minutes, depending on the length of the job queue. For all normal applications this time is independent of the amount of calculation to be done and therefore the gain over the RESPEKTRA board increases with the complexity of the calculation. If, for example, the total number of ratios required was fifteen the RESPEKTRA method might be quicker, but it should be appreciated that during the period results are being awaited from the computer the spectrographer is free to carry out other tasks. One disadvantage of the computer compared with the RESPEKTRA board method is that, owing to machine "down-time," the former cannot be relied on to be available at all times. Mostly, however, convenience and reliability of the calculations are more important than speed.

These comparisons pertain to the computer and RESPEKTRA board methods of calculation. If a RESPEKTRA board is not available and manual computation is the only alternative, the computer method becomes even more attractive.

Copies of the source listings of the program can be obtained on application to the authors.

Appendix

THE EMULSION CALIBRATION FUNCTION

The emulsion calibration function relates the transmittance (T) of the photographic image of a line to the spectral line intensity (I). As the exact form of this function is not known, an approximation has to be made which predicts as closely as possible the observed relationship between I and T. The approximation used in our calculation is

$$\log I = \frac{1}{\gamma} P + \log \mathrm{I}_0$$

$$\text{or } \log I_\mathrm{R} = \frac{1}{\gamma} P \qquad (1)$$

where γ and I_0 are constants and I_R is a relative intensity defined such that $I_\mathrm{R} = 1$ when $P = 0$.

P is the Baker - Sampson - Seidel transformation[4]

$$P = \kappa \log (1 - T) - \log T \qquad (2)$$

where κ is the transformation constant.

Combining (1) and (2)

$$\log I_\mathrm{R} = \frac{\kappa}{\gamma} \log (1 - T) - \frac{1}{\gamma} \log T \qquad (3)$$

In the two-step method of calibration the data are in the form of pairs of transmittances for the strong (s) and weak (w) steps, and the transmission ratio of the calibrating device (τ) is known.

$$\tau = \frac{I_\mathrm{s}}{I_\mathrm{w}}$$

Taking logarithms and substituting from (3)

$$\log \tau = \frac{\kappa}{\gamma} \log \left(\frac{1 - T_s}{1 - T_w} \right) + \frac{1}{\gamma} \log \left(\frac{T_w}{T_s} \right) \quad .. \quad .. \quad .. \quad (4)$$

Substitution of the strong and weak-step transmittances into equation (4) results in an over-determined set of linear equations in the constants $\frac{\kappa}{\gamma}$ and $\frac{1}{\gamma}$. The values of these constants, which minimise the sum of the squares of the residuals (S) are calculated by using a subroutine from the Harwell Subroutine Library.

$$S = \sum_{i=1}^{M} \left\{ \log \tau - \left[\frac{\kappa}{\gamma} \log \left(\frac{1 - T_{s,i}}{1 - T_{w,i}} \right) + \frac{1}{\gamma} \log \left(\frac{T_{w,i}}{T_{s,i}} \right) \right] \right\}^2 \quad .. \quad .. \quad (5)$$

where M is the number of pairs of readings.

For the seven-step method the readings are divided into pairs, 1 and 2, 2 and 3, 3 and 4, etc., and the same method of determining the constants can then be used.

In calculating the ratio of intensities, equation (3) is used to convert the transmittances to relative intensities.

References

1. Franke, H., Poste, K., and Schmotze, W., *Z. analyt. Chem.*, 1965, **212**, 269.
2. "Methods for Emission Spectrochemical Analysis," Fifth Edition, American Society for Testing Materials, Philadelphia, 1968.
3. Kaiser, H., *Spectrochim. Acta*, 1951, **4**, 351.
4. Margoshes, M., and Rasberry, S. D., *Ibid.*, 1969, **24B**, 497.

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The Determination of Alumina in Iron Ores, Slags and Refractory Materials by Atomic-absorption Spectroscopy

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As chemical methods of determining alumina are time-consuming, the simpler, more rapid atomic-absorption technique was adapted to iron ores, slags and refractory materials.

The basic technique comprises fusion of the sample with a sodium tetraborate - sodium carbonate mixture, extraction with dilute nitric acid, appropriate dilution and spraying under recommended conditions for aluminium. As the flux materials enhance the aluminium absorption, sample and corresponding calibration solutions should contain equivalent amounts.

Interference tests on synthetic solutions of the other constituents showed that the inhibiting effect of silica was suppressed by lanthanum chloride. A standard addition of lanthanum chloride was therefore incorporated and calibration conditions were developed to cover the ranges 0 to 1 per cent., 0 to 5 per cent., 0 to 10 per cent. and 10 to 35 per cent. of aluminium.

Applications to miscellaneous B.C.S. materials showed good agreement with accepted values and reproducibilities of $\pm 0{\cdot}035$ per cent., $\pm 0{\cdot}12$ per cent., $\pm 0{\cdot}18$ per cent. and $\pm 0{\cdot}38$ per cent. of aluminium, respectively, at the above levels.

SENSITIVITIES reported for aluminium are largely dependent upon the type of flame and apparatus used and range from nil with an air - acetylene mixture[1] to the 1 μg ml^{-1} obtained by Amos and Willis[2] when using the nitrous oxide - acetylene flame. Experiments with oxygen-enriched air - acetylene,[3] fuel-rich oxygen - acetylene[4,5] and other flames[6,7] have met with reasonable success, but the nitrous oxide - acetylene flame is now generally preferred for its superior sensitivity and comparative safety in operation. Most workers prefer the 309·3 nm line as it appears to provide the best signal-to-noise ratio.

Other factors governing sensitivity are the spectral intensity of the source, efficiency of the nebuliser coupled with burner design, and performance of the monochromator and amplification systems.[8]

Aluminium has been determined at concentrations of up to about 5 per cent. in a range of metallurgical materials[9] and more recent work has covered the range 3·3 to 6·4 per cent. in cements.[10]

The particular application described in the present paper arose from a considerable increase in the demand for analyses of refractory materials; prior to the adoption of the atomic-absorption technique, chemical determinations of alumina in our works' materials were made by the current B.S. procedure,[11] which is tedious and time-consuming.

Recently, more rapid new techniques published by the British Ceramic Research Association have also been used with success, but it was soon realised that the input of samples could be matched only by the use of a method based on an even faster principle such as atomic absorption.

The object of the present investigation, therefore, was to devise suitable procedures for determining alumina in home and foreign iron ores, iron and steel-making slags and various types of refractory materials over wide ranges of content. Performance in the higher ranges (about 20 to 60 per cent.) was of particular interest, and the results obtained compared favourably with those of the classical method. A considerable saving in time was also achieved.

Experimental

The instrument used was the Techtron Model AA-4 with the following conditions and settings—

Wavelength	309·3 nm	Setting	Gauge reading 18 p.s.i.
Lamp	High spectral output	Fuel	Acetylene, cylinder pressure 11 p.s.i.
Current	8 mA		
Slitwidth	100 μm	Flow reading	The observed reading for the optimum flame conditions was within the range 6 to 9
Spectral band width	0·33 nm		
Flame	Nitrous oxide - acetylene		
Burner	A.B. 50 with grooved titanium head*	Damping	D
		Scale expansion	Ranges 1, 2 and 3: ×5; range 4: none
Observation height	1 mm		
Support gas	Nitrous oxide, cylinder pressure 36 p.s.i.		

* This burner is of special design, which considerably reduces carbon build-up.

The stainless-steel nebuliser has a platinum - iridium capillary and a Teflon throat to reduce acid attack.

Matrix effect—

The borax - carbonate fusion followed by an acid extraction constitutes a rapid and effective means of achieving complete dissolution of the types of sample under consideration. but it was readily appreciated that the flux, consisting of alkali salts, would affect the absorption reading. At the high temperature (about 3000 °C) of the nitrous oxide - acetylene flame some ionisation of the aluminium will occur, thus reducing the number of atoms in the ground state. The addition of a readily ionisable alkali metal is known to counter this effect by raising the proportion of non-ionised atoms, thus producing an enhancement of the absorbance, and so an experiment was designed to study the matrix effect.

Solutions were prepared containing the various matrix constituents and 20 p.p.m. of aluminium. They were sprayed under the conditions given in the procedure. The recoveries are compared in the upper part of Table I.

Table I

The effect of flux constituents in various dilutions

In 50 ml of solution containing 20 p.p.m. of aluminium—

Constituents of test solution	Aluminium found,* p.p.m.
5 ml of nitric acid (sp.gr. 1·42)	20·09
plus 1·0 g of sodium carbonate	22·57
plus 0·5 g of sodium tetraborate	23·54
plus 1·0 g of sodium carbonate *plus* 0·5 g of sodium tetraborate	24·69

In 100 ml of solution containing 20 p.p.m. of aluminium—

	Constituents of test solution	Aluminium found,* p.p.m.	Blank, p.p.m. of aluminium
A.	10 ml of nitric acid (sp.gr. 1·42) *plus* 2·0 g of sodium carbonate *plus* 1·0 g of sodium tetraborate	25·22	1·58
B.	20 ml of A diluted to 100 ml	22·66	0·79
C.	10 ml of A diluted to 100 ml	21·67	0·59

The dilutions A, B and C are those recommended in the Procedure to give the three lowest ranges of aluminium content.

* The found aluminium contents are derived from a calibration graph prepared by using pure aqueous solution.

Further solutions containing different concentrations of sodium carbonate and borax, together with 20 p.p.m. of aluminium, were then prepared and sprayed. The amounts used corresponded with the dilutions used when calibrating for the three lowest ranges of aluminium content. The recoveries are compared in the lower part of Table I.

These tests showed that sodium carbonate and sodium tetraborate enhance the aluminium absorbance, the effect being greater when they are combined. Progressive dilution diminishes the effect. A slight increase due to nitric acid is also observed.[5]

Hence the calibration solutions should contain the same concentrations of these reagents as the corresponding sample solution.

EFFECTS OF OTHER MAJOR ELEMENTS—

It was appreciated that interference tests should preferably be made over the lowest range of aluminium content, *viz.*, 0 to 1·0 per cent., at which the concentration of salts would be at its highest. Additions of the other elements were therefore made to solutions having final concentrations of 10 per cent. v/v of nitric acid, 2 per cent. w/v of sodium carbonate, 1 per cent. w/v of sodium tetraborate and 20 p.p.m. of aluminium, and the solutions were sprayed. The recoveries are compared in Table II.

The results indicate an interference by silica, when it is present alone, which increases with concentration. This could be ascribed to the formation of aluminium silicate in the flame, thus reducing the number of aluminium atoms in the ground state and hence the absorption. This effect is counteracted by some elements when they are present, probably as a result of the preferential formation of other silicates, *e.g.*, of calcium.

TABLE II

INTER-ELEMENT INTERFERENCE

Range: 0 to 1·0 per cent. of aluminium

	Additions to the base solution,* per cent. w/w											
Silicon dioxide	12·0	8·0	30·0	30·0	—	—	—	—	100·0	—	—	—
Iron(III) oxide	15·0	20·0	10·0	—	—	—	—	—	—	90·0	—	—
Calcium oxide	50·0	40·0	40·0	—	50·0	—	—	—	—	—	—	—
Manganese(II) oxide ..	6·0	2·0	10·0	—	—	10·0	—	—	—	—	—	—
Magnesium oxide ..	5·0	10·0	5·0	—	—	—	10·0	—	—	—	—	—
Phosphorus pentoxide..	12·0	20·0	5·0	—	—	—	—	20·0	—	—	—	—
Chromium(III) oxide ..	—	—	—	—	—	—	—	—	—	—	50·0	—
Titanium(IV) oxide ..	—	—	—	—	—	—	—	—	—	—	—	2·0
Aluminium found,† p.p.m.	19·41	19·32	19·41	16·44	19·32	19·49	19·49	19·67	13·73	19·49	20·03	19·55

* The base solution contained 10 per cent. v/v of nitric acid (sp.gr. 1·42), 1 per cent. w/v of sodium tetraborate, 2 per cent. w/v of sodium carbonate and 20 p.p.m. of aluminium.

† The found aluminium contents are derived from a calibration graph prepared by using the base solution.

When signal suppression occurs, a spectroscopic buffer is usually employed as a "releasing agent" to increase the ground-state atom population of the element concerned. Further tests were therefore devised, as in Table III, to test the effect of adding lanthanum chloride solution to synthetic solutions of high silica content, which showed various degrees of suppression, depending on the nature and amount of boric oxide present. The recoveries of aluminium recorded on spraying with and without 2 ml of lanthanum chloride solution (≡ 0·2 g of lanthanum) indicated, in every instance apart from 100 per cent. of silica, the elimination of interference and a considerable improvement in the consistency of absorption.

Regarding the matrix effect, the use of nitric acid in conjunction with the lanthanum solution resulted in an aluminium recovery of 20·61 p.p.m.; the inclusion of sodium carbonate increased this value to 25·21 p.p.m., *i.e.*, a little above the previous representative value for the flux contents reported in Table I.

The lanthanum chloride addition was therefore incorporated in the method as described below, the calibration solutions being made up to contain the appropriate concentrations of lanthanum chloride and the flux reagents.

TABLE III

SUPPRESSION OF INTER-ELEMENT INTERFERENCES BY THE ADDITION OF LANTHANUM CHLORIDE

Range: 0 to 1·0 per cent. of aluminium

Additions to the base solution* with and without lanthanum chloride	Aluminium found,† p.p.m.	
	Without lanthanum	With 0·2 g of lanthanum
100 per cent. of silicon dioxide	13·53	19·64
40 per cent. of silicon dioxide	18·04	20·41
40 per cent. of silicon dioxide *plus* 20 per cent. of iron(III) oxide ..	17·25	20·41
40 per cent. of silicon dioxide *plus* 4 per cent. of calcium oxide ..	17·61	20·41
40 per cent. of silicon dioxide *plus* 40 per cent. of calcium oxide ..	19·06	20·21
40 per cent. of silicon dioxide *plus* 10 per cent. of manganese(II) oxide	17·90	20·79
40 per cent. of silicon dioxide *plus* 10 per cent. of magnesium oxide ..	19·04	20·41
40 per cent. of silicon dioxide *plus* 10 per cent. of phosphorus pentoxide	16·00	20·41

* The base solution contained 10 per cent. v/v of nitric acid, 1 per cent. of sodium tetraborate, 2 per cent. w/v of sodium carbonate and 20 p.p.m. of aluminium.

† The found aluminium contents are derived from a calibration graph prepared from the base solution with and without added lanthanum.

METHOD

APPLICATION—

The method is suitable for home and foreign ore, blast-furnace and basic open-hearth slags, magnesite, silica brick, chrome ore, fire-brick and sillimanite.

RANGE AND REPRODUCIBILITIES—

	Aluminium per cent.	
	Range	Reproducibility
1.	0 to 1·0	±0·035
2.	0 to 5·0	±0·12
3.	0 to 10·0	±0·18
4.	10·0 to 35·0	±0·38

INSTRUMENT CONDITIONS—

As under "Experimental."

NOTE—

In general the optimum burner height is found by raising the burner until it just begins to obstruct the light path. This position is indicated by a left deflection of the meter needle. The burner is then lowered by 1 mm.

The optimum flame setting is found by starting with a fuel-rich flame and slowly reducing the acetylene flow until the white luminosity just disappears, leaving a red "feather" approximately 15 mm in height.

REAGENTS—

Sodium carbonate, anhydrous—AnalaR grade.

Sodium tetraborate, fused—AnalaR grade.

Nitric acid, 20 per cent. v/v, pure.

Hydrogen peroxide—100-volume concentration, AnalaR grade.

Lanthanum solution—Dissolve 26·7 g of analytical-reagent grade lanthanum chloride in water and dilute to 100 ml.

1 ml of solution ≡ 0·1 g of lanthanum.

Standard aluminium solution—

(*a*) *For the lower ranges*—Dissolve 0·8792 g of potassium aluminium sulphate in water and dilute to 500 ml.

1 ml of solution ≡ 100 μg of aluminium.

(*b*) *For the highest range*—Dissolve 1 g of pure metal in 20 ml of hydrochloric acid (sp.gr. 1·18) and cautiously evaporate to dryness. Add a further 10 ml of nitric acid (sp.gr. 1·42) and again cautiously evaporate to dryness. Add 10 ml of nitric acid (sp.gr. 1·42), digest until dissolution is complete, cool and dilute to 1 litre.

1 ml of solution ≡ 1000 μg of aluminium.

Store solutions in polythene containers when appropriate.

PREPARATION OF CALIBRATION SOLUTIONS—

1. *Range* 0 *to* 1 *per cent. of aluminium*—To each of six 150-ml conical beakers transfer 2 g of sodium carbonate and 1 g of sodium tetraborate and add 50 ml of 20 per cent. v/v nitric acid. Heat to dissolve solids and expel carbon dioxide. Cool and add 2 ml of lanthanum solution. Add 0, 4, 8, 12, 16 and 20 ml of standard aluminium solution (*a*) (≡ 0, 0·2, 0·4, 0·6, 0·8 and 1·0 per cent. of aluminium) and dilute to 100 ml in calibrated flasks. Store in polythene containers.

2, 3 *and* 4. *Ranges* 0 *to* 5, 0 *to* 10 *and* 10 *to* 35 *per cent. of aluminium*—Dissolve 5 g of sodium carbonate and 2·5 g of sodium tetraborate in 125 ml of 20 per cent. v/v nitric acid and heat to expel the carbon dioxide. Cool, add 5·0 ml of lanthanum solution and dilute to 250 ml for the base solution.

(2) *Range* 0 *to* 0·5 *per cent. of aluminium*—To 20-ml fractions of the base solution add 0, 4, 8, 12, 16 and 20 ml of aluminium solution (*a*) (≡ 0, 1, 2, 3, 4 and 5 per cent. of aluminium) and dilute to 100 ml in calibrated flasks. Store in polythene containers.

(3) *Range* 0 *to* 10 *per cent. of aluminium*—To 10-ml fractions of the base solution add 0, 4, 8, 12, 16 and 20 ml of aluminium solution (*a*) (≡ 0, 2, 4, 6, 8 and 10 per cent. of aluminium) and dilute to 100 ml in calibrated flasks. Store in polythene containers.

(4) *Range* 10 *to* 35 *per cent. of aluminium*—To 20-ml fractions of the base solution add 4, 6, 8, 10, 12 and 14 ml of aluminium solution (*b*) (≡ 10, 15, 20, 25, 30 and 35 per cent. of aluminium) and dilute to 100 ml in calibrated flasks. Store in polythene containers.

PREPARATION OF SAMPLE SOLUTION—

Mix 0·2 g of sample with 2 g of sodium carbonate and 1 g of sodium tetraborate in a small platinum capsule. Melt over a Meker burner and, when dissolution is apparent, raise to full heat (900 to 1000 °C) and maintain this temperature for about one minute (Note 1).

Cool, place the capsule in a 150-ml tall-form beaker containing 50 ml of 20 per cent. v/v nitric acid warmed to a temperature not exceeding 80 °C, add two or three drops of hydrogen peroxide (100-volume) and swirl to effect dissolution.

Cool, transfer to a 100-ml calibrated flask, add 2 ml of lanthanum solution and dilute to the calibration mark with water.

This solution serves for the range 0 to 1 per cent. of aluminium (Note 2). For the higher ranges, dilute as follows—

Range	Dilution
0 – 5 per cent. of aluminium	20 ml to 100 ml
0 – 10 per cent. of aluminium	10 ml to 100 ml
10 – 35 per cent. of aluminium	20 ml to 100 ml

NOTES—

1. Some refractory materials may require an additional period of 5 to 10 minutes in a muffle furnace maintained at 1100 °C.

2. For samples containing up to 40 per cent. of silica complete dissolution should be achieved. With silica bricks some silica hydrolyses out of solution so, after dilution to 100 ml, the solution is filtered through a Whatman No. 41 paper preparatory to spraying.

DETERMINATION OF ALUMINIUM—

Set the instrument according to the table of instrument conditions.

Lower ranges—Spray the appropriate calibration solutions, followed by the sample solutions. Repeat this procedure. Spray water between each test and set to 100 per cent. transmission.

Plot absorption (per cent.) against element concentration, draw a calibration graph and read off the percentage of aluminium.

Percentage of aluminium × 1·8895 = alumina, per cent.

NOTE—

For greater accuracy the system used under "High range" can be used.

High range—Spray the sample solution and select two calibration solutions containing concentrations of aluminium immediately above and below those present in the sample.

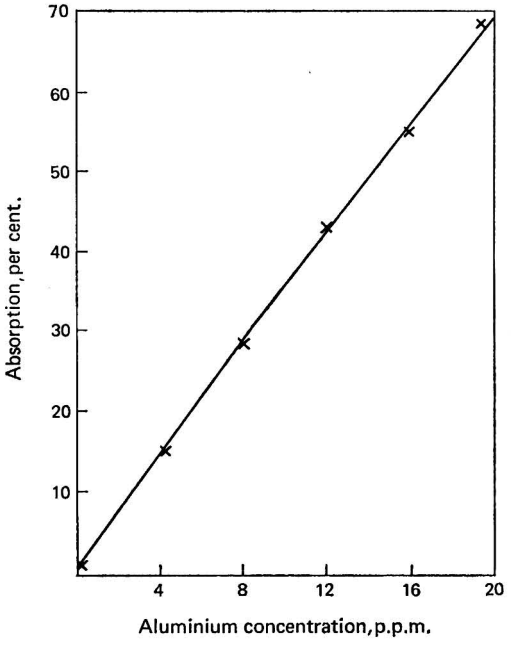

Fig. 1. Aluminium calibration curve

Then spray the sample and calibration solutions several times, spraying water between tests and setting to 100 per cent. transmission.

From the mean absorbance readings calculate the percentage of aluminium in the sample in relation to each calibration solution. Convert the results into percentage of alumina.

ACCURACY AND REPRODUCIBILITY TRIALS—

The above procedure was then applied to a series of British Chemical Standards including home and foreign ore, blast-furnace and basic open-hearth slag, magnesite, silica brick, chrome ore, firebrick and sillimanite.

TABLE IV

ALUMINA IN IRON ORES, SLAGS AND REFRACTORY MATERIALS: ACCURACIES AND REPRODUCIBILITIES (LOWER RANGES PROCEDURE)

B.C.S. No.	302	301	367	175/1	174/2	319	314
Type of material	Northants iron ore	Lincs iron ore	Blast-furnace slag	Liberian iron ore	Basic slag	Mag-nesite	Silica brick
Alumina, per cent., certificate value	7·24	4·26	20·0	1·10	0·77	1·00	0·77
Alumina, per cent., by atomic-absorption spectroscopy	7·07	4·19	20·18	1·12	0·78	1·01	0·79
	7·26	4·07	20·00	1·08	0·72	0·96	0·74
	7·22	4·22	20·27	1·08	0·71	0·93	0·72
	7·26	4·15	20·00	1·09	0·68	0·91	0·75
	7·07	4·19	20·18	1·11	0·72	0·97	0·79
	7·30	4·19	20·37	1·06	0·71	0·92	0·75
	7·36	4·15	20·18	1·11	0·69	0·98	0·79
	7·34	4·24	19·80	1·08	0·73	1·00	0·77
	7·37	4·34	20·09	1·09	0·71	0·97	0·75
	7·17	4·02	20·00	1·06	0·70	0·93	0·77
Mean	7·24	4·18	20·11	1·09	0·72	0·96	0·76
Reproducibility (95 per cent.) $\pm$ 2 s	0·22	0·18	0·33	0·04	0·05	0·07	0·05

For the blast-furnace slag a further calibration point was prepared containing the equivalent of 12 per cent. of aluminium, although the range 0 to 10 per cent. of aluminium will cover modern blast-furnace practice.

A typical calibration graph is shown in Fig. 1.

Determinations on each sample were carried out on ten separate occasions. The results shown in Tables IV and V were obtained.

Comparison of the certificate values with the corresponding mean values found by atomic-absorption spectroscopy shows an acceptable degree of accuracy for the method, whilst the reproducibilities compare favourably with those of existing chemical procedures.

Six determinations can be completed in less than three hours, compared with about three days by the standard hydroxyquinoline chemical procedure.

Table V

Alumina in iron ores, slags and refractory materials: accuracies and reproducibilities (high range procedure)

B.C.S. No. Type of material	269 Firebrick	309 Sillimanite	308 Chrome ore
Alumina, per cent., certificate value	33·9	61·1	19·4
Alumina, per cent., by atomic-absorption spectroscopy	33·35	61·1	19·7
	32·85	61·3	19·3
	33·7	61·05	19·55
	33·95	61·45	19·8
	33·75	61·75	19·65
	33·65	61·15	19·5
	34·0	61·0	19·4
	33·55	61·6	19·6
	33·3	61·6	19·7
	33·95	61·6	19·6
Mean	33·61	61·36	19·58
Reproducibility (95 per cent.) $\pm$ 2 s	0·72	0·55	0·30

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References

1. Gilbert, P. T., *Analyt. Chem.*, 1962, **34**, 210R.
2. Willis, J. B., *Nature*, 1965, **207**, 715.
3. Amos, M. D., and Thomas, P. E., *Analytica Chim. Acta*, 1965, **32**, 139.
4. Slavin, W., and Manning, D. C., *Analyt. Chem.*, 1963, **35**, 253.
5. Elwell, W. T., and Gidley, J. A. F., "Atomic Absorption Spectrophotometry," Second Edition, Pergamon Press, Oxford, London, Edinburgh, New York, Toronto, Sydney, Paris and Braunschweig, 1966, p. 76.
6. Chakrabarti, C. L., Lyles, G. R., and Dowling, F. B., *Analytica Chim. Acta*, 1963, **29**, 489.
7. ——, ——, ——, *Ibid.*, 1963, **28**, 392.
8. Slavin, W., "Atomic Absorption Spectroscopy," Interscience Publishers, New York, 1968.
9. Nikolaev, G. I., and Aleskovskh, V. B., *Zh. Analit. Khim.*, 1963, **18**, 816.
10. Capacho Delgado, L., and Manning, D. C., *Analyst*, 1967, **92**, 553.
11. B.S. 1121 : Part 43, British Standards Institution, London, 1963.

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The Atomic-fluorescence Determination of Mercury by the Cold Vapour Technique

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A method for the determination of low levels of mercury by using atomic fluorescence in conjunction with the cold vapour technique is described, and shows significant advantages over the corresponding absorption technique.

The determination of mercury in solution by using atomic absorption in conjunction with the cold vapour technique has been reported by many workers[1–6]; Manning[7] has published a review on the subject. The methods utilise the fact that mercury is the only element (other than the inert gases) that has an appreciable vapour pressure at room temperature, and whose vapour is practically wholly monatomic. Mercury also has a very low affinity for oxygen, and therefore a relatively high concentration of mercury atomic vapour can be maintained in air at room temperature. Because of its relatively high vapour pressure, no thermal energy from a flame (or other source) is required for the vaporisation and atomisation of elemental mercury. At 20 °C, 1 litre of air saturated with mercury contains 14 μg of mercury.

Most methods generate mercury vapour by first reducing it to the elemental state, *e.g.*, with tin(II) chloride or sulphate, and then blowing air through the solution to expel the mercury. The stream of air is passed through a cell and the absorption of the 253·7-nm mercury resonance line emitted by a low pressure mercury lamp is monitored. To improve the sensitivity, various methods are used to concentrate the vapour. In one method, air is continuously circulated in a closed system until all of the mercury is liberated before an absorption reading is taken.[4,6] This procedure can be time consuming, and also requires the use of a drying column to remove traces of water vapour, which can cause slight spurious broad band absorption at 253·7 nm. Traces of organic vapours can also cause broad band absorption. The use of automatic background correction by measuring the broad band absorption with a hydrogen lamp at 253·7 nm can overcome these problems[6] as long as the broad band absorption at 253·7 nm is not too great.

Other methods liberate the mercury by using the same principle, but the mercury is then absorbed on a suitable substance such as iodised charcoal[8] or silver.[9] The absorbing substance is heated and the mercury evolved is carried into a suitable absorption cell and the absorption at 253·7 nm is monitored. This method is time consuming and errors can be caused by organic contaminants being absorbed by the absorbent and subsequently driven off, causing broad band absorption at 253·7 nm.

The fluorescence technique shows distinct advantages over the absorption technique in that it is simple, there is no enclosed cell (hence no fogging of the cell windows), no spurious signal from broad band absorption by organic contaminants, no re-circulation system or drying column required, the sensitivity is high, and the calibration graph is linear over a wide concentration range.

Experimental

A Southern Analytical A3000 atomic-absorption - emission spectrophotometer with the burner and lenses removed is used. A low-pressure OZ4W Philips mercury lamp is mounted in a suitable housing in the fluorescence position, so as to minimise specular reflection from components mounted near the monochromator. It is essential that the specular reflection is minimised. The light from the mercury lamp is directed over the top of a 10-mm i.d. Pyrex tube, which is connected to a mercury generation system. The apparatus is shown in Fig. 1. Mercury is liberated in cell A, and air or argon is bubbled through this cell and through expansion chamber B. This tends to smooth out the flow and also prevents any accidental carry-over of corrosive solutions caused by sudden excessive gas flows into the

instrument compartment. The optimum size of the expansion chamber was found to be approximately 200 ml. The mercury passes up through tube C and fluoresces in region D. It is not necessary to use a drying column. The fluorescence signal is displayed on a Bryans Series 27 000 recorder. The measurement procedure was as follows. The reducing agent [tin(II) chloride, hydrochloric acid and sulphuric acid] was added to cell A and argon was bubbled through this solution until a stable base-line on the recorder was obtained. The mercury solution, containing between 0·01 and 2 μg of mercury, was then added and the fluorescence signal monitored on the recorder.

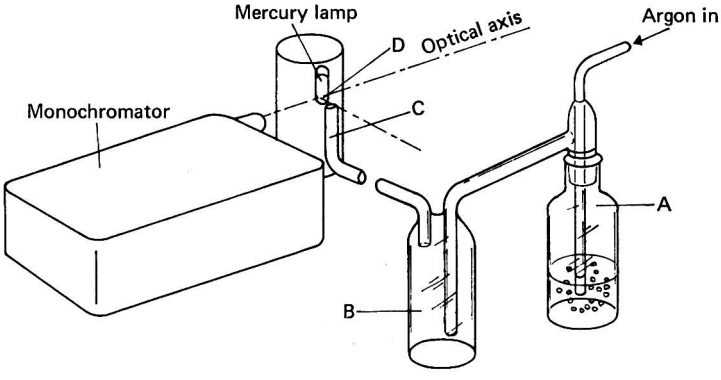

Fig. 1. Schematic diagram of mercury fluorescence detector

OPTIMISATION OF OPERATING PARAMETERS—

Damping—The A3000 was operated at maximum damping (the time constant was 5 seconds). This usually gave well defined peaks, but occasionally sharp spikes were observed above the smooth trace. The recorder was further damped by using an *RC* network attached to the recorder terminals ($R = 12$ kΩ, $C = 400$ μF, time constant = 4·8 seconds). With the extra damping, reproducible peaks as shown in Fig. 2 were obtained.

The recorder output of the A3000 was set to 0 to 25 mV full-scale deflection and the recorder to 0 to 10 mV full-scale deflection.

Choice of gas—For similar amounts of mercury, the peak height with argon was approximately four times greater than that with nitrogen and thirty-five times greater than that

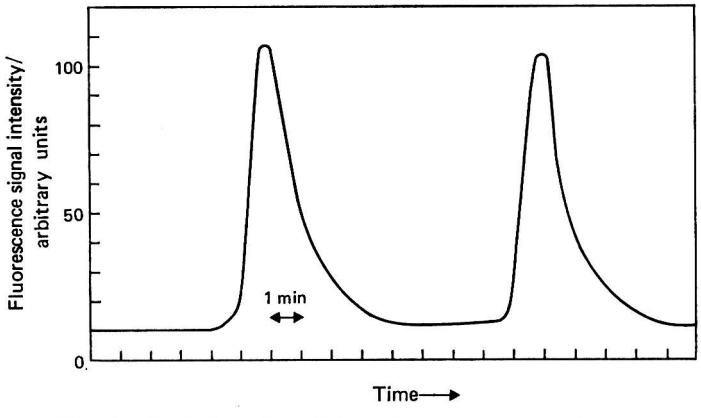

Fig. 2. Typical peaks obtained for mercury by using spectral band pass, 6 nm; 0·06 μg (1 ml containing 0·06 p.p.m.) of mercury added to cell A; and argon at a flow-rate of 1·4 l min^{-1}

with air. This is obviously caused by the quenching of excited mercury atoms in the $^3P_1$ state by nitrogen and oxygen molecules. Oxygen is a far more efficient quenching agent than nitrogen because the excited mercury atoms and the ground-state oxygen molecules are both in the triplet state, thus facilitating energy transfer. The optimum flow-rate was 1·4 l min^{-1} for air, nitrogen and argon. The fluorescence signal was not very dependent on the gas flow-rate. At low flow-rates a spiky trace was obtained and at high flow-rates a decrease in peak height was observed. Argon was used in all further measurements unless otherwise stated.

Choice of gas bubbling arrangement—To increase the rate of uptake of the mercury from the solution, a glass sinter was sealed across the end of the gas inlet to cell A (Fig. 1). This should have increased the solution - gas interface area appreciably. However, an increase in the blank value, caused by fine droplets of solution being carried through the system and causing specular reflection, was observed. On adding a known amount of mercury, the glass sinter increased the signal by 5 per cent. This showed that an efficient uptake of mercury occurred without the sinter, and that all the sinter did was to saturate the gas with water vapour and also cause a fine mist of droplets to be carried up to region D. The sinter was not used in further studies. Throughout this work, no condensation was observed in expansion chamber B, which indicated that when the sinter was removed the gas was not saturated with water vapour.

The diameter of tube C was fairly critical, the optimum internal diameter being 1 cm. When this tube was sheathed with argon, only a very slight increase in signal was observed, which indicated that little mixing with air occurred in region D. The sheath was not used in further measurements.

Lamp current—The optimum lamp current was found to be 0·32 A.

Reagents for mercury generation—Various systems have been reported in the literature. In this study the following reagents were used. Solution 1 was a 10 per cent. w/v solution of tin(II) chloride in 5 N hydrochloric acid, and solution 2 was a mixture of 2 N nitric acid and 10 N sulphuric acid.

The mercury solutions were freshly made before use from a stock solution containing 1000 p.p.m. of mercury that was prepared by dissolving 1 g of mercury in 50 ml of nitric acid and diluting it to 1 litre with distilled water. All reagents were of analytical grade.

Results

For mercury concentrations between 0·01 and 2 p.p.m., 10 ml of solution 1, 20 ml of solution 2 and 20 ml of distilled water were added to cell A and argon was bubbled through until a stable base-line was obtained. This procedure ensured that any traces of mercury, either in solutions 1 and 2 or accidentally transferred to cell A, would be removed from the system. This effective elimination of the blank from the reagents was important when working at maximum sensitivity.

Between 0·1 and 1 ml of the mercury solution was added to cell A, the peak recorded (Fig. 2), and the peak height measured. The recorder returned to the base-line within 5 minutes of adding the sample and the next sample could then be added directly to the contents of cell A. This procedure could be repeated until the total volume reached 60 ml. [The use of argon prevents the oxidation of tin(II) salts in cell A by atmospheric oxygen.]

For mercury concentrations below 0·01 p.p.m. the same procedure was followed except that between 5 and 10 ml of the sample were added to cell A and the solution in the cell was discarded after only one or two measurements, *i.e.*, when the total volume reached 60 ml.

For the determination of mercury in urine samples, the use of potassium permanganate to break down any protein mercury present would be necessary.[5,7] In the limited time available these procedures could not be tested. However, standard additions of mercury(II) were made to acidified urine samples (5 ml of urine and 1 ml of nitric acid), which were then added to cell A. To prevent foaming, a trace of silicone anti-foaming agent was added to the cell. The response was linear with respect to the amount of mercury added, and as little as 0·003 μg of mercury could be detected in a 5-ml sample of urine.

The calibration graphs for mercury in air, nitrogen and argon are shown in Fig. 3.

Effect of organic solvents—

The presence of 2 per cent. v/v of acetone in cell A (which, in an original 1-ml sample added to the 50 ml in cell A, would represent 100 per cent. of acetone in the original sample)

did not affect the base-line, and with a 0·3-μg sample of mercury (1 ml $\equiv$ 0·3 p.p.m. of mercury) gave a 33 per cent. reduction in peak height when argon was used. With 5 per cent. of acetone in cell A, the base-line was not affected, but the peak height for a 0·3-μg sample of mercury was reduced by 60 per cent. This decrease was thought to be caused by the quenching of excited mercury atoms by acetone molecules. When air was used instead of argon, no change in the base-line was observed until 5 per cent. of acetone was present in the cell. A 2-μg sample of mercury (1 ml $\equiv$ 2 p.p.m. of mercury) and 2 per cent. of acetone in cell A did not affect the peak height, while the presence of 5 per cent. of acetone in cell A gave only an 8 per cent. decrease in peak height. It would appear that the quenching effect of nitrogen and oxygen molecules had minimised any additional quenching from the low concentration of acetone vapour in the gas.

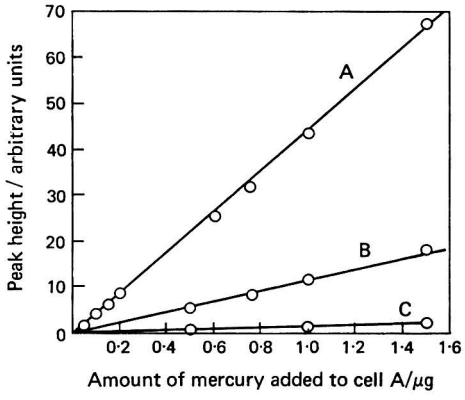

Fig. 3. Mercury calibration graphs at a spectral band-pass of 6 nm and a gas flow-rate of 1·4 l min^{-1} for: A, argon; B, nitrogen; and C, air

The presence of 2 per cent. of ethanol, chloroform or benzene in cell A did not affect the base-line when argon or air was used. However, when argon was used, the signal for 1 μg of mercury was reduced by 25, 22 and 93 per cent., respectively, and when air was used, the corresponding figures were <5, <5 and 60 per cent. The large decrease with benzene and air is thought to be caused by relatively strong absorption of the 253·7-nm radiation over the small path lengths of region D (Fig. 1). Although the presence of organic solvents gave a negligible change in the base-line, the absolute signal magnitudes were decreased appreciably when argon was used. It appears that air would be the better choice of carrier gas when organic solvents are known to be present, although this would reduce the sensitivity considerably (Fig. 3). Alternatively, the method of standard additions could be used with argon.

An absorption system similar to that of Hatch and Ott[4] was constructed. A cell with a 12-cm path length was used in conjunction with a re-circulating pump. The mercury generation system was similar to that shown in Fig. 1. A 1-μg sample of mercury gave an absorbance of 0·27. The presence of 2 per cent. of acetone in cell A (no mercury present) corresponded to 0·5 μg of mercury, while 2 per cent. of benzene (again with no mercury present) gave complete absorption of the radiation at 253·7 nm.

PRECISION—

A mixture of 10 ml of solution 1, 20 ml of solution 2 and 20 ml of distilled water was placed in cell A and argon bubbled through it until a stable base-line was obtained. Then 1 ml of a 0·06-p.p.m. mercury solution (containing 0·06 μg of mercury) was added to the cell, the peak recorded and, when the recorder had returned to the base-line, another 1ml of the solution containing 0·06 p.p.m. of mercury was added and the peak recorded. This was repeated until ten readings (spread over a period of 90 minutes) had been obtained. The relative standard deviation calculated from the peak height was 5 per cent.

SENSITIVITY—

The noise on the base-line gave a 3σ detection limit of 0·002 μg of mercury. The steady blank signal (caused mainly by specular reflection) corresponded to a peak fluorescence signal of 0·004 μg of mercury. It was essential to position the source so that this specular reflection signal was minimised. The peak height on adding 1 ml of distilled water to cell A corresponded to less than 0·0005 μg of mercury. The sensitivity with the A3300 atomic-absorption - fluorescence - emission spectrophotometer, which has improved amplification characteristics, was a factor of 2·5 times better.

It is difficult to compare the sensitivity of the fluorescence technique with that of the absorption technique because the sensitivity of the former is directly dependent on the source intensity and on the detector sensitivity.

Hatch and Ott[4] used a re-circulation system to obtain a steady absorbance reading of 0·29 for 1·1 μg of mercury. Lindstedt,[5] who used a straight-through system with small volumes, obtained a limit of detection of 0·002 μg of mercury in a 1-ml sample.

The present system yielded a 3σ detection limit of 0·002 μg of mercury.

CONCLUSIONS

The determination of mercury in solution by using atomic fluorescence in conjunction with the cold vapour technique is a simple, sensitive and specific method for determining low levels of mercury.

The main advantages over the corresponding absorption technique are: its simplicity, as no re-circulation system or drying column is required; the fluorescence is not viewed from an enclosed cell so that the cell window cannot fog and the memory effect is minimised; and background correction facilities to compensate for broad band absorption are not required. Broad band (molecular) absorption will be recorded as mercury in the absorption technique unless background correction facilities are used. In the fluorescence technique, any broad band absorption (which should be small because of the low path lengths used) will not be recorded as mercury. Even more important, molecular fluorescence at the 253·7-nm exciting wavelength is unlikely to occur with most common volatile organic compounds.

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REFERENCES

1. Ballard, A. E., and Thornton, C. W. D., *Ind. Engng Chem., Analyt. Edn*, 1941, **13**, 893.
2. Poluektov, N. S., and Vitkun, R. A., *Zh. Analit. Khim.*, 1963, **18**, 33.
3. Poluektov, N. S., Vitkun, R. A., and Zelyukova, Y. V., *Ibid.*, 1964, **19**, 873.
4. Hatch, W. R., and Ott, W. L., *Analyt. Chem.*, 1968, **40**, 2085.
5. Lindstedt, G., *Analyst*, 1970, **95**, 264.
6. Manning, D. C., *Atomic Absorption Newsletter*, 1970, **9**, 109.
7. ——, *Ibid.*, 1970, **9**, 97.
8. Moffitt, A. E., and Kupel, R. E., *Ibid.*, 1970, **9**, 113.
9. Kalb, G. W., *Ibid.*, 1970, **9**, 84.

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X-ray Spectrometric Determination of Rare Earth Elements by Using a Fusion Technique

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A general method for the determination of rare earth elements by X-ray fluorescence spectrometry is described. The sample is fused with sodium tetraborate, chromium is added to act as internal control-standard, and the resulting bead is analysed directly. This method overcomes variations in sample form and particle size. Individual rare earths can be determined at levels from 0·1 to 100 per cent., and by using the L spectra and a lithium fluoride 220 crystal, line overlap is kept to a minimum.

X-RAY fluorescence spectrometry has been used to determine rare earth elements in solution,[1,2,3] catalysts[4] and ores,[5] and traces of rare earths in high-purity oxides.[6] The purpose of this work was to develop a general method for the analysis of lanthanum, cerium, praseodymium, neodymium, samarium, europium and gadolinium in a wide range of materials including rare earth ores, alloys containing a high percentage of a rare earth, and mixed oxides. Analysis of alloy steels and nickel-base alloys containing rare earths was not attempted.

The use of a fusion technique reduces sample preparation to a minimum as solid samples can be fused directly. Various fluxes were tried, including sodium tetraborate, lithium tetraborate, lithium tetraborate - lithium carbonate in various proportions, and potassium pyrosulphate. Sodium tetraborate was found to be at least as satisfactory as other fluxes, and had the advantage of being readily available in a pre-fused form.

EXPERIMENTAL

APPARATUS—

A Philips 1220 semi-automatic spectrometer was used with the following conditions: the X-ray tube target was gold and the tube required 50 kV at a current of 40 mA; the crystal was a lithium fluoride 220 crystal; the collimator opening was 160 μm, the X-ray path was through a vacuum; the counter was flow-proportional with a counting time of 40 s; and automatic pulse height analysis was used.

It is possible to use either the K or L spectra of the rare earths for quantitative analysis. Even though the lithium fluoride 220 crystal gives reasonably good resolution of the K spectra, the resolution of the L spectra is much better. No advantage is gained by use of the K spectra from the point of view of intensity because it has been shown that, for those rare earths heavier than praseodymium, greater intensity is obtained from the L lines (under vacuum conditions).[7] Preliminary work showed that the use of an internal control-standard[8] was desirable; a suitable one for the rare earth L lines is the chromium Kα line.[1,2] This compensates satisfactorily for variations in the sample preparation technique by different operators, and serves for all the rare earth lines used (Table I).

TABLE I

ANALYTICAL LINES

Spectral line	Line °2θ	Background °2θ
Lanthanum Lα	138·70	137·60
Cerium Lα	128·11	127·00
Praseodymium Lβ	104·97	106·00
Neodymium Lβ	99·02	98·00
Samarium Lβ	89·10	90·00
Europium Lβ	84·78	83·90
Gadolinium Lβ	80·86	53·90
Chromium Kα	107·11	—

Some of the Lα lines were subject to line overlap but in most instances the intensity of the Lβ line was equal to, or greater than, the intensity of the Lα line. This is because of the greater absorption in the X-ray path and flow-counter window of the Lα compared with the Lβ line. It is therefore more marked if an air path is used.

The only serious line overlap occurs when holmium is present (the holmium Lα line is very near to the gadolinium Lβ line) so that a correction must be made for holmium.

Procedure—

Mix thoroughly 1·0 g of sample, 0·10 g of chromium(III) oxide (Cr_2O_3) and 15 g of sodium tetraborate and place them in a 95 per cent. platinum - 5 per cent. gold crucible. Particular care must be taken to weigh the chromium(III) oxide accurately. The crucible is heated at 1100 °C in a muffle furnace for 30 minutes, with swirling at 5-minute intervals. The mixture is then poured into a graphite mould at about 400 °C on a hot-plate and covered with a graphite lid. The mould is allowed to cool slowly to room temperature (for about 1 hour), and its contents are then analysed directly on the spectrometer by using the settings mentioned above.

Standards are made up by mixing individual rare earth oxides in various proportions. The mixes are dissolved in hydrochloric acid, precipitated as oxalates and ignited at 1000 °C for 1 hour. They are immediately weighed (because they pick up moisture and carbon dioxide very rapidly) and fused as for a sample.

Results and discussion

Table II shows the comparison between the total rare earth analysis obtained by summing the results for the individual rare earths and that obtained by chemical analysis of some typical samples.

Table II

Comparison of X-ray fluorescence and chemical results

Sample	Total rare earth oxides, per cent.	
	By X-ray fluorescence	By chemical method
Rare earth - iron silicide 1	30·8	31·0
Rare earth - iron silicide 2	39·1	39·8
Rare earth - calcium silicate slag 1	25·6	24·8
Rare earth - calcium silicate slag 2	31·7	31·7
Ore concentrate	70·6	70·9
Mixed oxides	98·9	99·8

The standard deviation was calculated from 126 separate determinations, in which the concentrations ranged from 0·1 to 100 per cent., and was found to be 0·123. Thus the 99·7 per cent. probability (3σ) is $\pm 0{\cdot}369$.

The main factor causing errors in the repeatability of the results is the sample preparation. No significant difference was found between the determinations of the separate elements. On analysing a number of routine samples, it was invariably found that any lack of agreement between duplicates resulted from an inhomogeneous melt.

Limit of detection—

This was taken as the concentration yielding a line intensity that exceeds the background by three standard deviations.[9] Calculated on this basis, the detection limit was found to be about 0·02 per cent., although for lanthanum and cerium it was about 0·01 per cent.

The author thanks the London and Scandinavian Metallurgical Co. Ltd., Rotherham, in whose laboratories this work was carried out.

References

1. Rekholainen, G. I., and Ivanova, L. I., *Zav. Lab.*, **1968**, **34**, 172.
2. Rekholainen, G. I., *Ibid.*, **1965**, **31**, 442.
3. Tertian, R., "Advances in X-ray Analysis," Volume **12**, Plenum Press, New York, **1969**.
4. Stone, I. C., and Rayburn, K. A., *Analyt. Chem.*, **1967**, **39**, 356.
5. Lytle, F. W., Botsford, J. I., and Heller, H. A., *Rep. Invest. U.S. Bur. Mines*, **1957**, No. 5378.
6. Lytle, F. W., and Heady, H. H., *Analyt. Chem.*, **1959**, **31**, 809.
7. Payne, K. W., *in* "Proceedings of the 5th Conference on X-ray Analytical Methods," Philips, Eindhoven, **1966**.
8. Bertin, E. P., "Principles and Practice of X-ray Spectrometric Analysis," Plenum Press, New York, **1970**.
9. Jenkins, R., Hurley, P. W., and Shorrocks, V. M., *Analyst*, **1966**, **91**, 395.

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The Use of a Shield for the Reduction of Fogging on Photographic Plates in Spark-source Mass Spectrography

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In spark-source mass spectrography, secondary effects cause pronounced fogging of the photographic plate in the vicinity of the isotope lines of the major elements, and the limit of detection of elements whose lines fall within this area is considerably raised.

A shielding device has been designed to reduce the amount of ions produced by secondary effects and to prevent them from reaching the photographic plate. This reduces the background in the region of the major isotope lines and enables elements in this region to be determined with increased sensitivity and precision.

ALTHOUGH the photographic plate is widely used in spark-source mass spectrography for recording spectra, it has several disadvantages. The method involving its use is slow, the intensity range over which the plate has a linear reponse is limited and the high background in the vicinity of the isotope lines of the major elements restricts the measurement of adjacent trace-element concentrations. The evaluation of mass spectra has been speeded up by the introduction of automatic microdensitometry with coupled punch tape and computer facilities,[1] but the problem of high photoplate background remains. The introduction of electrical detection[2,3] has eliminated the photographic plate and made it possible to produce directly a semi-quantitative record of mass spectra. Rapid quantitative determination of elements within a mass range of M to 2M for one setting of the magnet current is also made possible by using electrical detection and peak switching. This method is useful when a small number of elements has to be determined quantitatively, but it becomes less advantageous as the number of elements to be determined increases[2] and the mass range is extended. A very high degree of resolution is also required to discriminate instrumentally between interfering spectra, and the eye can more easily resolve such interferences on a microdensitometric trace from a photographic plate.

In these circumstances the photographic plate is still a useful technique. The method would be considerably improved by eliminating the background interference in the vicinity of the isotope lines of the major elements and a simple device to achieve this end is described in this paper.

The general background of the photographic plate under recommended conditions of operation is satisfactory. It is only in the region of the isotopes of the major elements, where secondary ionic species are produced in large numbers, that it becomes unacceptable. This latter effect is caused by the geometry of the instrument and the way in which charged species behave in that environment, which is illustrated in Fig. 1 as follows.

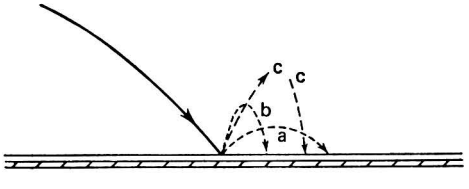

Fig. 1. Causes of secondary emission fogging on photographic plates: a, b and c are described in the text

(a) As an ion beam strikes the photoplate a small fraction of the ions is reflected. The energy of these ions is considerably reduced and the ions are rapidly deflected by the magnetic field so that they reach the photoplate in a slightly higher mass position.

(b) A situation arises, when a large ion current strikes the photoplate and raises the potential of the emulsion surface, where electrostatic repulsion of some of the ions occurs. These ions follow a path of small radius and return to the photoplate.

(c) Some of the ions leaving the photoplate may not return to the photoplate by the routes described in (a) and (b) because they collide with metal parts of the instrument in the neighbourhood of the photoplate. In doing so, they release secondary electrons, which are attracted to the photoplate by localised charge accumulations.

X-rays and luminescence are also produced when the positive ion beam strikes the photographic plate.

All of these factors combine to give the characteristic halo effect on photographic plates around the lines of the major components. Several attempts have been made to reduce the problem of fogging, the mode of attack falling into two categories: removal of the factors contributing to fogging, and special treatment of the photographic plate at the manufacturing and emulsion development stages.

METHOD 1—

(a) The segment of the photographic plate and plate holder where the major component normally strikes is removed.[4,5,6] In this way the ion beam due to the major component passes through the aperture and none of the interferences described above occur. The disadvantages are numerous, however, and are as follows: (i) each photoplate must be individually cut to size; (ii) the photoplate holder is modified in such a way that it can be used only for the analysis of one particular type of sample; (iii) the two pieces of the photoplate must be accurately aligned in the holder, which will be particularly important when determination of an element of mass number close to that of the major element is required; and (iv) the photoplate holders are no longer light-tight and precautions have to be taken when loading and unloading the plate holders.

(b) An earthed metallic strip is placed over the segment of the emulsion struck by the ions of the major component to avoid build-up of positive charge on the photographic plate.[5,7] This technique is not very successful and results are not as good as those obtained by method 1 (a).

(c) A suppressor plate is fitted at a high positive potential to reduce the effects of secondary electrons.[5] This removes only the least important cause of fogging.

METHOD 2—

Kennicott[8,9] investigated the rôle of photographic developers in spark-source mass spectrography and their relationship to photoplate background. By using a surface developer to obtain more reproducible results he found that the photoplate exhibited less fogging than usual. The surface developer resulted in an image of less intensity but this was compensated for by a large increase in signal-to-noise ratio. He also used an internal image developer and obtained a substantial reduction in background and an improvement in the reproducibility of the developing process. There was again a reduction in the absolute intensity of the image, but the increased signal-to-noise ratio compensated for this effect. Cavard[10] has also reported similar results.

METHOD 3—

Some work[11] has been carried out on photoplates containing a layer of a conducting oxide between the glass plate and the emulsions. The oxide layer is intended to conduct away excess charge so that fogging of the plate does not occur. Although a reduction in background is obtained, the plates have not been used other than for experimental purposes, because of manufacturing difficulties.

The methods described above have their inherent advantages and disadvantages, no one method being completely satisfactory. Thus the methods 1 (a), (b) and (c) show no decrease in intensity of signal but are limited in use and are not very practical. The techniques of method 2 are more widely applicable and, in general, show a greater reduction in background.

They also show a reduction in the absolute signal obtained and require a stricter control of the developing technique.

The work described here falls into the list of modifications given under method 1. Fig. 1 shows in diagrammatic form the way in which fogging can occur on the high mass side of a high-intensity ion beam. If a shield is placed on the photographic plate as shown in Fig. 2, then the primary ion beams of the intense line and the weak lines can still reach the photographic plate, but the secondary ion beams now strike the shield and do not reach those parts of the photographic plate which are of interest. As no secondary ions reach the photographic plate, fogging effects on the high mass side should be removed.

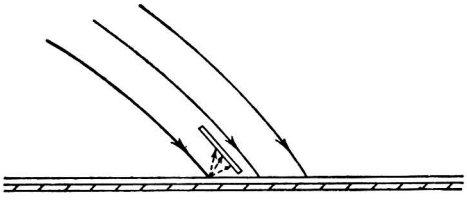

Fig. 2. Effectiveness of inserting a small shield at an angle of about 45° to the photographic plate to remove the causes of secondary emission fogging

Experimental

An MS7 double-focusing instrument of the Mattauch-Herzog type* was used. Ilford Q2 photographic plates were used for recording the mass spectra, and a microdensitometer† was used for measuring line intensities in the spectra. Electrode preparation and instrument parameters have been described previously.[12]

Discussion

The main problem is to design a shield that can be fitted into the limited space available. It is important that the shield and its fixtures do not protrude beyond the dimensions of the plate holder because otherwise the plate holder itself will not fit into its outer cover,

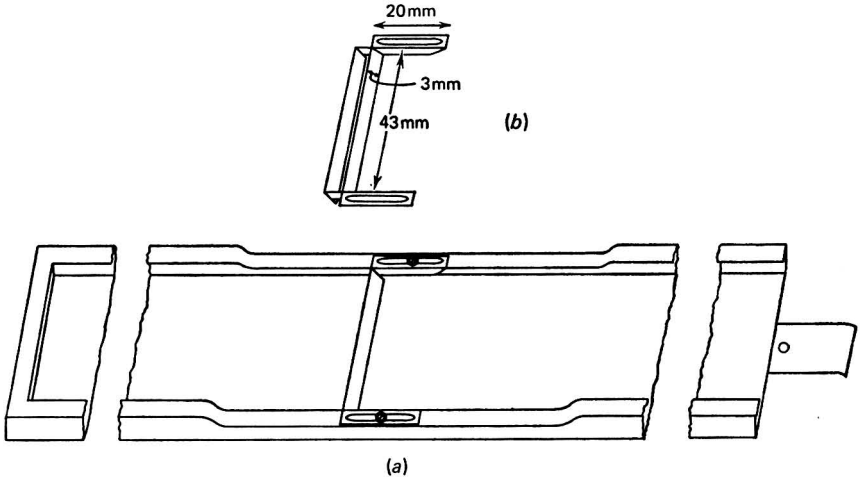

Fig. 3. Modified MS7 photoplate holder and single shield (*a*) and double shield (*b*)

* A.E.I. Scientific Apparatus Limited.
† Joyce-Loebl and Company Limited, Model MkIIIC.

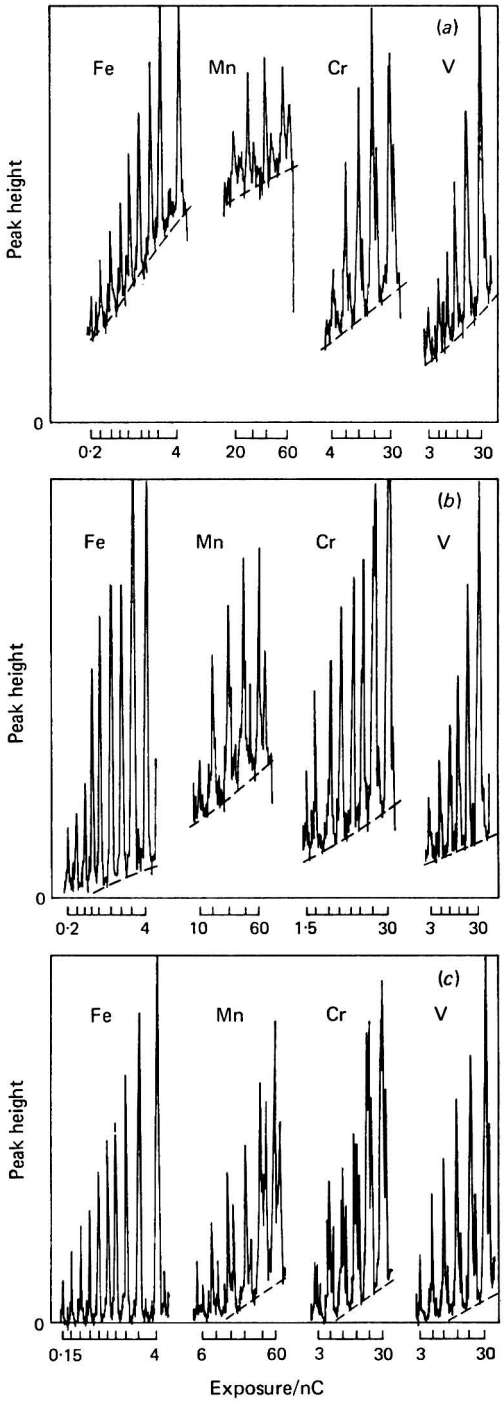

Fig. 4. Microdensitometer scans of ^{56}Fe, ^{55}Mn, ^{52}Cr and ^{51}V in a titanium dioxide matrix: (*a*), with no shield; (*b*), with single shield; and (*c*), with double shield. The exposures recorded on the photoplate were 60, 40, 30, 20, 10, 6, 4, 3, 2, 1·5, 1, 0·6, 0·4, 0·3, 0·2 and 0·15 nC. The longest and shortest exposures measured on the microdensitometer are shown; - - - represents the background level due to fogging

and that the position of the shield should be adjustable to allow greater versatility and to enable minor adjustments to be made to compensate for any variation in magnet current that would cause a shift in the position of the ion beams. Fig. 3 shows the modified MS7 plate holder with the single shield in place. The design of the double shield is also shown. The essential features of the modification are as follows.

The sides of the photoplate holder have been lowered over a length of about 50 mm to a depth of 1 mm to accommodate a piece of 0·79-mm brass sheet.

A small hole has been drilled at a position coinciding approximately with the major isotope lines of titanium on both sides of the holder, and each hole has been tapped to take a small screw.

The shields have been made from 0·79-mm brass sheet to the designs illustrated. The choice of 0·79-mm ($\frac{1}{32}$-inch) brass sheet gives sufficient rigidity to the shield. The thickness also represents about one half of the distance between two adjacent mass numbers on the photographic plate, thus allowing some leeway in the position and angle of the shield. The shield is made so that it subtends an angle of approximately 45° to the photographic plate. The exact shield dimensions and angle are found by experiment.

The shield is held in place by the two screws.

The metal strip at the inside front end of the outer case for the photoplate holder is removed.

Thin photoplates are used without the aluminium backing plate.

The design enables the position of the shield to be varied over a range of about 20 mm, which corresponds to 16 mass units about a mean mass number of 50 (magnet current 248 mA). Although it has not been necessary in the present work it should be possible to cover a much larger mass range, which could be achieved by increasing the length of the modified part of the photoplate holder and by drilling a series of holes at regular intervals along the edges of the photoplate holder.

To adjust the shield to the correct position, insert an exposed photoplate of the type of sample to be analysed into the holder, and slide the shield along until the base edge of the shield just comes to the high mass side of the major isotope line to be shielded. Tighten the two retaining screws. Remove the exposed plate and insert an unexposed photoplate. Spark a sample in the normal way and then develop the photoplate. Any slight adjustments to the position or angle of the shield will be apparent from the exposed plate. After making the adjustments, repeat the above procedure to check that the shield is functioning satisfactorily. One or two plates exposed in this manner are normally sufficient to fix the position of the shield. No further adjustments will be necessary unless there is any drift in the magnet current.

Removal of the two screws and the shield leaves the photoplate holder available for any other analyses that may be required.

The shield has been applied to the determination of trace amounts of vanadium, chromium, manganese and iron (mass numbers 51, 52, 55 and 56, respectively) in titanium dioxide (titanium mass numbers 46 to 50 inclusive). Without the shield there is a very high level of background in the required mass range 51 to 56 [Fig. 4 (*a*)]. With the use of the single shield some improvement in the observed background is obtained [Fig. 4 (*b*)], but it has not been completely eliminated.

As there are five titanium isotope lines involved, the single shield is obviously inadequate in shielding all of them and some secondary ions arising from the titanium-46, titanium-47 and, possibly, titanium-48 lines are still able to pass the shield and cause an increase in background. To overcome this a modification was made by fixing a second shield to the first shield [Fig. 3 (*b*)] in such a way that direct shielding was applied at the titanium-48 and titanium-50 lines. In this way, the background on the high mass side of the titanium lines was almost completely eliminated [Fig. 4 (*c*)].

Normally, a single shield should give adequate results but for shielding several lines a double-shield arrangement is clearly superior. The result of the work reported above is, therefore, to increase the signal-to-noise ratio with no corresponding loss of absolute intensity. The modifications outlined are simple and, if required, the photoplate holders can be used normally after removal of the shield. Finally, and most important, once the shield has been positioned no change is required in the normal mode of operation used for photographic detection.

The authors acknowledge the technical assistance of Mr. B. R. Ellis and Mr. A. R. Collins in the manufacture and design of the photoplate shield. This work is published by permission of the Directors of Tioxide International Limited.

References

1. Degreve, F., and Champetier de Ribes, D., *Int. J. Mass Spectrom. Ion Phys.*, **1970**, **4**, 125.
2. Hull, C. W., *Ibid.*, **1969**, **3**, 293.
3. Bingham, R. A., Powers, P., and Wolstenholme, W. A., ASTM, 17th E14, Dallas, **1969**, p. 261.
4. Ahearn, A. J., and Malm, D. L., *Appl. Spectrosc.*, **1966**, **20**, 411.
5. Mai, H., "Advances in Mass Spectrometry," Volume 3, Elsevier Publishing Co., Amsterdam, 1966, p. 163.
6. ——, *J. Scient. Instrum.*, **1965**, **42**, 339.
7. Hannay, N. B., *Rev. Scient. Instrum.*, **1954**, **25**, 644.
8. Kennicott, P. R., *Analyt. Chem.*, **1965**, **37**, 313.
9. ——, *Ibid.*, **1966**, **38**, 633.
10. Cavard, A., "Advances in Mass Spectrometry," Volume 4, Elsevier Publishing Co., Amsterdam, 1968, p. 419.
11. "Proceedings of the Sixth Annual MS7 Mass Spectrometer Users' Conference," Associated Electrical Industries, Scientific Apparatus Department, Manchester, March, **1966**, p. 23.
12. Jackson, P. F. S., and Whitehead, J., *Analyst*, **1966**, **91**, 418.

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Automatic Radiofrequency Titration of Acids in Tertiary Butyl Alcohol - Acetone Medium*

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The mixed solvent t-butyl alcohol - acetone can be used as a differentiating medium for the titration of acids with a standard solution of tetra-n-butylammonium hydroxide dissolved in a mixture of toluene and methanol. Titration curves of various shapes can be obtained and the simultaneous determination of certain acids achieved. The differences in curve shapes obtained by radiofrequency titration can be used as the basis of separation. The low toxicity of t-butyl alcohol (compared with other solvents at present in widespread use for the titration of weak acids) combined with its low solvating power and good differentiating properties make it a suitable medium for the routine determination of such acids in admixture.

The use of t-butyl alcohol as a non-aqueous solvent for the titration of acids was first investigated by Fritz and Marple,[1] who noted the low acidity of the compound compared with methanol or ethanol and its good solvent properties, and pointed out its potential uses as an amphiprotic solvent. Other workers reported on its use in potentiometric,[2,3,4,5,6] conductimetric[7,8] and visual[7,9] titrations. It has been observed that this alcohol possesses differentiating properties for weak acids, which are attributed to the high degree of dissociation of ion-pairs, and to the fact that no appreciable association of the acid anion with free acid occurs in the solvent.[1,2,3,4,5,6] No thorough investigation has so far been reported on the differentiating titrations of carboxylic acids in the solvent, although an investigation on phenols has shown some encouraging results.[8] Radiofrequency end-point detection has not so far been reported.

The differentiating effect of the alcohol, coupled with the advantages of radiofrequency end-point detection, offers considerable selectivity and precision for the titration of mono- and dibasic acids and mixtures of these acids. The low dielectric constant (10·6) of the pure solvent imposes some limitations on instrument response, because the operational frequency of the oscillator (of which the titration cell forms an integral part) must be rather low if reasonably high admittance is to be achieved. The radiofrequency titrimeter described by Scott, Quigg and Svehla[10] is equipped with a continuously variable operational frequency covering the range 0·5 to 30 MHz and could be applied to monitor such titrations at the lower end of this frequency range. Experiments showed that the addition of about 20 per cent. v/v of acetone to the solvent increases the dielectric constant slightly (to 13·5). The optimum operational frequency for such media, which is about 2 MHz, is safely within the working range of the instrument. The presence of acetone does not interfere in the resolution of mixtures of acids as it is not itself a levelling solvent.[11] To ensure that the solvent does not freeze, 10 per cent. v/v of toluene has to be added also. If the operational frequency is correctly selected, instrument response is satisfactory and there is no superimposition of background noise on the titration curves. With tetra-n-butylammonium hydroxide[12,13,14,15,16,17] as a titrant dissolved in a mixture of toluene and methanol, sharp, well defined end-points can be obtained.

Experimental

Reagents—

Titrant—A 0·1 M solution of tetra-n-butylammonium hydroxide in toluene - methanol (9 + 1 v/v).† This solution is standardised against analytical-reagent grade benzoic acid

* Presented at the National Conference of Analytical Chemistry, Mamaia, Romania, September 24th to 28th, 1969.

† This solution is available from B.D.H. Chemicals Ltd.

with radiofrequency end-point detection. The titrant must be protected from contamination with carbon dioxide and moisture by the use of a drying tube containing soda-lime and calcium chloride.

Solvent—t-Butyl alcohol was dried by the method of Lund and Bjerrum[18] by using ethyl bromide as a catalyst. As the pure alcohol just melts at room temperature (m.p. 25·5 °C), a volume of analytical-reagent grade toluene sufficient to give a 1 + 9 mixture was added immediately after distillation so as to depress the melting-point; as toluene is used as a solvent for the titrant, it does not interfere in the titration. To raise the dielectric constant of the solvent 20 per cent. by volume of anhydrous, analytical-reagent grade acetone is added to the solvent immediately prior to titration. The acid blank of the solvent was often checked and was found to be less than 0·001 milli-equivalents per 50 ml. During the titration an atmosphere of pure dry nitrogen was maintained over the solution in the cell (described below) so as to exclude carbon dioxide. If titrations are completed within a few minutes, this precaution can be omitted except when the compounds are sensitive to atmospheric oxygen (as are, for example, dihydric phenols).

Acids and phenols—The acids and phenols were, whenever possible, of analytical-reagent grade; if these were not available, general-purpose grades were used.

Apparatus—

The radiofrequency titrimeter described earlier by the authors[10] was used. An automatic burette and a T - Y chart recorder were added to the basic instrument, thus making the whole set-up completely automatic. A Radiometer ABU 1c piston burette of 25-ml capacity and a Sunvic pen recorder were used. The volume of dispensed titrant is read on a digital counter of the burette. To slow down the rate of delivery and to increase the precision of volume reading, we used the slow gear system (normally used with the 0·25-ml burette tube) and the faster counting rate; therefore, the full delivery of 25·00 ml corresponded to a reading of 100·00 on the counter. The rate of delivery was about 2 ml min^{-1} and the chart speed was usually 5 cm min^{-1}. A special switch was built into the burette, in parallel with the push-button by which the burette could be operated manually, which activated both the burette and the chart-delivery motor (T-axis) of the recorder. The optimal operational frequency for these titrations was 1·9 MHz. A low, but not zero, beat frequency was adjusted when commencing the titration and the variation of beat frequency was plotted on the Y-axis of the chart recorder.

The titration cell is a thin-walled glass cylinder, 5 cm in diameter, with two sheets of copper foil (each 2 × 7 cm) acting as capacitor plates, which were held firmly to the outside by Sellotape. The Quickfit stopper is equipped with three outlets, to accommodate an "Electrothermal" stirrer, a gas inlet tube and a combined burette inlet - gas outlet tube. The polythene outlet tube of the burette, 0·2 cm in diameter, enters the cell through the burette inlet - gas outlet orifice and terminates in a fine 5-cm long glass capillary. The tip of the capillary dips below the surface of the solution to be titrated. Photographs of the cell and of the instrument panel are shown in Figs. 1 and 2.

Precision of volume measurement—

With the automatic titration system used in these investigations, the accuracy of the results depends mainly on the precision with which the volume is measured. This measurement is made in the following way: the starting position of the pen is marked on the chart and the titration carried out beyond the end-point. The final position of the pen is marked again on the chart and the corresponding figure, a, on the digital counter is read. (Because of the gear setting used, the volume of titrant delivered is $\frac{1}{4}a$ ml.) The titration chart is then examined, the end-point determined graphically and the full l_a distance between starting and final position as well as the l_x distance from the start to the end-point are measured with a ruler. The V_x volume corresponding to the end-point is then calculated from the equation

$$V_x = \frac{a\,l_x}{4\,l_a}$$

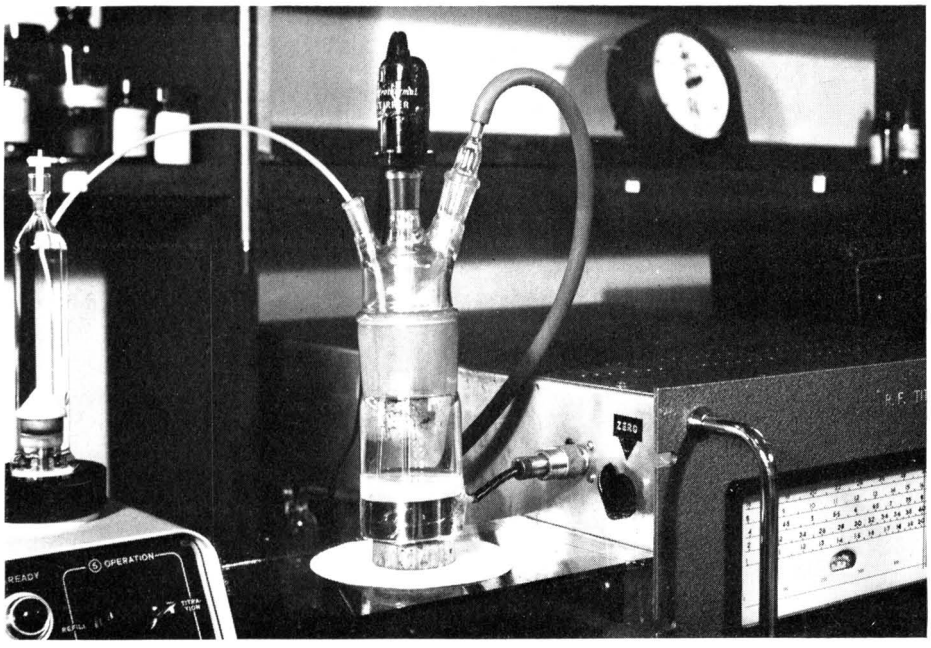

Fig. 1. View of the capacitive cell complete with nitrogen supply

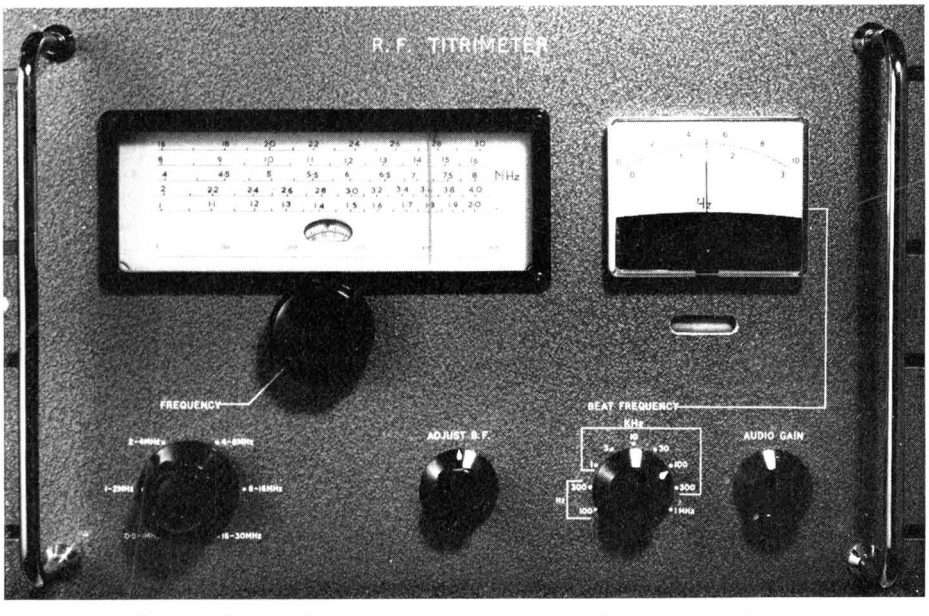

Fig. 2. View of the instrument panel of the radiofrequency titrator

[To face page 786

By applying the law of propagation of errors to these measurements, the s_V/V coefficient of variation of volume measurements can be expressed as

$$\frac{s_V}{V} = \pm\sqrt{\left(\frac{s_a}{a}\right)^2 + 2\left(\frac{s_l}{l}\right)^2} \quad .. \quad .. \quad .. \quad (1)$$

where s_a/a is the coefficient of variation of the burette delivery. We determined this quantity by operating the burette to the same digital read-out several times and determining the volume of the liquid delivered by weighing it. This s_a/a coefficient of variation was found to be $\pm 0{\cdot}0017$. The coefficient of variation of chart travel, s_l/l, was determined by operating the burette again to the same digital read-out several times and by measuring the distance travelled by the chart. This s_l/l coefficient of variation was found to be $\pm 0{\cdot}008$. By using these values in equation (1) the coefficient of variation of volume measurement was found to be

$$\frac{s_V}{V} = \pm 0{\cdot}009 \text{ or } \pm 0{\cdot}9 \text{ per cent.}$$

which is the degree of reproducibility that one can expect in the final results. With a different burette and a different chart recorder a different level of reproducibility can be expected.

PROCEDURE—

Accurately weigh a sample containing about 0·3 milli-equivalents of active ingredient and transfer it into the titration cell with 50 ml of solvent. (This amount will consume 2 to 3 ml of titrant up to the first equivalence-point.) Add 10 ml of acetone and adjust the stirring rate so that the vortex does not extend below the top of the capacitor plates. With the operational frequency set at 1·9 MHz, tune the reference oscillator with the capacitor control to give a low beat frequency. After filling the burette with the titrant and adjusting the chart recorder, start the titration by operating the start switch. At a suitable time after the equivalence-point, stop the titration by using the same switch. Determine the volume of the titrant corresponding to the end-point from the titration graph and calculate the result.

STANDARDISATION OF THE TITRANT—

By following the procedure given above, titrate analytical-reagent grade benzoic acid (equivalent weight, 122·13).

RESULTS AND DISCUSSION

TITRATION OF SINGLE ACIDS—

The groups examined were *(i)* inorganic acids, *(ii)* monocarboxylic aliphatic and aromatic acids, *(iii)* dicarboxylic aliphatic and aromatic acids and *(iv)* phenols.

(i) Inorganic acids—Hydrochloric, sulphuric, nitric and phosphoric acids were investigated, mainly for the sake of comparison. The titration curves were easy to evaluate. Hydrochloric and nitric acids give titration curves of the "elbow" type, the end-point being marked by the change in slope of the curve. Sulphuric acid gives a "chair"-shaped curve

TABLE I

TITRATION OF MONOCARBOXYLIC ACIDS

Group	Acid	pK_1 (H_2O) (COOH)	pK_2 (H_2O) (phenolic OH)	Number of end-points	Shape of curve
Aliphatic	Formic	3·75	—	1	Elbow
	Acetic	4·75	—	1	Elbow
	Hexanoic	4·88	—	1	Elbow
	Glycollic	3·83	—	1	Elbow
	Lactic	3·08	—	1	Elbow
Aromatic	Benzoic	4·19	—	1	Elbow
	Mandelic	3·85	—	1	Elbow
	Anthranilic	6·97	—	1	Elbow
	Salicylic	2·97	13·40	1	Elbow
	3-Hydroxybenzoic	4·06	9·92	1	Elbow
	4-Hydroxybenzoic	4·48	9·32	1	Elbow

with two changes in the slope corresponding to the two equivalence-points. Titration curves of phosphoric acid show one sharp and a second less distinct end-point, which obviously correspond to the neutralisation of the first and second acidic hydrogen atoms, respectively. These results were, however, not quantitative and reproducible, because the strong acids react readily with t-butyl alcohol.[1] The titration of strong acids is, of course, possible in aqueous solutions.[10]

(ii) Aliphatic and aromatic monocarboxylic acids—The titration curves of these acids consist of two lines (sometimes slightly curved) of different slopes, the end-point corresponding to their intersection. These elbow-like titration curves can easily be evaluated. Organic hydroxy-acids fall into two categories. Some of these acids, mainly aliphatic acids but also salicylic acid, show only one end-point, corresponding to the carboxyl group only, while others, mainly phenolic acids but excluding salicylic acid, show two end-points with a chair-shaped titration curve corresponding to the neutralisation of the carboxyl and phenolic hydroxyl groups. The monobasic behaviour of salicylic acid has been reported by other workers.[19] Results are summarised in Table I. The pK values (corresponding to aqueous solutions) are shown for the sake of comparison.[20] The high value given for the phenolic hydroxyl group of salicylic acid is in accordance with the fact that it shows only one end-point.

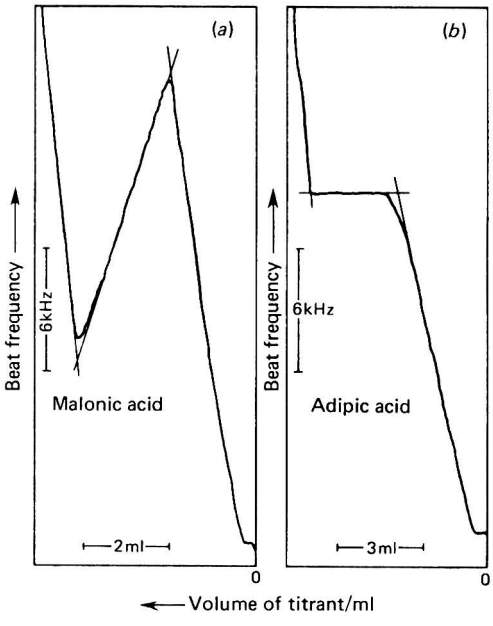

Fig. 3. (*a*) N-curve and (*b*) chair-curve for the homologous series of aliphatic dicarboxylic acids

(iii) Aliphatic and aromatic dicarboxylic acids—The lower aliphatic dicarboxylic acids, both saturated and unsaturated, show two very sharp end-points, which correspond to the neutralisation of the first and second acidic hydrogen atoms. These titration curves resemble the letter N [see Fig. 3 (*a*)]. As one proceeds along the homologous series, the strength of these acids decreases and the difference in the pK values of the first and second dissociations decreases also (*cf.* Table II), and therefore the sharpness of the two end-points decreases as well. The N-shaped titration curve changes into a chair-like trace [see adipic acid, Fig. 3 (*b*)], then the sharpness decreases further until an elbow-type titration curve is obtained in which only the second end-point is clearly marked [see pimelic and sebacic acids; *cf.* Fig. 4 (*a*) and (*b*)]. The sharpness of end-points and the pK values of the first and second dissociations (referred to aqueous media) are in a similar correlation also with aromatic dicarboxylic acids.

TABLE II

TITRATION OF DICARBOXYLIC ACIDS

Group	Acid	pK_1 (H_2O)	pK_2 (H_2O)	Number of end-points	Shape of curve
Aliphatic	Oxalic	1·23	4·19	2	N
	Malonic	2·83	5·69	2	N
	Succinic	4·16	5·61	2	N
	Glutaric	4·34	5·41	2	N
	Adipic	4·43	5·41	2	Chair
	Pimelic	4·71	5·43	2	Chair
	Suberic	4·52	5·41	2	Chair
	Azelaic	5·30	6·40	2	Chair
	Sebacic	5·59	—	1	Elbow
	Maleic	1·83	6·07	2	N
	Fumaric	3·08	4·44	2	N
	Itaconic	3·85	5·45	2	N
	Malic	3·40	5·11	2	N
Aromatic	Phthalic	2·89	5·51	2	N
	Isophthalic	3·62	4·60	2	Chair
	Terephthalic	3·54	4·46	Insoluble	—

These results obtained for the titration of dicarboxylic acids illustrate well the advantages of the solvent system. While the trend in the sharpness and separation of end-points, as discussed above, has been noted also for other solvents,[15,21,22] sharpness and separation deteriorate more quickly in most of these solvents than in t-butyl alcohol as the chain length of the compound investigated increases. The explanation of this phenomenon lies in the fact that the solvent has a very low solvating power,[21] which is a distinct advantage in differentiating titrations. It is difficult to make more quantitative comparisons, or predictions of the behaviour of acids in other solvents, because the dissociation constants of these acids and the ionic conductivities of their dissociation products in non-aqueous solvents are generally not known.

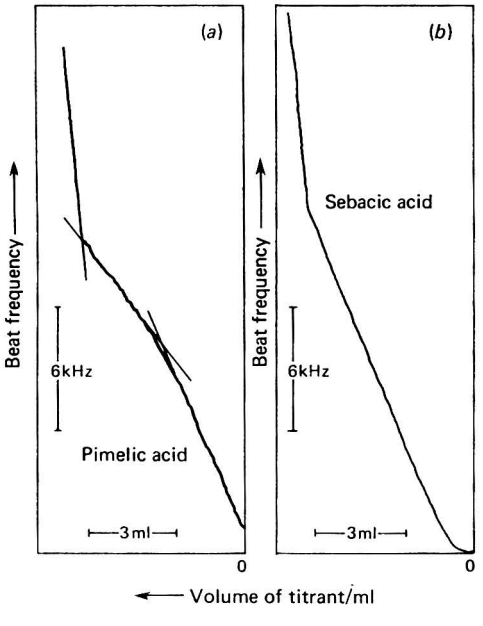

Fig. 4 (*a*) Intermediate-curve and (*b*) elbow-curve for the homologous series of aliphatic dicarboxylic acids

(iv) Phenols—The phenols investigated, as distinct from phenolic acids, which were discussed under *(ii)*, yield elbow-shaped titration curves in all instances apart from the trihydric phenol phloroglucinol, which gave a titration curve with three distinct end-points corresponding to the three hydroxyl groups. The shape of the titration curve resembles the letter N but has a horizontal ending (N^{-}). Results are shown in Table III and are in agreement with low-frequency conductimetric results.[23]

TABLE III

TITRATION OF PHENOLS

Group	Compound	pK_1 (H_2O)	pK_2 (H_2O)	Number of end-points	Shape of curve
Monohydric	Phenol	9·99	—	1	Elbow
	2-Nitrophenol	7·23	—	1	Elbow
	3-Nitrophenol	8·38	—	1	Elbow
	4-Nitrophenol	7·15	—	1	Elbow
	2-Bromophenol	8·39	—	1	Elbow
	3-Bromophenol	8·87	—	1	Elbow
	4-Bromophenol	9·34	—	1	Elbow
	o-Cresol	10·26	—	1	Elbow
	m-Cresol	10·04	—	1	Elbow
	p-Cresol	10·20	—	1	Elbow
	2-Phenylphenol	10·01	—	1	Elbow
	2,4-Dinitro-1-naphthol	(?)	—	1	Elbow
	Picric acid	0·29	—	1	Elbow
	2,3-Xylenol	10·50	—	1	Elbow
	2,4-Xylenol	10·45	—	1	Elbow
	2,5-Xylenol	10·21	—	1	Elbow
	2,6-Xylenol	10·59	—	1	Elbow
	3,4-Xylenol	10·32	—	1	Elbow
	3,5-Xylenol	10·15	—	1	Elbow
Dihydric	Catechol	9·12	12·08	1	Elbow
	Resorcinol	9·15	11·32	pK_3 (H_2O) 1	Elbow
	Quinol	9·91	12·03	1	Elbow
Trihydric	Phloroglucinol	8·45	8·88	(?) 3	—

TITRATION OF MIXTURES OF ACIDS—

The titration of binary mixtures of the acids mentioned was also attempted. Instead of classifying them according to chemical structure we classified these acids according to the shape of titration curves (N-acid, chair-acid and elbow-acid), as preliminary experiments showed that resolution of acids by such titrations is dependent mainly on the form of individual titration curves. Mixtures that gave good resolution can be classified into four groups:

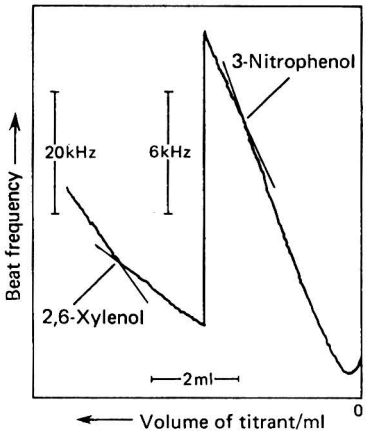

Fig. 5. Differentiating titration of a mixture comprising 3-nitrophenol and 2,6-xylenol

(i), elbow *plus* elbow; *(ii)*, elbow *plus* N; *(iii)*, elbow *plus* chair; and *(iv)*, N *plus* chair. Other combinations, such as N *plus* N, etc., were tested but did not yield good resolution and are not mentioned here.

(i) Elbow plus *elbow mixtures*—Mixtures of compounds characterised by elbow curves were resolved without difficulty. Fig. 5 shows the results obtained with the titration of a mixture of 3-nitrophenol and 2,6-xylenol. (The break in the middle of the curve originates from the fact that as the titration proceeded and the beat frequency became very low, it was felt necessary to increase the sensitivity of the beat-frequency meter, that is, to "magnify" the frequency axis of the titration graph. The volume axis remains the same.) Information on the resolution of such titrations is shown in Table IV. None of the ternary mixtures investigated gave good resolution, which is in agreement with the results of potentiometric titrations,[1] although other workers[8] were able to resolve the isomers of cresol.

TABLE IV

TITRATION OF MIXTURES OF ELBOW-ACIDS (PHENOL MIXTURES)

Mixture	pK (H_2O)	Δ pK	Results
4-Nitrophenol	7·15	3·44	Two end-points
2,6-Xylenol	10·59		
3-Nitrophenol	8·39	2·21	Two end-points
2,6-Xylenol	10·59		
4-Bromophenol	9·34	1·25	Two end-points
2,6-Xylenol	10·59		
2,4-Xylenol	10·45	0·14	Two end-points
2,6-Xylenol	10·59		
2,3-Xylenol	10·50	0·09	Two end-points
2,6-Xylenol	10·59		
4-Nitrophenol	7·15	0·08	One end-point
2-Nitrophenol	7·23	1·15	
3-Nitrophenol	8·38		
2-Bromophenol	8·39	0·48	One end-point
3-Bromophenol	8·87	0·47	
4-Bromophenol	9·34		
3,5-Xylenol	10·35	0·17	One end-point
3,4-Xylenol	10·32	0·27	
2,6-Xylenol	10·59		

Results in Table IV indicate that resolution might be expected if the difference between the aqueous pK values of the acids involved is larger than 0·1. Such rules are usually drawn with potentiometric titrations, for which the shapes of the titration curves are closely and simply related to the equilibrium constants of the reactions involved. The correlation between curve shape and equilibrium constants in radiofrequency titrations is much more complicated because factors such as ionic mobilities, relaxation times and the variation of dielectric constant during the titration influence the actual shape of the titration curve. An attempt to express the resonance frequency of the oscillator, *i.e.*, a quantity that differs only by a constant from the variable monitored in these titrations, as a function of hydrogen-ion concentration was made by K. I. Millar of this Department. The very complex equation (covering several pages) is not given here, as its practical application requires a special computer programme. Details of such a calculation will be published shortly in a Ph.D. thesis.[24]

(ii) Elbow plus *N mixtures*—When titrating elbow and N-acids together, two types of titration curves are obtained. If there is complete resolution, as with malonic and acetic acids (Fig. 6), three end-points are shown on the titration curve. Experiments with various amounts of the two acids showed that the first end-point corresponds to the neutralisation of the first acidic hydrogen atom of malonic acid, the second to that of acetic acid and the third to the neutralisation of the second acidic hydrogen atom of malonic acid. This order corresponds to the order of aqueous pK values of these acids. Although the order established by experiments generally followed this rule, there were some notable exceptions, *e.g.*, salicylic

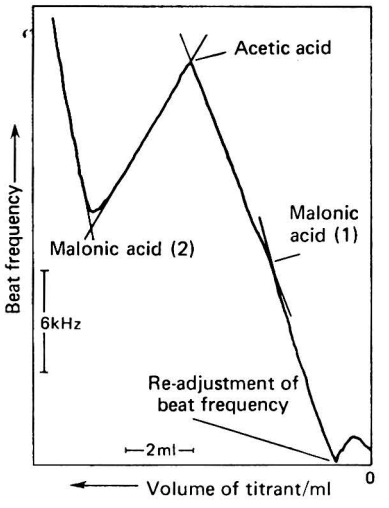

Fig. 6. Complete resolution of a mixture of N- and elbow-type acids. Malonic + acetic acids

and malonic acids showed end-points in an unexpected order (first the salicylic acid and then the two malonic acid end-points).

Other pairs of elbow *plus* N-acids showed only two end-points. The general rule is that initially the first acidic hydrogen atom of the dibasic acid and the monobasic acid are titrated together, while the difference between the second and first end-points corresponds to the neutralisation of the second acidic hydrogen atom of the dibasic acid. This was found to be true even if the aqueous pK values suggested a different pattern, *e.g.*, titration of oxalic and sebacic acids together. Predictions from aqueous pK values cannot reliably be made; titration of salicylic and glutaric acids, for example, gave only two end-points, although from the pK values one would expect three end-points. In any event, if mixtures of acids are titrated, the order of end-points must be established experimentally.

Table V shows the pairs of acids that can be titrated, together with aqueous pK values and the numbers of end-points on the titration curves.

TABLE V

TITRATION OF AN ELBOW-TYPE AND AN N-TYPE ACID TOGETHER

Elbow-acid		N-acid								
Compound	pK_a (H_2O)	Oxalic	Maleic	Malonic	Phthalic	Fumaric	Malic	Itaconic	Succinic	Glutaric
Salicylic	2·97	2	3	3	2	2	2	2	2	2
Lactic	3·08	2	2	3	3	2	3	2	2	3
Formic	3·75	3	2	3	2	2	2	2	2	2
Glycollic	3·83	2	2	2	2	2	2	2	2	2
Mandelic	3·85	2	3	3	2	2	2	2	2	2
Benzoic	4·19	2	3	3	3	2	3	3	2	2
Acetic	4·75	3	3	3	2	2	3	2	3	2
Hexanoic	4·88	2	3	3	2	2	3	3	3	2
Anthranilic	5·00	3	3	3	3	2	3	3	3	2
Sebacic	5·59	2	3	3	2	2	3	3	2	3
	pK_{a_1} (H_2O)	1·23	1·83	2·83	2·89	3·03	3·40	3·85	4·16	4·34
	pK_{a_2} (H_2O)	4·19	6·07	5·69	5·51	4·44	5·11	5·45	5·61	5·41

2 ≡ two end-points on the titration curve.
3 ≡ three end-points on the titration curve.

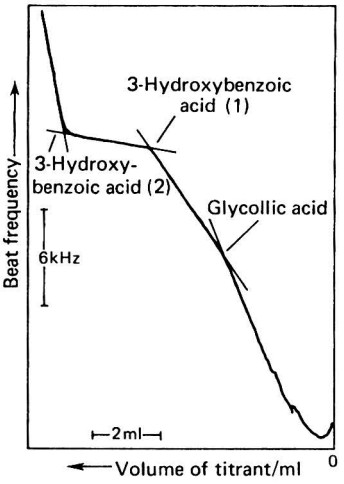

Fig. 7. Complete resolution of a mixture of chair- and elbow-type acids. 3-Hydroxybenzoic + glycollic acids

(iii) Elbow plus *chair mixtures*—Mixtures of elbow *plus* chair-acids show complete resolution in some instances, that is, three end-points are found on the titration curves, as with glycollic and 3-hydroxybenzoic acids (see Fig. 7). The order of end-points follows the order of the aqueous pK values. Other mixtures show only two end-points and their order follows the rule mentioned under *(ii)*, that is, generally the first end-point corresponds to the neutralisation of the first acidic hydrogen atom of the dibasic acid together with the monobasic acid, while the second end-point corresponds to the neutralisation of the second acidic hydrogen atom of the dibasic acid. Mixtures with adipic acid yield only two end-points, although according to the aqueous pK values one would expect three. Mixtures of anthranilic and isophthalic acids cannot be resolved as they yield only one end-point corresponding to the total acid content of the system. Results of titrations are summarised in Table VI.

TABLE VI

TITRATION OF AN ELBOW-TYPE AND A CHAIR-TYPE ACID TOGETHER

Elbow-acid		Chair-acid			
Compound	pK_a (H_2O)	3-Hydroxybenzoic	Adipic	4-Hydroxybenzoic	Isophthalic
Salicylic	2·97	3	2	3	2
Lactic	3·03	3	2	3	3
Formic	3·75	3	2	3	2
Glycollic	3·83	3	2	3	2
Mandelic	3·85	3	2	3	2
Benzoic	4·19	2	2	2	2
Acetic	4·75	2	2	2	2
Hexanoic	4·88	2	2	2	2
Anthranilic.. ..	5·00	2	2	2	1
Sebacic	5·59	2	2	2	2
	pK_{a_1} (H_2O)	4·06	4·43	4·48	3·62
	pK_{a_2} (H_2O)	9·92	5·41	9·32	4·60

2 ≡ two end-points on the titration curve.
3 ≡ three end-points on the titration curve.

(iv) N plus *chair mixtures*—Most of the pairs formed from N- and chair-acids show four end-points giving total resolution. Fig. 8 shows the titration curve for a mixture of malic acid and 3-hydroxybenzoic acid. The four end-points follow generally the order

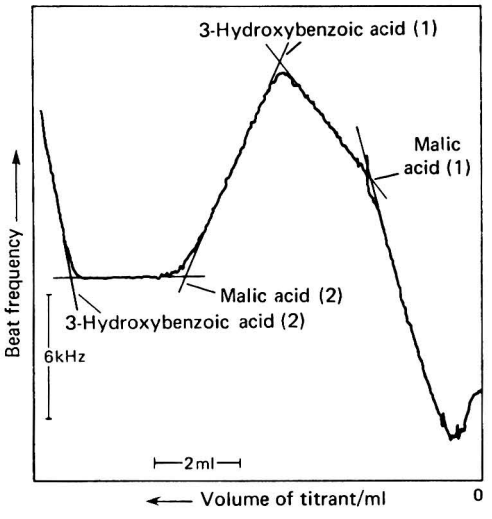

Fig. 8. Complete resolution of a mixture of N- and chair-type acids. 3-Hydroxybenzoic + malic acids

expected from the aqueous pK values. In a few instances, when two pK values were close together, only three end-points were obtained when the two corresponding acidic hydrogen atoms were titrated together. Mixtures with fumaric acid resulted in two end-points only, one when the first acidic hydrogen atoms of both acids were titrated together, followed by a second end-point when the second acidic hydrogen atoms were titrated. Unfortunately, therefore, the two acids cannot be resolved at all, the titration curve giving information only on the total acid content. In some instances the order of end-points does not follow the order predicted from the aqueous pK values. Thus, a mixture of maleic and 3-hydroxybenzoic acids was titrated in the order of maleic (1), 3-hydroxybenzoic (1), 3-hydroxybenzoic (2) and maleic (2), while one would expect the last two end-points to appear in the reverse order. The good resolving power of the solvent can again be emphasised here. While the mixture of oxalic and adipic acids, for example, yields four end-points (that is, giving complete resolution), in pyridine only one end-point occurs.[25] Results of titrations are shown in Table VII.

TABLE VII

TITRATION OF A CHAIR-TYPE AND AN N-TYPE ACID TOGETHER

N-acid			Chair-acid			
Compound	pK_{a_1} (H_2O)	pK_{a_2} (H_2O)	3-Hydroxybenzoic	Adipic	4-Hydroxybenzoic	Isophthalic
Oxalic	1·23	4·19	4	4	4	3
Maleic	1·83	6·07	4	4	4	4
Malonic	2·83	5·69	4	4	4	4
Phthalic	2·89	5·51	4	3	4	4
Fumaric	3·03	4·44	2	2	2	2
Malic	3·40	5·11	4	3	4	4
Itaconic	3·85	5·45	4	4	4	4
Succinic	4·16	5·61	4	4	4	3
Glutaric	4·34	5·41	4	3	4	4
	pK_{a_1} (H_2O)		4·06	4·43	4·48	3·62
	pK_{a_2} (H_2O)		9·92	5·41	9·32	4·60

4 ≡ four end-points on the titration curve.
3 ≡ three end-points on the titration curve.
2 ≡ two end-points on the titration curve.

TITRATION OF TERNARY MIXTURES—

In the course of this study attempts were made to titrate ternary mixtures consisting of N-, chair- and elbow-acids. The titration curves resembled with each attempt those obtained with a mixture of an N- and a chair-acid, the elbow-acid being titrated together with one of the acidic hydrogen atoms of the other acid. In some instances, therefore, the amounts of all of the component acids could be determined from the four end-points, while in other instances, when only three end-points were obtained, only one of the acids could be determined separately, with the sum of the other two. Even in the most favourable case, *i.e.*, when four end-points were obtained, one of the acids is determined indirectly from a difference of two volumes so that we did not pursue this line of approach, the error in the indirect determination being always considerably higher than that in a direct determination. A comprehensive study of ternary mixtures would have required the examination of a large number of combinations, but because of the limitations in accuracy such a study has not been undertaken.

ACCURACY AND PRECISION—

The accuracy of the determination of each acid was checked by titrating various amounts of the acid. In one range ten different samples were taken, the titrations were carried out, and the proportionality between sample weight and volume was checked by calculating the correlation coefficient and the intercept of the volume *versus* weight curve with the volume axis, which is supposed to be zero. The standard deviation of the intercept was calculated and the presumption that the intercept is different from zero was tested with 95 per cent. statistical significance. The correlation coefficient was in all instances better than (+)0·99, and the intercept was found to be zero in each instance. The slope of these curves is proportional to the equivalent weight of the acids, and these slopes were calculated for all samples. An "absolute" test of the accuracy, based on stoicheiometry, was not possible, as the titrant was obtained already made up, and the standardisation with benzoic acid presupposes the stoicheiometry in these reactions. Evidence from our work and other experiments, however, leaves no doubt about the stoicheiometric nature of such reactions.

The precision of these titrations was checked by six parallel measurements by titrating approximately equal amounts of the acids taken from the middle of the useful range of sample sizes. As all of the samples had to be weighed with a swinging balance by the method of swings, these samples could not be completely identical, and therefore the ratios of the weights calculated from the end-points and the weights of the samples were determined (this should be exactly unity) and the standard deviation of these ratios was also determined. As benzoic acid was used as a standard, precision of its titration was checked in four sets of different sample sizes.

TABLE VIII

RESULTS OF TITRATION OF SUCCINIC ACID *versus* 0·0929 N TETRA-n-BUTYL-AMMONIUM HYDROXIDE

Acid taken/mg	Volume to end-point/ml (1)	Acid found/mg	Amount found / Amount taken	Volume to end-point/ml (2)	Acid found/mg	Amount found / Amount taken
32·38	2·89	31·70	0·979	6·03	33·07	1·021
31·80	2·84	31·15	0·980	5·80	31·88	1·003
31·60	2·82	30·94	0·979	5·75	31·57	0·999
32·38	2·87	31·48	0·972	5·89	32·31	0·998
32·47	2·93	32·14	0·990	6·01	33·00	1·015
32·67	2·93	32·14	0·984	6·04	33·16	1·015
	Mean		0·981	Mean		1·008
	Standard deviation		0·006	Standard deviation		0·010
	Coefficient of variation, per cent...		0·580	Coefficient of variation, per cent...		0·990
	Error, per cent.		−1·9	Error, per cent.		−1·0

A typical set of results obtained for succinic acid is shown in Table VIII. The values given in this table indicate that the error and the coefficient of variation of these determinations is in the range of 1 to 2 per cent., a value similar to that predicted from the precision of volume measurements. With a more precise burette and recorder system the precision

could be increased, though we found that the variation in temperature, which results in changes in the specific volume of the titrant, is a considerable source of error. We did not attempt, however, to overcome this problem, as such variations in room temperature would occur normally in laboratories. In laboratories with air conditioning a better degree of precision might be expected. Such accuracy and precision can be achieved when titrating acids in the range 10^{-4} to 2×10^{-3} gram-equivalents.

With a slightly reduced accuracy and precision, samples containing not less than 6×10^{-5} gram-equivalents can still be analysed. In the higher concentration range more acetone might be needed to provide good titration curves that are free from instrument noise. Binary mixtures of acids can be resolved if the molar ratios are between 10:1 and 1:10. Accuracy and precision of titrations of acids in mixtures can be judged from Table IX, in which results for the titration of mixtures of malic acid and 3-hydroxybenzoic acid are shown. The coefficient of variation is in the same range (1 to 2 per cent.) as for the titration of single acids. The errors are somewhat larger and increase as higher end-points are used for evaluation because these errors accumulate. In extreme instances, *e.g.*, the determination of the lesser component in a 1:10 mixture, the reproducibility of the results is lower; the coefficient of variation may then be as high as 3 to 4 per cent.

TABLE IX

TITRATION OF MIXTURES OF MALIC AND 3-HYDROXYBENZOIC ACIDS

M taken/mg	Volume to end-point/ml (1)	M found/mg	Amount found / Amount taken	Volume to end-point/ml (3)	M found/mg	Amount found / Amount taken
27·28	2·09	26·68	0·978	2·10	26·92	0·987
27·25	2·11	27·00	0·991	2·12	27·06	0·993
28·19	2·17	27·71	0·983	2·19	28·05	0·995
28·53	2·18	27·93	0·979	2·22	28·42	0·996
28·64	2·20	28·10	0·981	2·24	28·61	0·999
28·47	2·21	28·38	0·997	2·20	28·21	0·991
	Mean		0·985	Mean		0·994
	Standard deviation		0·007	Standard deviation		0·006
	Coefficient of variation, per cent...		0·7	Coefficient of variation, per cent...		0·6

HB taken/mg	Volume to end-point/ml (2)	HB found/mg	Amount found / Amount taken	Volume to end-point/ml (4)	HB found/mg	Amount found / Amount taken
29·13	2·32	30·64	1·052	2·29	30·27	1·039
28·52	2·25	29·75	1·043	2·34	30·83	1·081
28·86	2·32	30·62	1·061	2·33	30·68	1·063
29·13	2·29	30·18	1·036	2·36	31·08	1·067
28·67	2·31	30·42	1·061	2·29	30·22	1·054
28·91	2·34	30·79	1·065	2·33	30·70	1·062
	Mean		1·049	Mean		1·064
	Standard deviation		0·012	Standard deviation		0·014
	Coefficient of variation, per cent...		1·2	Coefficient of variation, per cent...		1·4

M = malic acid; HB = 3-hydroxybenzoic acid.

A more comprehensive account of the whole of the work carried out is available in the form of a thesis.[26]

The authors thank Professor C. L. Wilson for his interest in this work. One of us (W.J.S.) thanks the Government of Northern Ireland for the provision of a Postgraduate Studentship. We are indebted to Mr. R. Donelly who took the photographs of the instrument.

REFERENCES

1. Fritz, J. S., and Marple, L. W., *Analyt. Chem.*, 1962, **34**, 921.
2. Crabb, N. T., and Critchfield, F. E., *Talanta*, 1963, **10**, 271.
3. Kreshkov, A. P., Drozdov, V. A., and Kolchina, N. A., *Zh. Analit. Khim.*, 1967, **22**, 123.
4. Wetzel, F. L., and Meloan, C. E., *Analyt. Chem.*, 1964, **36**, 2474.
5. Lin, S., and Blake, M. I., *J. Pharm. Sci.*, 1966, **55**, 781.
6. Marple, L. W., and Fritz, J. S., *Analyt. Chem.*, 1963, **35**, 1223.
7. ——, ——, *Ibid.*, 1963, **35**, 1305.

8. Riolo, C. B., and Soldi, T. F., *Annali Chim.*, 1964, **54**, 923.
9. Lickhova, N. V., and Dulova, V. I., *Izv. Vŷssh. Ucheb. Zaved., Khim. Khim. Tekhnol.*, 1964, **7**, 10.
10. Scott, W. J., Quigg, R. K., and Svehla, G., *Analyst*, 1970, **95**, 113.
11. Fritz, J. S., and Yamamura, S. S., *Analyt. Chem.*, 1957, **29**, 1079.
12. Cundiff, R. M., and Markunas, P. C., *Ibid.*, 1956, **38**, 792.
13. Bruss, D. B., and Harlow, G. A., *Ibid.*, 1958, **30**, 1836.
14. Marple, L. W., and Fritz, J. S., *Ibid.*, 1962, **34**, 796.
15. Harlow, G. A., *Ibid.*, 1962, **34**, 1482 and 1487.
16. Buell, B. E., *Ibid.*, 1967, **39**, 762.
17. Morales, R., *Ibid.*, 1968, **40**, 1148.
18. Lund, H., and Bjerrum, J., *Ber. dt. chem. Ges.*, 1931, **64**, 210.
19. Van Meurs, N., and Dahmen, E. A. M. F., *Analytica Chim. Acta*, 1959, **21**, 10.
20. Kortüm, G. F. A., Vogel, V., and Andrussow, K., "Dissociation Constants of Organic Acids in Aqueous Solutions," IUPAC Commission on Electrochemical Data; *Pure Appl. Chem.*, 1960, **1**, 187.
21. Van Meurs, N., and Dahmen, E. A. M. F., *J. Electroanalyt. Chem.*, 1959/60, **1**, 458.
22. Masui, M., *J. Pharm. Soc. Japan*, 1955, **75**, 1519.
23. Marple, L. W., and Scheppers, G. T., *Analyt. Chem.*, 1966, **38**, 553.
24. Millar, K. I., Thesis to be submitted for the Ph.D. degree, Queen's University, Belfast, 1972.
25. Van Meurs, N., and Dahmen, E. A. M. F., *Analytica Chim. Acta*, 1959, **21**, 443.
26. Scott, W. J., Ph.D. Thesis, Queen's University, Belfast, 1970.

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Improvements to the Nitrite-Diazo Dye (Blom's) Method of Determining Hydroxylamine as Used in the Determination of Residues of Aldicarb

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The precision of determination of hydroxylamine, and hence of residues of aldicarb, by Blom's method has been improved by controlling the pH of the solutions at the diazotisation and coupling stages and by removing the excess of iodine, after oxidation of the hydroxylamine, by extraction into bromobenzene. The latter previously required chemical reduction to iodide.

Blom's method[1] of determining hydroxylamine, by oxidation with iodine to nitrite, which is then utilised to form a diazo dye, has been used by Johnson and Stansbury[2] as the basis of an end-method for the determination of residues of the carbamoyloxime insecticide aldicarb.* Improvements to Blom's method made by Csáky[3] and Jámbor and Kiss[4] were not adopted by Johnson and Stansbury. Csáky recommended the use of arsenite, rather than thiosulphate, to reduce the excess of iodine because colloidal sulphur, which interferes with the colorimetric determination of the dye, is readily formed from thiosulphate in the high concentrations of acetic acid used. Jámbor and Kiss conducted an extensive investigation of Blom's method and recommended that the oxidation of the hydroxylamine by iodine should be carried out in the dark, the pH of the solution during the diazotisation

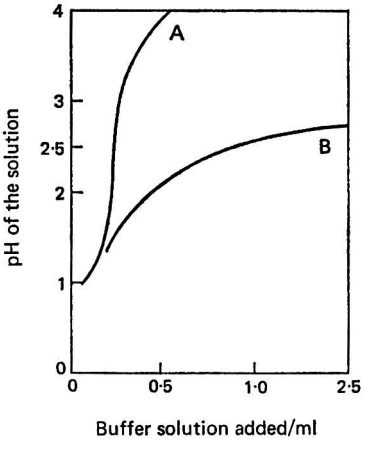

Fig. 1. Variation of pH with the volume of buffer solution added to a mixture of 0·5 ml of 0·1 N NaOH, 0·5 ml of N HCl, 0·5 ml of sulphanilic acid solution and 0·2 ml of glacial acetic acid: curve A, 2 M solution of potassium acetate as buffer; and curve B, 2 M solution of sodium dihydrogen phosphate as buffer

* Aldicarb is the B.S.I. name for 2-methyl-2-(methylthio)propionaldehyde *O*-(methylcarbamoyl)oxime.

and coupling stages should be maintained within a tenth of a unit of 2·5, and they also showed that the timing of the addition of the various reagents was critical. We confirmed that these were valid improvements but still had difficulty in obtaining reproducible results when working in the 0 to 6 μg of hydroxylamine range. Typically, within a group of determinations at the 3 μg (1·27 μg of nitrogen) level the final optical density varied between 0·39 and 0·73 units. These difficulties led us to make a detailed examination of Blom's method, which resulted in the improvements described below.

Previous workers have used potassium acetate for buffering the solutions for the diazotisation and coupling stages but we found it to be unsuitable because pH 2·5 lies in the range of pH where there is a rapid change when small increments of potassium acetate solution are added (see Fig. 1, curve A). Small volume errors in dispensing the solutions comprising the mixture at these stages can therefore result in large differences in final pH. Sodium dihydrogen phosphate was a more suitable buffer under the conditions used in our work (Fig. 1, curve B).

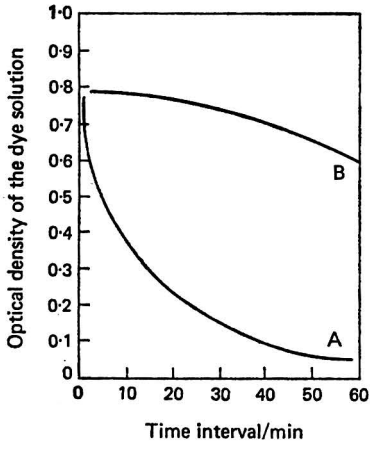

Fig. 2. Effect of the time interval between the removal of excess of iodine and the addition of 1-naphthylethylenediamine on the yield of dye: curve A, iodine reacted with thiosulphate; and curve B, iodine extracted into bromobenzene

As observed by Jámbor and Kiss, increasing the time interval between the removal of excess of iodine with thiosulphate (or arsenite) and the addition of the coupling reagent decreased the yield of dye (Fig. 2, curve A). This pointed to a rapid decomposition of the diazo ion caused by its reaction with the ionic species formed in the chemical reduction process. Such decomposition can be largely avoided by physically removing the excess of iodine by extraction into bromobenzene (Fig. 2, curve B). There is still some decay of the diazo ion but the loss during the first 10 minutes is insignificant (less than 1 per cent.) when compared with the loss in the same period with the thiosulphate system (greater than 50 per cent.). Thus the time interval between the removal of the excess of iodine with bromobenzene and the addition of the coupling reagent is not critical within a wide practical limit of several minutes. There is no interference with the subsequent development of the dye if the bromobenzene - iodine and aqueous phases are allowed to remain in contact and the optical density of the dye solution remains stable for several hours. 1-Naphthylamine was used as the coupling reagent by previous workers but as it is regarded as a potential carcinogen it was replaced in this investigation by 1-naphthylethylenediamine.

Experimental

Reagents—

Sodium hydroxide, 0·1 N aqueous solution.
Hydrochloric acid, 1·0 N aqueous solution.
Sulphanilic acid, 0·5 per cent. solution in 25 per cent. v/v acetic acid.
Sodium dihydrogen phosphate, 2·0 M aqueous solution.
Iodine, 0·5 per cent. in glacial acetic acid.
1-Naphthylethylenediamine dihydrochloride—Dissolve 0·5 g in 50 ml of glacial acetic acid *plus* 115 ml of water.
Acetic acid, glacial and 50 per cent. aqueous.
Bromobenzene, reagent grade.

One volume of the sulphanilic acid solution and two volumes of the sodium dihydrogen phosphate solution should be pre-mixed before use. The sulphanilic acid and the 1-naphthylethylenediamine solutions should be prepared freshly each week.

Standard solutions—

Prepare solutions of sodium nitrite in 0·1 N sodium hydroxide and of hydroxylamine in 1·0 N hydrochloric acid to contain 0·4, 1·0, 2·0, 3·0 and 4·0 μg of nitrogen per ml.

Apparatus—

This consisted of stoppered 10-ml calibrated cylinders fitted with removable light shields.

Procedure—

All solutions should be stored, and determinations conducted, away from direct daylight or high-intensity artificial illumination.

Nitrite calibration—To 0·5-ml aliquots of the standard nitrite solutions in the 10-ml cylinders add, in sequence, with mixing, 0·5 ml of 1·0 N hydrochloric acid, 1·5 ml of sulphanilic acid - sodium dihydrogen phosphate solution and 0·2 ml of glacial acetic acid. After 5 minutes add 1·0 ml of bromobenzene, stopper the cylinder and shake it vigorously for 30 s. Then allow the phases to separate, add 0·3 ml of 1-naphthylethylenediamine solution and gently invert the stoppered cylinder twice. After 5 minutes dilute the aqueous phase to 5·0 ml with 50 per cent. acetic acid and again gently invert the cylinder twice. Withdraw the upper phase and measure its optical density in a 10-mm cell at 530 nm against a matched 10-mm cell filled with water as a reference standard.

Nitrite - iodine calibration—The procedure is as described under *Nitrite calibration* except that the light shields are placed over the cylinders after the addition of the sulphanilic acid - sodium dihydrogen phosphate solution and the 0·2 ml of glacial acetic acid is replaced by 0·2 ml of the iodine solution.

Hydroxylamine calibration—The procedure is as described under *Nitrite - iodine calibration* above except that the nitrite solution is replaced by 0·1 N sodium hydroxide solution and the 1·0 N hydrochloric acid solution by 0·5 ml aliquots of the standard solutions of hydroxylamine in 1·0 N hydrochloric acid.

Results

By using the procedures outlined above, calibration graphs with the parameters shown in Table I were obtained over the range from 0 to 2·0 μg of nitrogen.

Table I

Parameters of calibration graphs for nitrite and hydroxylamine over the range 0 to 0·2 μg of nitrogen

System	Slope of least-squares fit, optical density units per μg of N*	Intercept on optical density axis	Root mean square deviation from least-squares fit,* optical density units
Nitrite	0·694	0·015	0·0243
Nitrite - iodine	0·654	0·010	0·0228
Hydroxylamine - iodine ..	0·582	0·005	0·0352

* Calculated from twenty-two points on each calibration.

The precision of these results shows a considerable improvement over the best that we were able to obtain with the excess of iodine being removed by chemical reduction when the root mean square deviations from the least-squares fit were of the order of 0·1 of an optical density unit. A concomitant improvement in the precision of determination of aldicarb was also obtained.

REFERENCES

1. Blom, J., *Ber. dt. chem. Ges.*, 1926, **59**, 121.
2. Johnson, D. P., and Stansbury, H. A., *J. Ass. Off. Analyt. Chem.*, 1966, **49**, 399.
3. Csáky, T. Z., *Acta Chem. Scand.*, 1948, **2**, 450.
4. Jámbor, B., and Kiss, J., *Acta Biol. Hung.*, 1956, **7**, 1.

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Determination of Orthophosphate in the Presence of Nitrate Ions

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A method is described for the spectrophotometric determination of orthophosphate in the presence of nitrate. Reduction of nitrate ions to ammonia is effected by aluminium metal and sodium hydroxide solution, and after the removal of all the ammonia produced (by heating) the phosphate is determined by the formation of the phosphomolybdate complex and reduction to molybdenum blue. The method is suitable for the determination of orthophosphate at a concentration of 10^{-4} M in the presence of more than 10^{-1} M of nitrate. It also overcomes interference by fluoride and other halide ions in the molybdenum-blue method.

Although numerous methods have been developed for the determination of fairly low levels of orthophosphate, one of the most widely applicable methods, the phosphomolybdate or molybdenum-blue method[1] (or its modifications[2,3]) is sensitive to interference by the nitrate ion and several halide ions, especially fluoride. The vanadatophosphomolybdate method[4] is relatively insensitive to interference by the nitrate ion, but unlike the molybdenum-blue method, it cannot be used for the determination of very low orthophosphate concentrations. Methods have been developed to overcome interference by nitrate in the molybdenum-blue determination of orthophosphate.[5,6,7] These methods involve either ashing the sample or introducing additional manipulative procedures, from which arise the possibility of unacceptably high experimental losses or contamination. More recently, methods have been developed for the determination of phosphorus by atomic-absorption spectroscopy,[8] when interference by nitrate should not occur. This technique does, however, require a fairly high initial capital equipment cost and may not be generally available.

The method described here is based on the well established molybdenum-blue method, whereby the reduction of orthophosphate and molybdate with hydrazinium sulphate yields a blue reduction product known as molybdenum blue. It is the absorption of this product that is interfered with by the nitrate and the halide ions. In the present method this interference is overcome by prior reduction of the nitrate ion to ammonia, which can be removed by heating. Quantitative collection of the ammonia evolved in standard hydrochloric acid, followed by titration with standard sodium hydroxide solution, may allow the simultaneous determination of nitrate and orthophosphate. The presence of aluminium in the solution results in the complexing of halide ions and the consequential removal of this source of interference. The method enables orthophosphate to be determined at or below the 10^{-4} M level in the presence of 10^{-1} M fluoride and M nitrate, providing that sufficient aluminium is used. It is useful, therefore, to have prior knowledge of the approximate levels of these ions so as to ascertain the amount of aluminium to be used.

Experimental

Reagents—

Sodium hydroxide solution (AnalaR), 10 M.

Aluminium wire (AnalaR), weight 10 *mg* cm^{-1}.

Sulphuric acid (AnalaR), 5 M.

Hydrazinium sulphate solution—Dissolve 1·5 g in 1 litre of de-ionised, distilled water.

Standard orthophosphate solution—Dissolve 0·2197 g of potassium dihydrogen orthophosphate in 1 litre of de-ionised, distilled water. (1 ml ≡ 0·05 mg of phosphorus.)

Standard nitrate solution, M—Dissolve 101·3 g of potassium nitrate in 1 litre of de-ionised, distilled water.

Standard fluoride solution, M—Dissolve 42·00 g of sodium fluoride in 1 litre of de-ionised, distilled water.

Molybdate solution—Dissolve 25 g of sodium molybdate in the minimum amount of water and add to 1 litre of 5 M sulphuric acid.

PROCEDURE—

A suitable volume of the sample solution containing both orthophosphate and nitrate was transferred by pipette into a 50-ml glass or polypropylene flask. AnalaR aluminium wire cut into five 2-cm lengths was added, followed by 2 ml of 10 M sodium hydroxide solution. Sufficient water was added to adjust the volume to about 10 ml. The flask was held in a water-bath maintained at a maximum temperature of 80 °C for between 25 and 30 minutes, during which time the aluminium wire dissolved and all the nitrate present was reduced to ammonia. By limiting the temperature of the water-bath to 80 °C, large reagent blanks that resulted from the glass of the apparatus being dissolved by alkali were avoided. If a simultaneous nitrate determination is required, the liberated ammonia can be collected in standard hydrochloric acid and titrated against a standard sodium hydroxide solution. Alternatively, any other preferred method of ammonia determination can be used. It was generally found that a flask was to be preferred to a beaker as the reduction proceeded more efficiently, probably by allowing the hydrogen produced to be retained for a longer period.

The orthophosphate solution, now free of nitrate, was cooled rapidly, and when the removal of ammonia was carried out in an uncalibrated flask, the contents of the vessel were quantitatively transferred to a 50-ml glass or polypropylene calibrated flask. Water (10 ml) was then added, together with one drop of phenolphthalein indicator. (Tests were undertaken to show that no interference occurred as a result of the use of this indicator.) The alkaline orthophosphate solution was neutralised with 5 M sulphuric acid. At the point of neutralisation a dense white precipitate, considered to be aluminium hydroxide, was formed. This was ignored, as it dissolved completely on adding a few (excess) drops of sulphuric acid. Then 2 ml of hydrazinium sulphate solution were added, followed by 5 ml of the molybdate reagent. The volume was adjusted to 50 ml and the contents of the flask were thoroughly shaken before the flask was placed in a boiling water bath for 20 minutes to allow full development of the blue colour. After rapid cooling, the absorbance of the solution was measured at 820 nm in 1-cm cells against a water blank subjected to the same experimental procedure. The phosphorus concentration of the solution was determined by reference to a suitable calibration curve constructed from solutions containing known amounts of orthophosphate. These solutions were subjected to the same experimental procedures as the samples containing unknown amounts of orthophosphate. Typical calibration curves for the normal molybdenum-blue method and for the modification reported here are shown in Fig. 1. It can be seen that there is little significant difference between the calibration curves for both methods.

RESULTS AND DISCUSSION

This procedure was evolved because of the need for the analysis of mother liquor arising from the synthesis of amorphous calcium orthophosphate from solutions containing calcium nitrate, sodium fluoride and disodium hydrogen orthophosphate.[9] In these solutions the nitrate concentration was often in the range 0·1 to 1 M, while the orthophosphate concentration was much lower. Although nitrate was known to interfere in the molybdenum-blue method, accurate details relating to the degree of interference were lacking. Accordingly, samples of a solution containing 0·05 mg of phosphorus as orthophosphate were taken and various amounts of standard nitrate solution were added. The apparent phosphorus concentration in these solutions was determined by the normal molybdenum method. The degree of interference, expressed as apparent phosphorus concentration *versus* nitrate concentration, is shown in Fig. 2 and indicates a rapid apparent loss of phosphorus in the presence of relatively small amounts of nitrate.

By using the method described here for the removal of nitrate from the orthophosphate solution, a method that is well known in nitrate analysis,[10] 0·05 mg of phosphorus in 50 ml of the determination solution (*i.e.*, 0·001 mg ml^{-1}) can be determined without interference by up to 2000 mg of nitrate in the determination solution (*i.e.*, 40 mg ml^{-1}). Higher nitrate concentrations can be accommodated by increasing the amount of aluminium wire and sodium

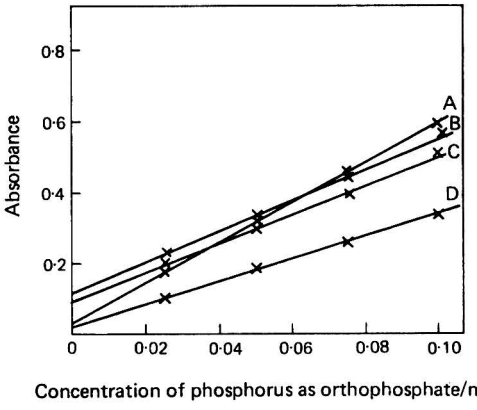

Fig. 1. Calibration graphs for the modified molybdenum-blue method with 2-cm cells. A, no nitrate added to glass flasks; B, 62 mg of nitrate added to 50-ml glass flasks and left overnight at room temperature; C, 62 mg of nitrate added to 50-ml glass flasks and left at 80 °C for half-an-hour; D, 62 mg of nitrate added to 50-ml polypropylene flasks and left at 80 °C for half-an-hour

hydroxide solution used. A slight increase (between 2 and 5 per cent.) in the absorbance of the reagent blank was observed on doubling the amounts of these two reagents used in nitrate removal. A calibration graph, obtained by using a total phosphorus concentration of up to 0·10 mg in 50 ml, appeared to be a straight line, indicating that Beer's law was obeyed within the limits of the experiment. At higher phosphorus concentrations the response was non-linear. The method is sensitive to a phosphorus concentration of 0·0004 mg ml^{-1}, *i.e.*, 0·02 mg of phosphorus added to the reagent blank. A possible slight disadvantage of this method is the tendency for the absorbance of the water blank to be somewhat higher than that obtained by the normal molybdenum-blue method, especially when the temperature of the water-bath used to effect the removal of ammonia is allowed to rise above 80 °C when glass apparatus is used. The high blank is undoubtedly caused by the walls of the containing vessel being slightly dissolved by the hot alkaline solution. This problem did not arise if the temperature of the water-bath was maintained at 80° C, or when polypropylene vessels were used. Neither was it observed if glass vessels were used and the nitrate reduction was allowed to proceed overnight at room temperature. The use of

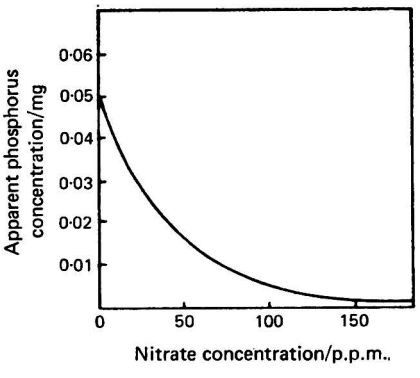

Fig. 2. Effect of nitrate ions on the determination of phosphorus by the molybdenum-blue method

aluminium to effect the reduction of nitrate did, however, result in an increase in the value of the reagent blank by some 2 to 5 per cent. compared with the value obtained by the normal molybdenum-blue method. This was minimised by the use of fresh sodium hydroxide solutions and the storage of all solutions in polypropylene containers. The increase in the absorbance of the reagent blank can be directly attributed to impurities in the aluminium wire and sodium hydroxide solution. The over-all increase in the absorbance has been estimated as being no more than a 3 per cent. increase over the water blank value from the normal molybdenum-blue method.

It is well known that fluoride causes bleaching of dyes used in many colorimetric determinations. As many of the sample solutions normally analysed for orthophosphate in these laboratories contain considerable amounts of fluoride and, on occasions, other halides, it was of interest to determine the fluoride concentration at which interference in the normal molybdenum-blue method of orthophosphate determination occurred. This determination was carried out on orthophosphate samples that were free from nitrate ions. Solutions containing 0·05 mg of phosphorus were used; the addition of a standard sodium fluoride solution was such that the final analytical solution contained up to 1000 mg of fluoride. By using the normal molybdenum-blue method the apparent phosphorus concentration was plotted against the fluoride concentration of the solution. The results obtained suggest that at a fluoride concentration of less than 500 mg, no interference with the orthophosphate determination occurred, although above this level severe interference was noted. However, no interference by fluoride at concentrations above 1000 mg was noted when the modified molybdenum-blue method described here was used. This is because of the formation of a complex of the type AlF_6^{3-} with the excess of aluminium present in the solution. A similar effect was noted with solutions containing chloride (interference in the normal molybdenum-blue method occurred when the chloride concentration was greater than 2·3 per cent. w/v) when the chloride concentration was 2·5 per cent. w/v or above. Here, complexing presumably resulted in the formation of either $AlCl_4^-$ or $AlCl_6^{3-}$. It was considered that it might be possible to overcome halide interference in the absence of nitrate ions by adding aluminium sulphate to the sample. Adding 2 ml of a 10^{-1} M aluminium sulphate solution to the orthophosphate samples containing 1000 mg of fluoride substantially reduced the interference by this ion in the normal molybdenum-blue method, if added before the molybdate reagent. It is apparent, therefore, that the formation of the AlF_6^{3-} complex must occur on, or immediately after, the removal of the nitrate from the solution. Presumably the presence of excess of sulphuric acid causes the preferential stabilisation of an $Al(SO_4)_3^{3-}$co mplex rather than the AlF_6^{3-} complex when aluminium sulphate is added after the addition of the reagent.

The use of ascorbic acid[3] instead of hydrazinium sulphate results in a more rapidc olour development. This modification of the basic method was examined by using the modified

TABLE I

ANALYTICAL RESULTS FOR MOTHER LIQUOR FOLLOWING PREPARATION OF CALCIUM ORTHOPHOSPHATE IN THE ABSENCE OF FLUORIDE*

	Concentration (mg ml^{-1}) of				
Time/hours	F^-†	Ca^{2+}	$H_2PO_4^-$	Na^+†	pH
0·00	$<10^{-4}$	$1{\cdot}65 \times 10^{-2}$	$5{\cdot}3 \times 10^{-2}$	$3{\cdot}3 \times 10^{-1}$	6·25
0·10	$<10^{-4}$	$1{\cdot}80 \times 10^{-2}$	$2{\cdot}3 \times 10^{-2}$	$3{\cdot}3 \times 10^{-1}$	6.32
0·20	$<10^{-4}$	$1{\cdot}75 \times 10^{-2}$	$9{\cdot}1 \times 10^{-3}$	$3{\cdot}3 \times 10^{-1}$	6·44
0·25	$<10^{-4}$	$1{\cdot}75 \times 10^{-2}$	$8{\cdot}4 \times 10^{-3}$	$3{\cdot}3 \times 10^{-1}$	7·00
0·50	$<10^{-4}$	$1{\cdot}75 \times 10^{-2}$	$7{\cdot}6 \times 10^{-3}$	$3{\cdot}3 \times 10^{-1}$	7·90
1·00	$<10^{-4}$	$1{\cdot}70 \times 10^{-2}$	$7{\cdot}4 \times 10^{-3}$	$3{\cdot}3 \times 10^{-1}$	8·12
2·00	$<10^{-4}$	$1{\cdot}75 \times 10^{-2}$	$7{\cdot}2 \times 10^{-3}$	$3{\cdot}3 \times 10^{-1}$	8·20
4·00	$<10^{-4}$	$1{\cdot}65 \times 10^{-2}$	$7{\cdot}1 \times 10^{-3}$	$3{\cdot}2 \times 10^{-1}$	8·09
24·00	$<10^{-4}$	$1{\cdot}70 \times 10^{-2}$	$7{\cdot}1 \times 10^{-3}$	$3{\cdot}2 \times 10^{-1}$	5·71
48·00	$<10^{-4}$	$1{\cdot}68 \times 10^{-2}$	$7{\cdot}0 \times 10^{-3}$	$3{\cdot}3 \times 10^{-1}$	5·57
72·00	$<10^{-4}$	$1{\cdot}71 \times 10^{-2}$	$7{\cdot}0 \times 10^{-3}$	$3{\cdot}2 \times 10^{-1}$	5·59
170·00	$<10^{-4}$	$1{\cdot}72 \times 10^{-2}$	$7{\cdot}1 \times 10^{-3}$	$3{\cdot}2 \times 10^{-1}$	5·59
250·00	$<10^{-4}$	$1{\cdot}67 \times 10^{-2}$	$7{\cdot}1 \times 10^{-3}$	$3{\cdot}2 \times 10^{-1}$	5·60
300·00	$<10^{-4}$	$1{\cdot}70 \times 10^{-2}$	$7{\cdot}1 \times 10^{-3}$	$3{\cdot}2 \times 10^{-1}$	5·58

* Taken from a paper to be published by E. J. Duff.[9]
† Determined by the method described in Ref. 11.

method reported here. It was found that the molybdenum-blue complex was de-stabilised when ascorbic acid was used. It was suggested that the solution should not be greater than 10^{-1} M in acid for the successful use of this, *i.e.*, ascorbic acid, modification. Such a concentration of acid was considerably exceeded in these samples and resulted in the rapid transformation of the blue coloration into a deep green colour on cooling the solution after colour development. Similar effects were observed on increasing the hydrazinium sulphate content of the solution.

The procedure described here provides a method that is especially applicable to samples containing small amounts of orthophosphate, as an alternative to other methods[4,6] of orthophosphate determination in the presence of nitrate. Typical results of analysis of mother liquor after the synthesis of amorphous calcium orthophosphate in the presence and absence of added fluoride are shown in Tables I and II, respectively. Theoretically, the method enables any amount of nitrate to be present and also effectively removes by complexing those halide ions that would otherwise interfere with the orthophosphate analysis.

Table II

Analytical results for mother liquor following preparation of calcium orthophosphate in the presence of fluoride*

Time/hours	Concentration (mg ml^{-1}) of F^-†	Ca^{2+}	$H_2PO_4^-$	Na^+†	pH
0·00	$2·2 \times 10^{-2}$	$7·0 \times 10^{-3}$	$7·3 \times 10^{-4}$	$3·3 \times 10^{-1}$	9·42
0·10	$2·3 \times 10^{-2}$	$4·96 \times 10^{-3}$	$7·5 \times 10^{-4}$	$3·3 \times 10^{-1}$	9·92
0·20	$2·1 \times 10^{-2}$	$4·57 \times 10^{-3}$	$6·7 \times 10^{-4}$	$3·2 \times 10^{-1}$	9·89
0·25	$2·1 \times 10^{-2}$	$4·63 \times 10^{-3}$	$6·0 \times 10^{-4}$	$3·3 \times 10^{-1}$	9·85
0·50	$2·1 \times 10^{-2}$	$4·57 \times 10^{-3}$	$6·1 \times 10^{-4}$	$3·2 \times 10^{-1}$	9·74
1·00	$2·0 \times 10^{-2}$	$3·68 \times 10^{-3}$	$5·7 \times 10^{-4}$	$3·2 \times 10^{-1}$	9·25
2·00	$1·4 \times 10^{-2}$	$3·13 \times 10^{-3}$	$5·4 \times 10^{-4}$	$3·1 \times 10^{-1}$	9·19
4·00	$2·0 \times 10^{-3}$	$2·70 \times 10^{-3}$	$5·2 \times 10^{-4}$	$3·1 \times 10^{-1}$	8·78
24·00	$2·0 \times 10^{-3}$	$2·69 \times 10^{-3}$	$5·25 \times 10^{-4}$	$2·7 \times 10^{-1}$	8·45
48·88	$1·5 \times 10^{-3}$	$1·69 \times 10^{-3}$	$5·3 \times 10^{-4}$	$2·5 \times 10^{-1}$	8·27
72·00	$1·2 \times 10^{-3}$	$1·38 \times 10^{-3}$	$5·3 \times 10^{-4}$	$2·3 \times 10^{-1}$	8·10
170·00	$1·2 \times 10^{-3}$	$1·13 \times 10^{-3}$	$5·2 \times 10^{-4}$	$1·8 \times 10^{-1}$	7·00
200·00	$1·0 \times 10^{-3}$	$1·05 \times 10^{-3}$	$5·1 \times 10^{-4}$	$1·5 \times 10^{-1}$	6·45
225·00	$1·0 \times 10^{-3}$	$1·00 \times 10^{-3}$	$5·2 \times 10^{-4}$	$1·4 \times 10^{-1}$	6·25
250·00	$0·85 \times 10^{-3}$	$9·25 \times 10^{-4}$	$5·05 \times 10^{-4}$	$1·3 \times 10^{-1}$	6·05
300·00	$0·85 \times 10^{-3}$	$9·50 \times 10^{-4}$	$5·1 \times 10^{-4}$	$1·3 \times 10^{-1}$	6·10

* Taken from a paper to be published by E. J. Duff.[9]
† Determined by the method described in Ref. 11.

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References

1. Vogel, A. I., "Textbook of Quantitative Inorganic Analysis," Third Edition, Longmans, Green & Co. (Publishers) Ltd., London, 1961, p. 810.
2. Ammon, R., and Hinsberg, K., *Z. physiol. Chem.*, **1939**, **239**, 207.
3. Chen, P. S., Tonbara, T. Y., and Warner, H., *Analyt. Chem.*, 1956, **28**, 1756.
4. Elwell, W. T., and Wilson, H. N., *Analyst*, 1956, **81**, 136.
5. Michelsen, O. B., *Analyt. Chem.*, 1957, **29**, 60.
6. Fogg, D. N., and Wilkinson, N. T., *Analyst*, 1958, **83**, 406.
7. Archer, K., Flint, D., and Jordan, J., *Fuel, Lond.*, 1958, **37**, 421.
8. Keuber, J. D., Barnett, W. B., and Kahn, H. L., *Atomic Absorption Newsletter*, 1970, **9**, 39 (and references cited therein).
9. Duff, E. J., *J. Chem. Soc., A*, in the press.
10. Belcher, R., and Nutten, A. J., "Quantitative Inorganic Analysis," Second Edition, Butterworth & Co. (Publishers) Ltd., London, 1960, p. 198.
11. Duff, E. J., and Stuart, J. L., *Analyst*, in preparation.

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The Determination of Epichlorohydrin in Aqueous Solutions in the Presence of Glycerin, Monochlorohydrin and Glycidol

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Epichlorohydrin can be extracted from aqueous solutions containing glycerin, monochlorohydrin and glycidol into carbon tetrachloride and determined by infrared spectrophotometry. The high-frequency component of the complex band at a wavenumber 1274 cm^{-1} is used as the analytical band. A three-fold excess of carbon tetrachloride over the aqueous phase is necessary for the quantitative extraction. A cell thickness of up to 1 mm can be used; the concentration limit of the solute in the aqueous phase is then 0·3 per cent. v/v.

A COMPLETE analysis of the reaction mixture formed in the preparation of synthetic glycerin from epichlorohydrin is rather complicated as, in addition to the initial reactants and final product, and mineral salts, the aqueous reaction solution contains monochlorohydrin and, depending on the method of preparation, also glycidol. The extent of reaction can be determined if the amount of unreacted epichlorohydrin is accurately known.

In general, the presence of chlorine and of the epoxy group can be utilised in the determination of epichlorohydrin. In the mixtures studied organochlorine present in the admixtures interferes. The epoxy group can be determined in non-aqueous media by the addition of hydrogen chloride to the epoxy group[1] by using pyridinium chloride, pyridinium perchlorate, etc. The method devised by Ross[2] is based on the addition of thiosulphate and the titration of the alkalinity formed, and requires the application of empirical correction factors.

Infrared spectroscopy was used in the determination of epichlorohydrin in aqueous solutions by Le Noble and Duffy[3] in the course of their study of the acid-catalysed hydrolysis.

PRINCIPLE OF THE METHOD

To facilitate the determination of epichlorohydrin in a mixture with monochlorohydrin and glycerin, the different solubilities of the components can be utilised. Glycerin and monochlorohydrin are soluble in water in all proportions and almost insoluble in carbon tetrachloride, whereas epichlorohydrin is only slightly soluble in water and completely miscible with carbon tetrachloride. Glycidol is soluble in water as well as in carbon tetrachloride; when extracted, however, it remains quantitatively in the aqueous phase. Epichlorohydrin can therefore be extracted from an aqueous mixture into carbon tetrachloride and determined by an appropriate method.

Infrared spectrophotometry can serve as a convenient analytical technique for the determination. Epichlorohydrin gives an infrared spectrum with a series of sharp bands. The complex band with the main maxima at 1264 and 1273 cm^{-1} can be used as the analytical band. No absorption appears above 1300 cm^{-1}, and therefore this range can serve for the construction of the base-line for the spectrum of the mixture. Additionally, the other components have no interfering bands at 1200 to 1300 cm^{-1}.

EXPERIMENTAL

In order to study the method for the determination of epichlorohydrin in aqueous solutions a stock solution A was prepared by dissolving 0·5 ml of epichlorohydrin in 15 ml of water. An aliquot of solution A was then diluted with water (see Table I) and shaken

with carbon tetrachloride on a shaking machine. After separation, the organic phase was measured on a Perkin-Elmer 325 grating infrared spectrophotometer (slit program 5) in sodium chloride cells (cell thickness 1·02 mm).

Results and discussion

The measurements showed that none of the three main admixtures are sufficiently soluble in carbon tetrachloride to influence the infrared spectrum. The conditions for the quantitative extraction of epichlorohydrin were examined; the examination revealed that carbon tetrachloride should be in a three-fold excess with respect to the aqueous phase, the extraction time being 1 hour.

Glycerin does not interfere, even in a one hundred-fold excess: the spectra obtained with solutions extracted from a mixture of 1·5 ml of solution A and 5 ml of water and from a mixture of 1·5 ml of solution A and 5 ml of glycerin were identical in the range studied.

Comparison of the values obtained for the two band components showed that the high-frequency component leads to more accurate results. This can be attributed to the greater effect of absorption by the solvent that occurs in the 1-mm cells at frequencies lower than 1270 cm^{-1}.

Table I

Determination of epichlorohydrin in aqueous solutions by infrared spectrophotometry

Amount of solution A per 10 ml (m)/ml	Absorbance (A)	km*	$\delta \times 10^3$†	$\delta^2 \times 10^6$
1	0·068	0·067	1	1
2	0·136	0·134	2	4
3	0·202	0·201	1	1
4	0·263	0·268	−5	25
5	0·337	0·335	2	4
6	0·400	0·402	−2	4
7	0·459	0·469	−10	100
8	0·544	0·536	8	64
9	0·598	0·603	−5	25
10	0·678	0·670	8	64

* k = 0·067 04 (from linear equation $A = km$).
† $\delta = A - km$.
$\Sigma\delta^2 = 292 \times 10^{-6}$.

The analytical band component was at 1274 cm^{-1}. The solutions for analysis were obtained by extracting m ml of solution A *plus* (10 − m) ml of water with 30 ml of carbon tetrachloride.

The results of the determination of epichlorohydrin in standard solutions are given in Table I. The linear relationship between absorbance and the volume of solution taken was treated by the least-squares method. The straight-line graph can be expressed as $A = km$ with k = 0·067 04. The standard deviation of scatter was shown by the equation—

$$s = [\Sigma\delta^2/(n - 2)]^{\frac{1}{2}} = 0{\cdot}006$$

while the standard deviation of the proportionality coefficient was shown by—

$$s_k = s/[\Sigma m_i^2 - \frac{1}{n}(\Sigma m_i)^2]^{\frac{1}{2}} = 0{\cdot}0007$$

Taking into account the specific gravity of epichlorohydrin (1·17) and the molecular weight (92·53), then

1 ml of solution A ≡ 0·5 ml of solute/15 ≡ 39 mg of epichlorohydrin,

1 ml of solution A shaken with 30 ml of carbon tetrachloride gives 1·30 mg of solute per ml of carbon tetrachloride and the absorptivity is given by—

$$a = A/cd = \frac{6{\cdot}70 \times 10^{-2}}{1{\cdot}30 \times 10^{-3}\ \text{g cm}^{-3} \times 0{\cdot}102\ \text{cm}} = 505\ \text{cm}^2\ \text{g}^{-1}$$

or

$$a = \frac{6{\cdot}70 \times 10^{-2}}{(1{\cdot}30/92{\cdot}53)\ \text{mol l}^{-1} \times 0{\cdot}102\ \text{cm}} = 46{\cdot}7\ \text{l mol}^{-1}\ \text{cm}^{-1}$$

where c is the concentration of epichlorohydrin and d is the path length.

When limited to a cell thickness of 1 mm (absorption by the solvent interferes when thicker cells are used) the solution comprising 1 ml of solution A *plus* 9 ml of water represents the limit for quantitative determination; the corresponding concentration is approximately 0·3 per cent. v/v.

References

1. Schrade, J., *Kunststoffe*, **1953**, **43**, 266.
2. Ross, W. C. J., *J. Chem. Soc.*, **1950**, 2257.
3. Le Noble, W. J., and Duffy, M., *J. Phys. Chem.*, **1964**, **68**, 619.

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The Use of Back-flushing with Electron-capture Gas Chromatography

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An apparatus is described that enables materials with a longer retention time than those of interest to be back-flushed out of electron-capture gas chromatographs. Shorter analysis times, a longer column life and less frequent cleaning of the detectors have been achieved with this device.

The reversal of flow through a gas-chromatographic column so as to elute more quickly compounds with longer retention times than those of interest (back-flushing), has been a recognised technique for many years.[1] The major advantage of the technique is the shortened analysis time. During the analysis of residual chemicals, particularly of pesticides in soil, water and crops, by electron-capture gas chromatography, both columns and detectors become contaminated with long retained co-extracted materials. The use of back-flushing in these analyses should, therefore, give the additional advantages of lengthened column life and increased intervals between detector cleaning operations. Although back-flushing has been used for residue analysis with a flame-ionisation detector,[2] its use with electron-capture detectors has not been reported, probably because of the sensitivity of that detector to changes in operating conditions, particularly gas flow. Two systems that appeared likely to minimise changes in operating conditions have been described by Crossley[2] and Deans.[3]

The techniques as reported were found to be unsuitable for use with electron-capture detectors, but a suitably modified system has given satisfactory results.

Experimental

Initially, the two back-flushing systems were constructed as reported. When in operation, the Crossley[2] system gave large base-line deviations that were caused by the different gas flows reaching the detector in the injection and back-flush gas flow patterns, by the build up of contaminants in the carrier gas in sections of the system where the gas was static during one or other gas flow pattern, and by the diaphragm valves used (British Oxygen Co. and Fisher) being unable to maintain a sufficiently constant pressure under the fluctuating gas flow conditions. Although the Deans[3] system overcame the first problem, the other two remained. The base-line deviations (70 per cent. full-scale deflection at attenuation 5×10^2) did not return to zero for about 10 minutes after changing to back-flush.

The system shown in Fig. 1 was therefore designed with these points in mind. The gas restrictor had a flow resistance equal to that of the main column, and CB a flow resistance equal to the pre-column AB. Valve V was opened to inject, and closed to back-flush. The system minimised static conditions and maintained the gas flow through the pressure control valve at an almost constant level.

The flow changes to the detector were not completely eliminated because of the different flow resistances of the two pre-columns in parallel *plus* the column during injection, and the one pre-column *plus* the column during back-flushing. The effects were minimised, however, and base-line deviation was, at the most, a small percentage of full scale at the maximum usable sensitivity of the detector (about $2{\cdot}5 \times 10^{-11}$ A). This effect, the magnitude of which differed with different instrument conditions, was not observed to affect the quantitative or qualitative analysis of any compound investigated. The majority of the analyses have been of organochlorine insecticides, phenoxyacetic acid herbicides and acrylamide in water.

In preliminary experiments, a pre-column length of 100 mm was chosen arbitrarily. As shorter pre-columns should reduce pressure differences at point B (Fig. 1), 50 and 75-mm

columns were also used. They were not successful, however, as clean fraction cutting could not be achieved. It is suspected that a portion of the longer retained materials was forced through to the main column by the sudden increase in pressure caused by the flash evaporation of 5 μl of solvent. Pre-columns 100 mm in length were the shortest that could be used successfully with the solvents tested (petroleum ether, diethyl ether and ethyl acetate).

CONSTRUCTION AND OPERATION—

The unit was constructed as in Fig. 1 with the pre-column forming AB. A needle valve adjusted to have the same flow resistance as the pre-column, or a second pre-column, formed the restriction at CB.

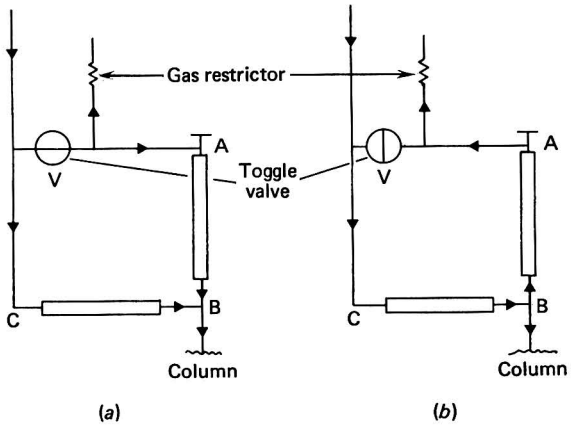

Fig. 1. (*a*), Injection and (*b*), back-flushing apparatus

In the analysis of pesticide residues it is often important to use an all-glass system so as to avoid sample decomposition.[4] The unit was designed to meet these requirements. A replaceable glass injection area was included, which minimised back-diffusion effects; this was joined to the pre-column by a glass-lined connector. Detailed diagrams of the injection zone (A) and the pre-columns-to-column T-joint (B) are shown in Figs. 2 and 3, respectively.

To avoid any possibility of the detector or column becoming contaminated by the break-down of non-volatile materials in the injection area, the unit was normally operated in the back-flush mode (V closed). Immediately before injection, valve V was opened. After injection it was left open until all the components of interest had passed point B and then closed. The length of time that valve V was open was determined by trial and error, and

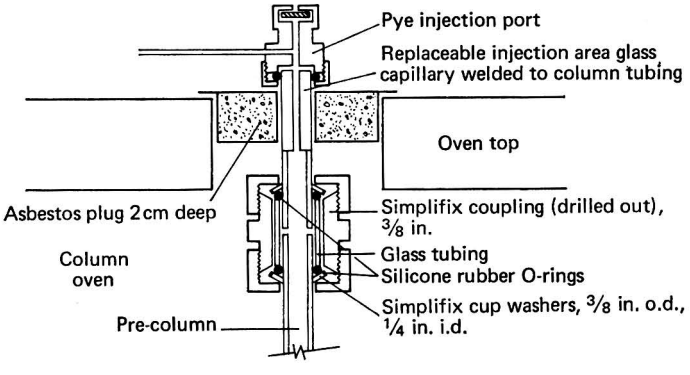

Fig. 2. Injection area

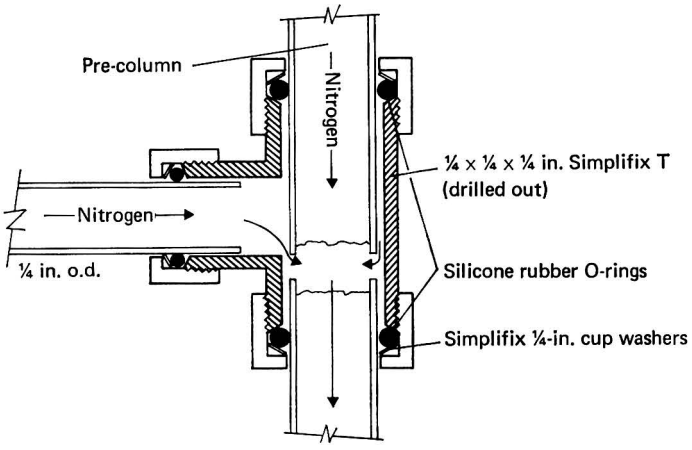

Fig. 3. T-joint

was the minimum time that gave no reduction in the area of the peaks produced by the compounds of interest when compared with the area if there was no back-flushing. After prolonged back-flushing, contaminants, probably from the valve diaphragm, built up in valve V where there was no gas flow. These were released during injection causing large base-line fluctuations. It was advisable to clear these by switching to injection until the base-line had returned to the normal level before injecting a sample. This procedure was always followed at the beginning of each day. Operation then proceeded as above.

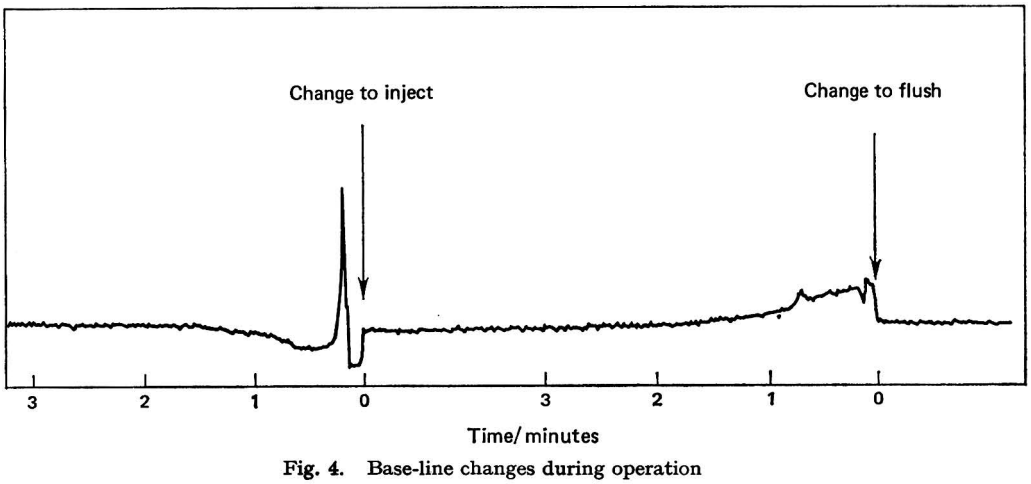

Fig. 4. Base-line changes during operation

Results

The base-line perturbations obtained on changing from back-flush to injection and *vice versa* are shown in Fig. 4. These results were obtained at the maximum usable sensitivity of a Pye 104 gas chromatograph at which 1 pg of lindane gave a recorder response of 5 per cent. full-scale deflection (attenuation 5×10^2; pulse interval 150 μs). It can be seen that the base-line returned to the steady state after 2 minutes, but that for many purposes a usable base-line was achieved within a few seconds of changing from one mode to the other.

Fig. 5 shows the type of separation possible with this unit when using an injection of

1 ng of 2,4-D methyl and isopropyl esters (at attenuation 10×10^2). The first chromatogram was obtained with the apparatus in its injection mode for the whole analysis. In the second analysis, the pre-column was back-flushed from 1 minute 20 seconds after injection. It can be seen that the second component has been removed from the chromatogram without any loss of the first, and also that the retention time of the 2,4-D methyl ester peak is marginally larger when back-flushing is used. This effect is caused by the lower gas flow through the pre-column. The small difference in gas flow to the detector can give rise to sensitivity changes between back-flushed and non-back-flushed chromatograms in some detectors. This effect was not noticed in the Pye 104 detector, and neither of the above effects was detrimental to quantitative analysis provided that calibrations were made with the same back-flushing conditions as for the samples.

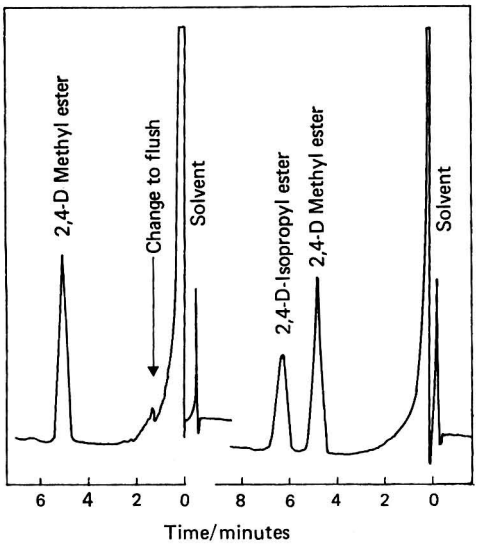

Fig. 5. An example of back-flushing

The system has been used regularly in these laboratories with successful results for more than 6 months. A chromatograph with a tritium foil d.c. detector has also been converted. In this instrument, the intervals between detector cleaning have at least doubled since the modification. Successful analyses have been made with various sizes of glass and metal columns with liquid-phase coatings of 6 per cent. FFAP, 1 per cent. FFAP, 1 per cent. neopentylglycol succinate, 5 per cent. QF-1, 3 per cent. XE-60, 1 per cent. Apiezon M and 2·5 per cent. OV-1. The operating temperature of these columns varied from 25 to 225 °C and the nitrogen flow-rates from 25 to 200 ml min^{-1}.

I thank the Director of the Water Research Association for permission to publish this paper.

References

1. Coates, V. J., Noelbels, A. J., and Fayerson, I. S., *Editors*, "Gas Chromatography," Academic Press, New York, 1958, p. 87.
2. Crossley, J., *Chem. & Ind.*, **1966**, 1969.
3. Deans, D. R., *J. Chromat.*, **1965**, **18**, 477.
4. de Faubert Maunder, M. J., Egan, H., and Roburn, J., *Analyst*, **1964**, **89**, 157.

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An Enzymic Method for the Determination of Dried Skimmed Milk in Mashed Potato Powders

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An enzymic method is described for the determination of dried skimmed milk in mashed potato powders. The method is based on the determination of free lactose by its hydrolysis with β-galactosidase, the glucose formed being determined by the hexokinase method. The determination is free of interference from varying concentrations of reducing sugars found in dried potatoes. Accuracy and reliability are greater with this method than with other methods currently in use.

EXISTING methods for the determination of dried skimmed milk in mashed potato powders rely upon the chemical determination of total nitrogen or lactose.

The determination based on total nitrogen can be unreliable because of the natural variation in nitrogen content of dried potatoes, the main ingredient of mashed potato powders. This variation, normally 1 to 2 per cent.,[1] may vitiate the method as only 1 per cent. of nitrogen would account for over 15 per cent. of dried skimmed milk. On the other hand, the direct determination of lactose content by Lane and Eynon's method[2] is liable to interference from the varying concentrations of other reducing sugars found in dried potatoes. The content of these reducing sugars may vary from 0·25 to 3 per cent.[1] but can exceed even 3 per cent. in the dried matter prepared from the stored potatoes, depending on the stage of maturity and temperature of storage of the potatoes.[1] Selective fermentation with yeast to eliminate these interfering sugars is tedious and not practical for routine laboratory use.

This paper describes an enzymic method for the determination of dried skimmed milk in mashed potato powders. The method is similar to that previously developed for the determination of skimmed milk powder in sausages,[3] and is based on the enzymic determination of free lactose. The free lactose is hydrolysed with β-galactosidase to glucose, which is determined by the hexokinase method.[3]

EXPERIMENTAL

APPARATUS—

All readings, at a wavelength of 340 nm, were carried out on a Pye Unicam SP800 spectrophotometer by using silica cells with a light path of 1 cm. A Marburg pipette (20 μl) was used for transferring small amounts of β-galactosidase.

REAGENTS—

*Glucose test combination kit (hexokinase method).** According to the supplier's instructions, prepare the following three solutions, and use suspension (*iv*) undiluted: solution (*i*), 0·3 M with respect to triethanolamine buffer (pH 7·5) and 0·004 M with respect to magnesium sulphate; solution (*ii*), 0·012 M nicotinamide-adenine dinucleotide phosphate (NADP); solution (*iii*), 0·016 M adenosine triphosphate (ATP); and suspension (*iv*), 1 mg ml^{-1} of hexokinase (HK) and 1 mg ml^{-1} of glucose-6-phosphate dehydrogenase (G-6-PDH).

β-Galactosidase, pure, specific activity 30 Units mg^{-1}.†

Dialysed iron solution, about 5 per cent. iron(III) oxide, laboratory-reagent grade.

Sodium sulphate solution—Dissolve 200 g of laboratory-reagent grade sodium sulphate decahydrate in de-ionised water and make the volume up to 1 litre.

* Obtainable from the Boehringer Corporation (London) Ltd., Catalogue No. 15931 TGAB.
† Obtainable from the Boehringer Corporation (London) Ltd., Catalogue No. 15079 EGAY.

PREPARATION OF AN AQUEOUS EXTRACT OF MASHED POTATO POWDER—

Macerate 2·5 g of well mixed mashed potato powder with 15 ml each of the dialysed iron and sodium sulphate solutions and 220 ml of water. Filter the mixture through a 15-cm Whatman No. 4 filter-paper. Dilute 20 ml of the filtrate to 100 ml with de-ionised water (test solution).

LACTOSE DETERMINATION—

Prepare a mixture of solutions (*i*), (*ii*) and (*iii*) and suspension (*iv*) in the proportions 2·0:0·1:0·1:0·02. In sequence, transfer by pipette 1 ml of test solution and 2 ml of the mixture into each of two silica cells.

To one cell (blank cell) add 0·02 ml of the de-ionised water and to the other cell (test cell) add 0·02 ml of β-galactosidase suspension. Mix the contents of each cell by using a separate small plastic paddle or a glass rod with a flattened end. After incubation at 25 °C for 1 hour measure the increase in the optical density of the test cell (against the blank) at a wavelength of 340 nm. Repeat this measurement after a further 10 minutes to ensure that the reaction is complete.

The concentration (C) of lactose in the test solution ($\mu g\ ml^{-1}$) is calculated from the equation—

$$C = \frac{E \times V \times MW}{\epsilon \times v \times d}$$

where E is the measured increase in optical density change at a wavelength of 340 nm, V is the total volume of the solution in the cell, ϵ is the extinction coefficient of reduced nicotinamide-adenine dinucleotide phosphate (NADPH) at wavelength 340 nm (6·22 $cm^2\ \mu mol^{-1}$), MW is the molecular weight of lactose, d is the light path of the cell and v is the volume of the test solution.

The enzyme mixture is stable for 12 hours at 25 °C. For routine determinations it is desirable to prepare the daily requirement freshly every day. The reactions for a batch of samples can be carried out in small test-tubes (75 × 12 mm) and the extinction measured in a single pair of matched silica cells that can be washed and dried for immediate re-use.

RESULTS

The accuracy of the proposed method for the determination of lactose was established as described in an earlier paper,[3] assays of analytical-reagent grade lactose monohydrate by this method being compared with those by the titrimetric method of Lane and Eynon.[2]

To test the suitability of this method for determining dried skimmed milk in mashed potato powders, recovery tests were carried out on laboratory-prepared samples with known concentrations of dried skimmed milk of known lactose content. The results, given as the average of six determinations at each concentration with their standard deviations, are presented in Table I.

TABLE I

RECOVERY OF DRIED SKIMMED MILK FROM LABORATORY-PREPARED SAMPLES OF MASHED POTATO POWDERS

Dried skimmed milk added, per cent.	Dried skimmed milk found, per cent.	Standard deviation	Recovery, per cent.
0	0	0	0
5	4·90	±0·04	98·0
10	9·92	±0·08	99·2
15	14·84	±0·17	98·9
20	19·60	±0·21	98·0

The results show satisfactory recoveries over a wide range of concentrations of dried skimmed milk in mashed potato powders (0 to 20 per cent.). It has been established previously that various supplies of dried skimmed milk available for commercial use in the United Kingdom contained different concentrations of lactose.[3] The lactose contents of fourteen different supplies, calculated as the monohydrate, gave an average of 51·3 per cent., with a standard deviation of ±2·1.[3] By using this average lactose monohydrate figure of 51·3 per

cent., the dried skimmed milk contents of retail mashed potato powders sold in London were determined. Table II lists the results obtained from different batches of four brands sampled over 6 months.

TABLE II

DRIED SKIMMED MILK IN RETAIL MASHED POTATO POWDERS

	Dried skimmed milk in six samples, per cent.					
Brand	1	2	3	4	5	6
1	15·4	14·8	15·2	12·5	12·9	13·0
2	12·3	11·8	11·2	12·2	13·9	14·4
3	13·8	12·1	14·6	14·2	14·9	14·0
4	7·4	7·2	7·6	6·7	7·0	6·9

CONCLUSIONS

Study of the proposed method shows that it is precise and accurate in respect of over-all procedure and recovery efficiency. The only factor that may affect the determination is the variation in the lactose content of the various skimmed milk powders available for commercial use. However, by using the average figure of 51·3 per cent. of lactose monohydrate, the result given by the analysis can be expected to be within 1 per cent. of the recipe. The accuracy of the determination will be further enhanced for products made from dried skimmed milk manufactured in the United Kingdom, for which the range of this variation is small.[3]

The method is rapid and simple and the complete determination does not take longer than 1½ hours, of which the actual working time does not exceed 15 minutes; the method is free of any interference from reducing sugars present in dried potatoes, the error being eliminated by the use of a sample blank. Ingredients such as salt, milk fat, pepper, glycerol monostearate, emulsifying salts, sorbitan tristearate, sodium bisulphite and antioxidants such as butylated hydroxytoluene or butylated hydroxyanisole do not interfere in this method.

The successful use of the method depends upon the strict observation of the usual precautions necessary with enzymic assays.

The author thanks the Directors of J. Sainsbury Ltd. for permission to publish this work, Mr. E. F. Williams for his advice throughout the investigation and Mr. P. W. Ratcliff and Mr. Dennis Neck for their help in the preparation of this paper.

REFERENCES

1. Burton, W. G., "The Potato," Second edition (completely revised), H. Veenman & Zonen N.V., Wageningen, The Netherlands, 1966, p. 146.
2. Lane, J. H., and Eynon, L. J., *J. Soc. Chem. Ind., Lond.*, 1923, **42**, 32.
3. Bahl, R. K., *Analyst*, 1971, **96**, 88.

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Analyst, November, 1971, Vol. 96, *pp.* 817–823

Analytical Methods Committee

REPORT PREPARED BY THE PROPHYLACTICS IN ANIMAL FEEDS SUB-COMMITTEE

The Determination of Carbarsone in Animal Feeds

THE Analytical Methods Committee has received the following Report from its Prophylactics in Animal Feeds Sub-Committee. The Report has been approved by the Analytical Methods Committee and its publication has been authorised by the Council.

REPORT

The constitution of the Prophylactics in Animal Feeds Sub-Committee responsible for the preparation of this Report was: Mr. S. G. E. Stevens (Chairman), Mr. R. J. Anderson, Mr. M. D. Beach, Mr. A. G. Croft, Mr. C. E. Dodd, Mr. G. Drewery, Mr. J. Hartley, Mr. R. S. Hatfull, Mr. S. P. Hayes, Mr. J. S. Leahy, Mr. I. McLachlan, Mr. J. Markland, Mr. D. H. Mitchell, Mr. R. C. Spalding, Mr. J. A. Stubbles, Mr. R. E. Weston and Dr. D. R. Williams, with Mr. P. W. Shallis as Secretary.

INTRODUCTION

Carbarsone (4-ureidophenylarsonic acid) is an organic arsenical having anti-blackhead activity, and is used as an additive in poultry feedingstuffs, usually at a level of about 375 p.p.m. Few analytical methods have been proposed for the determination of carbarsone. The drug is, however, the subject of a monograph in the British Pharmacopoeia 1963, in which the assay specified is a total arsenic determination. The Sub-Committee was of the opinion that a method based on a total arsenic determination was insufficiently specific for recommendation. It was known that carbarsone is readily hydrolysed by alkali to arsanilic acid, which can then be determined by diazotisation and coupling with *N*-1-naphthylethylenediamine dihydrochloride, and the Sub-Committee decided to investigate the possibility of providing a method based on this principle.

EXPERIMENTAL

In the first instance, one laboratory applied the principle of diazotisation and coupling to the determination of carbarsone in a feedingstuff. The drug was extracted from the feed with dilute hydrochloric acid, a portion of the filtered extract was hydrolysed with sodium hydroxide solution and an equal portion was taken through the remainder of the procedure without hydrolysis. After treatment with sodium nitrite and ammonium sulphamate, *N*-1-naphthylethylenediamine dihydrochloride was added to each solution and the absorptions were measured at 545 nm against water. The carbarsone content of the sample was calculated from the arsanilic acid equivalent of the increase in absorption after alkaline hydrolysis, read from a standard graph prepared with pure arsanilic acid. This laboratory obtained recoveries of carbarsone of 90 to 93 per cent. by the method.

Other laboratories then applied this method to the determination of carbarsone in a circulated feedingstuff, but with little success. One of these laboratories carried out a detailed re-appraisal of the method and concluded that several factors were responsible for the difficulties encountered. The greatest difficulty was found to be the variability of the blank value on the feed owing to turbidity of the solution, and this, it was thought, could be overcome by extraction of the coloured product into an organic solvent. Further difficulty owing to turbidity in the unhydrolysed solution was found to be overcome, without affecting the recovery of carbarsone, by the addition of sodium chloride to the acid solution used for extracting the drug from the feed. There was also evidence that hydrolysis of the carbarsone with boiling sodium hydroxide solution caused some degradation of the arsanilic acid produced, giving absorbance values for the hydrolysed solution somewhat lower than the true values. Solutions of carbarsone did not, therefore, give 100 per cent. recovery when

TABLE I

RESULTS OF CARBARSONE COLLABORATIVE TEST

Laboratory	Sample	Weight of carbarsone added to 10-g sample/mg	Weight of carbarsone found/mg	Recovery, per cent.
Results on Sample 1—				
A	1a	3·88	2·85	73·5
	1b	3·70	3·26	88·1
	1c	3·70	2·90	78·4
B	1a	3·90	3·16	81·0
	1b	3·90	3·33	85·4
	1c	3·86	3·43	88·9
C	1a	4·09	3·88	94·9
	1b	3·65	3·50	95·9
	1c	3·72	3·49	93·8
D	1a	4·00	3·80	95·0
	1b	3·70	3·50	94·6
	1c	3·90	3·80	97·4
E	1a	3·77	3·63	96·3
	1b	3·91	3·70	94·6
	1c	3·96	3·88	98·0
F	1a	3·90	3·59	92·1
	1b	3·77	3·53	93·6
	1c	3·90	3·75	96·2
Results on Sample 2—				
A	2a	3·88	3·63	93·6
	2b	3·88	3·97	102·3
	2c	3·88	4·16	107·2
B	2a	3·86	3·40	88·1
	2b	3·82	3·52	91·2
	2c	3·90	3·41	87·4
C	2a	4·07	3·96	97·3
	2b	3·96	3·76	95·0
	2c	4·08	3·85	94·4
D	2a	3·90	3·70	94·9
	2b	3·80	3·70	97·4
	2c	3·90	3·70	94·9
E	2a	3·83	3·64	95·0
	2b	3·91	3·85	98·5
	2c	3·76	3·56	94·7
F	2a	3·74	3·25	86·9
	2b	3·96	3·40	85·9
	2c	3·87	3·70	95·6
Results on Sample 3—				
A	3a	3·88	3·77	97·2
	3b	3·88	3·77	97·2
	3c	3·88	3·32	85·6
B	3a	3·95	3·44	87·1
	3b	3·94	3·27	83·0
	3c	3·76	3·27	87·0
C	3a	4·02	3·88	96·5
	3b	3·87	3·71	95·9
	3c	4·12	3·92	95·9
D	3a	4·00	4·00	100·0
	3b	4·00	3·80	95·0
	3c	3·80	3·60	94·7
E	3a	3·90	3·68	94·4
	3b	3·82	3·80	99·5
	3c	3·95	3·78	95·7
F	3a	3·86	3·70	95·8
	3b	3·96	3·70	93·4
	3c	3·96	3·80	96·0

compared with the arsanilic acid standard graph, and it was considered that, as a further loss occurred when the determination was carried out on a feed extract, the effect could be reduced by using carbarsone for the preparation of the standard graph.

The method was modified in accordance with these observations and a collaborative test arranged, but further difficulties were encountered. Erratic and low recoveries were obtained, which were found to be caused by the extraction of silica from the glassware during hydrolysis with boiling sodium hydroxide solution. The silica collected at the butanol - water interface and preferentially absorbed the colour. It was found that this effect could be overcome by the addition of sodium fluoride. With this modification it was shown that there was no destruction of arsanilic acid in the hydrolysed solution, and the carbarsone standard graph was virtually a straight line. The wavelength of maximum absorption of the colour in butanol was found to be 542 nm.

With these modifications incorporated, a collaborative test of the method was arranged involving six laboratories. Three feed samples from different manufacturers were circulated, together with a common sample of pure carbarsone. Each laboratory medicated three separate 10-g portions of each meal with between 375 and 400 p.p.m. of carbarsone and then determined the drug content by the proposed method. The results of these tests are shown in Table I. In addition, each laboratory carried out blank tests in duplicate on all three meals; the results are shown in Table V. A statistical assessment of the results obtained on the medicated feed samples is given in Tables II, III and IV.

INTERFERENCES—

Carbarsone can be found in animal feeds in various combinations with several other prophylactic additives. To assess the interference that might be expected from other drugs present in a feed with carbarsone, one laboratory investigated the effects of the presence of 150 p.p.m. of a range of drugs on the recovery of 375 p.p.m. of carbarsone. Acinitrazole, amprolium, arsanilic acid, clopidol, decoquinate, dimetridazole, furazolidone, nitrofurazone, sulphadimidine, sulphaquinoxaline and procaine penicillin were found not to interfere. Arsanilic acid, sulphadimidine and procaine penicillin did, however, give colour reactions that were unchanged by hydrolysis and allowance is therefore made for this as the carbarsone content is measured from the absorption difference before and after hydrolysis. Positive interference was caused by the presence of dinitolmide and positive interference from pay-zone was also indicated, but here the level tested, 150 p.p.m., was more than ten times greater than the concentration used in feeds.

TABLE II

ANALYSIS OF VARIANCE OF RESULTS FROM TABLE I

Source of variation	Degrees of freedom	Mean square	"F" ratio	Significance level
Between laboratories	5	122·5	9·05	$P < 0·001$
Between samples	2	63·2	4·66	$P < 0·05$
Interaction, laboratories/samples	10	64·0	4·73	$P < 0·001$
Residual	34	13·5	—	—

This indicates that (*i*), variance between laboratories is highly significant, and (*ii*), variance between samples is significant.

RESULTS AND STATISTICAL ASSESSMENT—

The results obtained in a collaborative test of the recommended method (see Appendix I) involving six laboratories and three different samples of feedingstuff are shown in Table I. An analysis of variance of these results is given in Table II, and in Table III the mean recovery values for each sample are summarised. It can be seen from Table II that the difference between laboratories is highly significant at $P < 0·001$, and this may be partly explained by the following observations.

(*i*) Laboratory A shows the greatest range in the results of its triplicate tests (Table III) and therefore the greatest variance on all samples. It has the lowest mean recovery (80·0 per cent.) and the highest mean recovery (101·0 per cent.) for triplicate tests.

(*ii*) Laboratory B has the lowest over-all mean recovery, for all samples, at 86·7 per cent.

(*iii*) From Table III it can be seen that there is no significant difference between the means of laboratories A, C, D, E and F, but as previously observed, laboratory A has the greatest range between its triplicate tests.

Table III shows that the variations between samples are just significantly different at $P = 0{\cdot}05$ with a difference of 3·28, the critical value being 3·1. It is possible that this is partly due to the fact that medication of the feeds was carried out separately in each laboratory. This variation can, however, be regarded as satisfactory.

TABLE III

RECOVERY OF CARBARSONE, MEANS OF TRIPLICATE TESTS PER LABORATORY

	Sample 1 recovery, per cent.		Sample 2 recovery, per cent.		Sample 3 recovery, per cent.		
Laboratory	Mean	Range	Mean	Range	Mean	Range	Over-all mean
A	80·0	14·6	101·0	13·6	93·3	1·6	91·4
B	85·1	7·9	89·2	3·8	85·7	4·1	86·7
C	94·9	2·1	95·5	2·9	85·8	0·6	95·4
D	95·7	2·8	95·7	2·5	96·6	5·3	96·0
E	96·3	3·4	96·1	3·8	96·5	5·1	96·3
F	93·9	4·1	89·6	9·7	95·1	2·6	92·8
Over-all	91·0	—	94·5	—	93·8	—	93·1

Critical difference between individual means is 11·3 at $P = 0{\cdot}05$.
Critical difference between sample means is 3·1 at $P = 0{\cdot}05$.
Critical difference between laboratory means is 5·2 at $P = 0{\cdot}05$.

As regards mean recovery of carbarsone, the following examples may be noted—
Sample 1 is significantly different from sample 2.
Sample 2 and sample 3 are not significantly different.
Sample 1 and sample 3 are not significantly different.

From Table III it can also be seen that five laboratories could expect to return results within $\pm 5{\cdot}2$ per cent. of their over-all mean percentage recovery. So, although the mean recovery for laboratory B at 86·7 per cent. is not significantly different from that of laboratory A at 91·4 per cent., it is significantly different from the over-all means of laboratories C, D, E and F. It may also be noted that the over-all means of laboratories A, C, D and F are not significantly different.

The over-all performance of the method is shown in Table IV, from which it can be seen that for a single test any reasonably experienced laboratory could expect to obtain a result within $\pm 7{\cdot}36$ per cent. of the mean percentage recovery, which would be the result of a large number of tests. Thus if 375 p.p.m. of carbarsone are present in a sample, the over-all mean recovery for a large number of tests would be about 93·1 per cent. (349 p.p.m). A laboratory's single test could therefore be expected to lie within the range 85·7 per cent. (321 p.p.m.) to 100·5 per cent. (377 p.p.m.).

TABLE IV

OVER-ALL PERFORMANCE OF THE METHOD

Number of tests	54
Mean over-all recovery	93·1 per cent.
Minimum recovery	73·5 per cent.
Maximum recovery	107·2 per cent.
Standard deviation of a single test ..	3·68
Coefficient of variation	3·95

95 per cent. confidence limits $\pm$ 7·36 for a single test.

INFLUENCE OF FEEDINGSTUFF ON DETERMINATION OF CARBARSONE—

All six laboratories taking part in the collaborative work on the recovery of carbarsone also carried out duplicate determinations of the apparent carbarsone contents of the three unmedicated meals; the results are shown in Table V. These indicate that in most instances the blank meal makes a contribution to the result obtained for carbarsone (no explanation has been found for the negative value shown in Table V). It was known that one of the

TABLE V

RESULTS ON NON-MEDICATED SAMPLES TESTED FOR CARBARSONE

Laboratory	Sample	Absorbance before hydrolysis *a*	Absorbance after hydrolysis *b*	Difference *b*−*a*	Apparent carbarsone found	
					mg	p.p.m.
A	1 (a)	0·008	0·066	0·058	0·54	54
	1 (b)	0·018	0·061	0·043	0·40	40
	2 (a)	0·060	0·080	0·020	0·19	19
	2 (b)	0·082	0·082	0·000	0·00	0
	3 (a)	0·020	0·088	0·068	0·63	63
	3 (b)	0·020	0·057	0·037	0·34	34
B	1 (a)	0·014	0·017	0·003	0·03	3
	1 (b)	0·043	0·018	−0·025	−0·23	−23
	2 (a)	0·003	0·025	0·022	0·20	20
	2 (b)	0·003	0·016	0·013	0·12	12
	3 (a)	0·010	0·010	0·000	0·00	0
	3 (b)	0·002	0·002	0·000	0·00	0
C	1 (a)	0·012	0·041	0·029	0·27	27
	1 (b)	0·010	0·032	0·022	0·20	20
	2 (a)	0·011	0·028	0·017	0·16	16
	2 (b)	0·013	0·035	0·022	0·20	20
	3 (a)	0·018	0·030	0·012	0·11	11
	3 (b)	0·013	0·025	0·012	0·11	11
D	1 (a)	0·031	0·042	0·011	0·10	10
	1 (b)	0·017	0·030	0·013	0·12	12
	2 (a)	0·025	0·030	0·005	0·05	5
	2 (b)	0·015	0·030	0·015	0·14	14
	3 (a)	0·020	0·035	0·015	0·14	14
	3 (b)	0·028	0·040	0·012	0·11	11
E	1 (a)	0·010	0·033	0·023	0·21	21
	1 (b)	0·009	0·033	0·024	0·22	22
	2 (a)	0·010	0·026	0·016	0·15	15
	2 (b)	0·009	0·028	0·019	0·18	18
	3 (a)	0·013	0·032	0·019	0·18	18
	3 (b)	0·014	0·033	0·019	0·18	18
F	1 (a)	0·022	0·038	0·016	0·15	15
	1 (b)	0·015	0·027	0·012	0·11	11
	2 (a)	0·020	0·038	0·018	0·17	17
	2 (b)	0·013	0·025	0·012	0·11	11
	3 (a)	0·013	0·029	0·016	0·15	15
	3 (b)	0·013	0·030	0·017	0·16	16
						*Mean 17·5

* Omitting negative value on laboratory B, sample 1 (b).

blank meals was a laboratory-prepared mix to a commercial formulation made with ordinary raw materials as delivered to the factory. All organic drugs had been deliberately omitted yet, by inspection, differences in results for the blank meals do not appear to hold any relationship with differences in the blank meals themselves. It is clear, however, that the method would give lower assay results if any correction for blank meal were applied.

CONCLUSIONS

From the results obtained in the collaborative work and the statistical assessment of these results the Sub-Committee has concluded that the method given in Appendix I to this Report is satisfactory for the determination of carbarsone, and it is recommended that it should be used for determining the drug in poultry feeds.

RECOVERY OF CARBARSONE FROM PELLETED FEEDS—

After the Sub-Committee had completed its work, an investigation of the recovery of carbarsone from pelleted feeds was carried out by the Compound Animal Feeding Stuffs Manufacturers National Association Ltd. (CAFMNA). The Report of this work is given in Appendix II.

Appendix I

Recommended method for determining carbarsone in poultry feeds

Principle of method—

A brine - acid extract of the feedingstuff is refluxed with sodium hydroxide, and the arsanilic acid produced is determined spectrophotometrically after diazotisation and coupling with *N*-1-naphthylethylenediamine dihydrochloride, and extraction of the coloured product into butanol.

Applicability—

The method is applicable to the determination of carbarsone in poultry feedingstuffs of the types currently marketed. The presence of dinitolmide in the feed might give rise to apparent high recoveries of carbarsone.

Reagents—

Hydrochloric acid, 5 M.
Sodium nitrite solution, 0·1 *per cent. w/v*—Freshly prepared.
Ammonium sulphamate solution, 0·5 *per cent. w/v*.
N-1-*Naphthylethylenediamine dihydrochloride solution*, 0·1 *per cent. w/v*.
Sodium fluoride solution, 1·0 *per cent. w/v*.
Butanol.
Sodium hydroxide, pellets.
Sodium chloride.
Carbarsone standard solution—Dissolve 0·100 g of pure carbarsone in 100 ml of water containing 5 ml of 5 M hydrochloric acid, and dilute to 500 ml with water (5 ml ≡ 1 mg of carbarsone).

Procedure—

Weigh 10 ± 0·01 g of feed sample and transfer it to a 250-ml calibrated flask. Add 2 ml of 5 M hydrochloric acid, 10 g of sodium chloride and about 100 ml of water, and shake the flask on a suitable shaker for 1 hour. Dilute to volume with water, mix well, and allow to settle for 10 minutes. Filter the extract through a Whatman No. 1 or equivalent filter-paper. Reject the first 20 ml of filtrate and collect the remainder.

To 25 ml of the filtrate in a 100-ml conical flask add 3 g of sodium hydroxide and reflux for 1 hour. Cool, add 10 ml of 1 per cent. sodium fluoride solution and 30 ml of 5 M hydrochloric acid (*Note*), and again cool. Transfer the solution to a 100-ml calibrated flask, and dilute to volume with water (solution A).

To a further 25-ml portion of the filtrate in a 100-ml calibrated flask add a cooled mixture of 10 ml of 1 per cent. sodium fluoride solution, 3 g of sodium hydroxide and 30 ml of 5 M hydrochloric acid (*Note*). Dilute to volume with water (solution B).

Take 10-ml portions of solutions A and B in separate, stoppered test-tubes and to each add 2 ml of sodium nitrite solution. Mix well, and set aside for 3 minutes. Add 2 ml of ammonium sulphamate solution to each, mix well, and set aside for 2 minutes. Add 1 ml of naphthylethylenediamine dihydrochloride to each, and mix well. After 10 minutes, add 5 g of sodium chloride and 15 ml of butanol to each, and shake the tubes for 1 minute. Spin the tubes in a centrifuge to clear the upper layers and then remove the upper butanol layers and measure their absorptions at 542 nm in 10-mm cells against butanol.

Note.—The spectrophotometric determination should be carried out as soon as possible after the addition of acid, as there is a danger of loss of arsanilic acid in the presence of feed extract.

Preparation of standard graph—

Transfer 0, 5, 10, 15, 20 and 25-ml portions of the carbarsone standard solution, equivalent to 0, 1, 2, 3, 4 and 5 mg of carbarsone, to separate 250-ml calibrated flasks. Add to each 10 g of sodium chloride and 2 ml of 5 M hydrochloric acid, and dilute to volume with water. Take 25-ml portions of these solutions and proceed with the hydrolysis and colour development as for the feed extract. Take a further 25-ml portion of each solution to determine the absorptions of the unhydrolysed solutions.

Calculate the differences in absorptions of the solutions before and after hydrolysis and plot this difference against milligrams of carbarsone present.

From the absorption difference of the sample extract before and after hydrolysis, read from the standard graph the carbarsone content of the sample in milligrams and hence the concentration (p.p.m.) of carbarsone in the feed.

Appendix II

Recovery of carbarsone from pelleted feeds

A collaborative investigation of the recovery of carbarsone from pelleted feeds was carried out under the auspices of the Compound Animal Feeding Stuffs Manufacturers National Association Ltd. A report of this work is given below.

Objective—

To test the suitability of the method recommended in Appendix I for its application to both pelleted and unpelleted feeds.

Experimental—

Two 5-ton batches of poultry feed were manufactured and a sampling scheme was designed so that ten spot samples of meal were taken before pelleting and ten spot samples of the pellets were taken immediately after passing through the die. The two series of samples for each run were mixed to provide average samples of the feed before and after pelleting, designated A and B, respectively.

Analytical method—

The method used was that given in Appendix I. Bulk samples of the material before and after pelleting were sent to three laboratories. Each laboratory prepared three sub-samples of each sample and analysed these sub-samples singly, giving three results per sample.

Results—

Table VI

General analysis of samples

	Sample	Protein, per cent.	Moisture, per cent.	Oil, per cent.
1st Batch	1A	26·0	10·6	3·3
	1B	26·2	11·4	3·3
2nd Batch	2A	25·8	10·7	3·2
	2B	25·9	11·4	3·6

Table VII

Recovery of carbarsone before and after pelleting

All results corrected to basis of 10·6 per cent. of moisture

	Carbarsone found, p.p.m.*			
Sample	Laboratory 1	Laboratory 2	Laboratory 3	Mean
1A (before)	341	330	347	339
1B (after)	314	338	358	337
2A (before)	337	334	347	339
2B (after)	331	349†	368	349

* Each laboratory result is the mean of three analyses. Over-all standard deviation (36 results) is 15 p.pm.

† Two aberrant results were discarded on statistical grounds.

Conclusions—

The mean levels of carbarsone in the samples before and after pelleting are not significantly different.

Book Review

APPLIED GAMMA-RAY SPECTROMETRY. By C. E. CROUTHAMEL. Second Edition. Revised and enlarged by F. ADAMS and R. DAMS. Pp. xviii + 752. Oxford, New York, Toronto, Sydney and Braunschweig: Pergamon Press. 1970. Price £12; $32.

All users of gamma-ray spectrometry will welcome the appearance of a comprehensive up-to-date book on the subject. Great advances in this technique have occurred in the past ten years, particularly the advent and development of high-resolution lithium-drifted germanium and silicon detectors. The revision of Crouthamel's original monograph "Applied Gamma-Ray Spectrometry" by Adams and Dams provides a source book of considerable authority to fill a notable gap in the literature.

The revised and enlarged volume is a weighty tome compared with the original, and now comprises nine chapters and seven appendices. The first chapter covers nuclear decay processes and the interaction of gamma rays with matter. The following three chapters deal, respectively, with the manufacture and properties of scintillation detectors, semi-conductor detectors and proportional detectors. An entirely new chapter on instrumentation includes discussion of amplifiers, analogue-to-digital converters, multi-channel analysers and counter arrangements. Energy and time resolution are dealt with next, followed by the calibration of detectors. The penultimate chapter is new and includes the important topics of qualitative and quantitative interpretation of gamma-ray spectra. Applications covered in the final chapter are: tracer methods, activation analysis, fission-product studies, whole-body measurements and non-dispersive X-ray spectrometry. The appendices make up rather more than half of the book. The two largest are appendix II, which includes sodium iodide detector gamma-ray spectra of some 214 nuclides, and appendix III, which includes lithium-drifted germanium detector gamma-ray spectra of about 230 nuclides. Appendix VI is a compilation of nuclides in photon energy, atomic number and half-life sequence, while appendix VII is a compilation of precise gamma-ray energies of isotopes produced by neutron bombardment. The additional appendices are I, on X-ray critical absorption and emission energies, IV, on intrinsic efficiencies for sodium iodide crystals, and V, on internal conversion coefficients.

The treatment of gamma-ray spectrometry given in this book is thorough. Some readers might call for less information on the manufacture of detectors and more on topics such as spectrum interpretation and specific applications, especially as the book is entitled "Applied Gamma-Ray Spectrometry." The catalogue of high-resolution spectra is extremely welcome and the most comprehensive available, and many will wish to acquire the book simply to obtain this catalogue. A disappointing feature is afforded by the glaring inconsistencies in the data presented in appendices II, III, VI and VII. The best values only of energy and half-life should have been used throughout. The precise gamma-ray energies listed by the authors are of excellent quality as judged by practical experience. With little extra work they could have annotated Crouthamel's original sodium iodide spectra with their values, and ensured that they were also used in appendix VI, which in its present state is of limited use to those who use high-resolution detectors.

Despite these few reservations, the quality of this publication is on the whole excellent, and it is a must for all those with a serious interest in gamma-ray spectrometry.

J. W. MCMILLAN

APPOINTMENTS VACANT

Determination of Orthophosphate in the Presence of Nitrate Ions

A method is described for the spectrophotometric determination of orthophosphate in the presence of nitrate. Reduction of nitrate ions to ammonia is effected by aluminium metal and sodium hydroxide solution, and after the removal of all the ammonia produced (by heating) the phosphate is determined by the formation of the phosphomolybdate complex and reduction to molybdenum blue. The method is suitable for the determination of orthophosphate at a concentration of 10^{-4} M in the presence of more than 10^{-1} M of nitrate. It also overcomes interference by fluoride and other halide ions in the molybdenum-blue method.

E. J. DUFF and J. L. STUART
Department of Preventive Dentistry, Turner Dental School, The University, Manchester, M15 6FH.

Analyst, 1971, **96**, 802–806.

The Determination of Epichlorohydrin in Aqueous Solutions in the Presence of Glycerin, Monochlorohydrin and Glycidol

Epichlorohydrin can be extracted from aqueous solutions containing glycerin, monochlorohydrin and glycidol into carbon tetrachloride and determined by infrared spectrophotometry. The high-frequency component of the complex band at a wavenumber 1274 cm^{-1} is used as the analytical band. A three-fold excess of carbon tetrachloride over the aqueous phase is necessary for the quantitative extraction. A cell thickness of up to 1 mm can be used; the concentration limit of the solute in the aqueous phase is then 0·3 per cent. v/v.

PETR ADÁMEK
Institute of Chemical Technology, Prague 6, Czechoslovakia.

and VLASTIMIL PETERKA
Research Institute of the Fat Industry, Rakovník, Czechoslovakia.

Analyst, 1971, **96**, 807–809.

The Use of Back-flushing with Electron-capture Gas Chromatography

An apparatus is described that enables materials with a longer retention time than those of interest to be back-flushed out of electron-capture gas chromatographs. Shorter analysis times, a longer column life and less frequent cleaning of the detectors have been achieved with this device.

B. T. CROLL
The Water Research Association, Medmenham, Marlow, Buckinghamshire.

Analyst, 1971, **96**, 810–813.

An Enzymic Method for the Determination of Dried Skimmed Milk in Mashed Potato Powders

An enzymic method is described for the determination of dried skimmed milk in mashed potato powders. The method is based on the determination of free lactose by its hydrolysis with β-galactosidase, the glucose formed being determined by the hexokinase method. The determination is free of interference from varying concentrations of reducing sugars found in dried potatoes. Accuracy and reliability are greater with this method than with other methods currently in use.

R. K. BAHL
J. Sainsbury Ltd., Stamford House, Stamford Street, London, S.E.1.

Analyst, 1971, **96**, 814–816.

The Determination of Carbarsone in Animal Feeds

Report prepared by the Prophylactics in Animal Feeds Sub-Committee.

ANALYTICAL METHODS COMMITTEE
9/10 Savile Row, London, W1X 1AF.

Analyst, 1971, **96**, 817–823.

Normex

Concentrated Buffer Solutions

A) range of concentrated solutions giving 500 ml. of specific pH Buffer Solution, by dilution with distilled water.

pH 1,00 (Potassium Chloride. Hydrochloric acid)
pH 1,50 (p. Toluene Sulphonic acid. Sodium Hydroxide)
pH 2,00 (p. Toluene Sulphonic acid. Sodium Hydroxide)
pH 2,00 (Potassium Chloride. Hydrochloric acid)
pH 3,00 (Sodium Hydrogen Citrate. Hydrochloric acid)
pH 4,00 (Potassium Hydrogen Phtalate. Sodium Hydroxide)
pH 5,00 (Potassium Hydrogen Phtalate. Sodium Hydroxide)
pH 6,00 (Pot. dihydrogen Phosphate. Sodium Hydroxide)
pH 6,20 (Pot. dihydrogen Phosphate. Sodium Hydroxide)
pH 6,40 (Pot. dihydrogen Phosphate. Sodium Hydroxide)
pH 6,60 (Pot. dihydrogen Phosphate. Sodium Hydroxide)
pH 6,80 (Pot. dihydrogen Phosphate. Sodium Hydroxide)
pH 7,00 (Pot. dihydrogen Phosphate. Sodium Hydroxide)
pH 7,20 (Pot. dihydrogen Phosphate. Sodium Hydroxide)
pH 7,40 (Pot. dihydrogen Phosphate. Sodium Hydroxide)
pH 7,60 (Pot. dihydrogen Phosphate. Sodium Hydroxide)
pH 7,80 (Pot. dihydrogen Phosphate. Sodium Hydroxide)
pH 8,00 (Pot. dihydrogen Phosphate. Sodium Hydroxide)
pH 9,00 (Sodium Borate. Sodium Hydroxide)
pH 10,00 (Sodium Borate. Sodium Hydroxide)

B) A range of concentrated solutions giving 500 ml. of variable pH Buffer Solution.

pH 1,00 ÷ pH 2,20 (Potassium Chloride) (by adding HCl N/1)
pH 1,40 ÷ pH 2,20 (p. Toluene Sulphonic acid) (by adding NaOH N/2)
pH 2,20 ÷ pH 6,20 (Potassium Hydrogen Phtalate) (by adding NaOH N/2)
pH 6,00 ÷ pH 8,00 (Potassium dihydrogen Phosphate) (by adding NaOH N/2)
pH 7,80 ÷ pH 10,00 (Sodium borate) (by adding NaOH N/2)

CARLO ERBA DIVISIONE CHIMICA INDUSTRIALE / VIA C. IMBONATI 24 / 20159 MILANO

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