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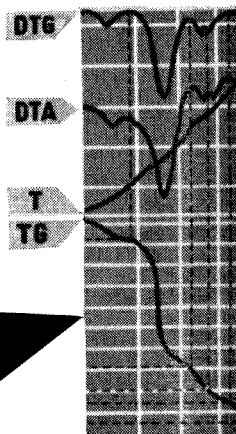
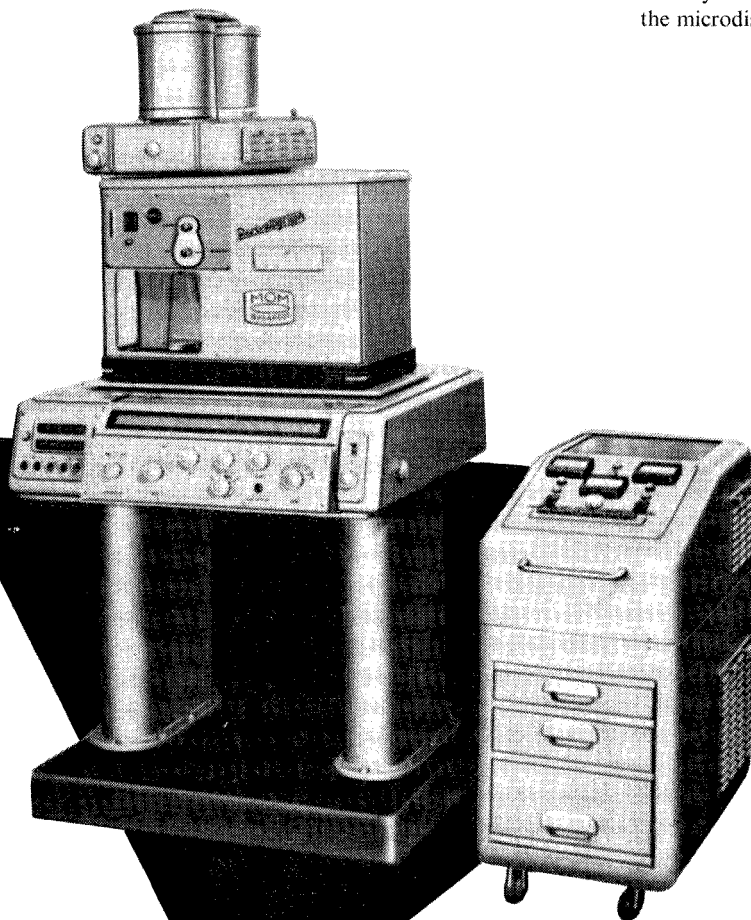
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1. Swamer, F. W. and Hauser, C. R., *J. Amer. Chem. Soc.*, 1950, **72**, 1352-6

2. Wheatley, N. B. and Cheney, L. C., *J. Amer. Chem. Soc.*, 1949, **71**, 64-6; 3795-7

3. Daub, G. H. and Johnson, W. S., *J. Amer. Chem. Soc.*, 1950, **72**, 501-4

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1. Salesin, E. D. and Gordon, L., *Talanta*, 1960, **4**, 75-7

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1. Dixon, B. E. and Hands, G. C., *Analyst*, 1959, **84**, 463-4



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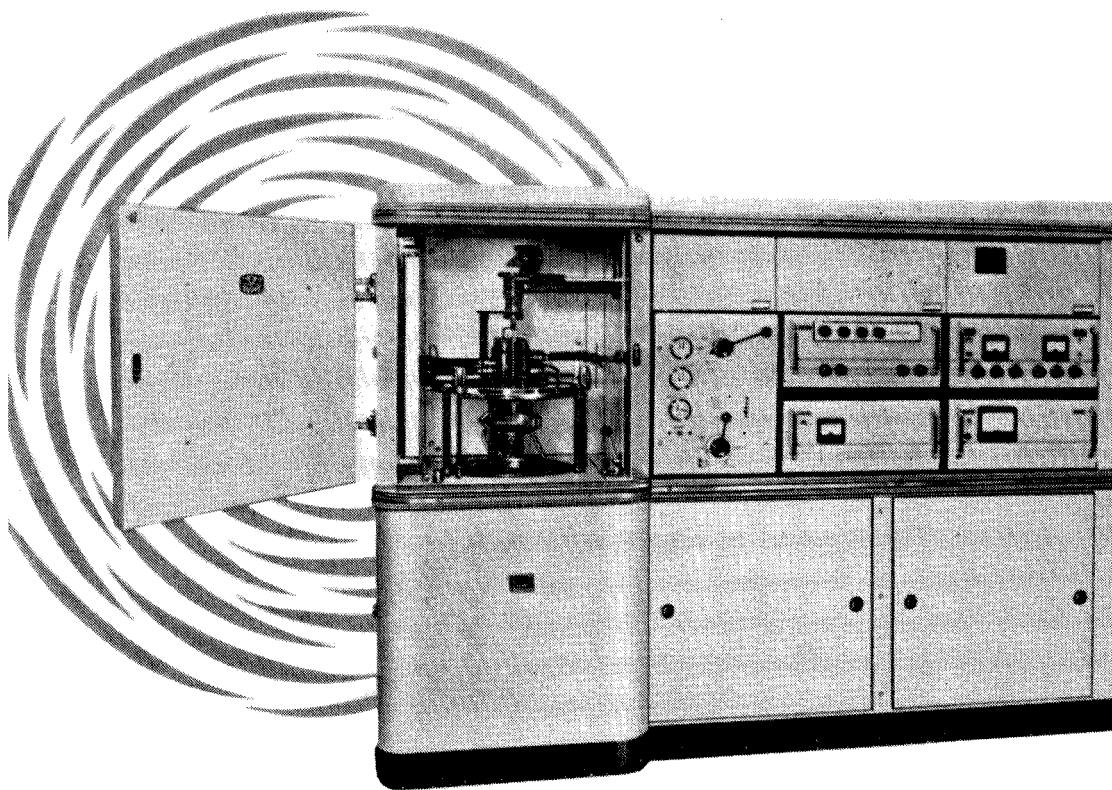
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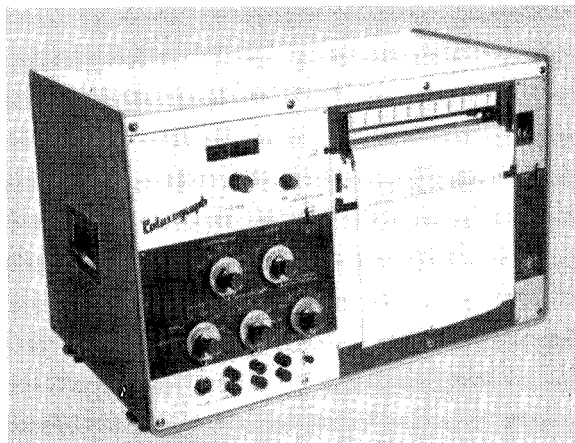
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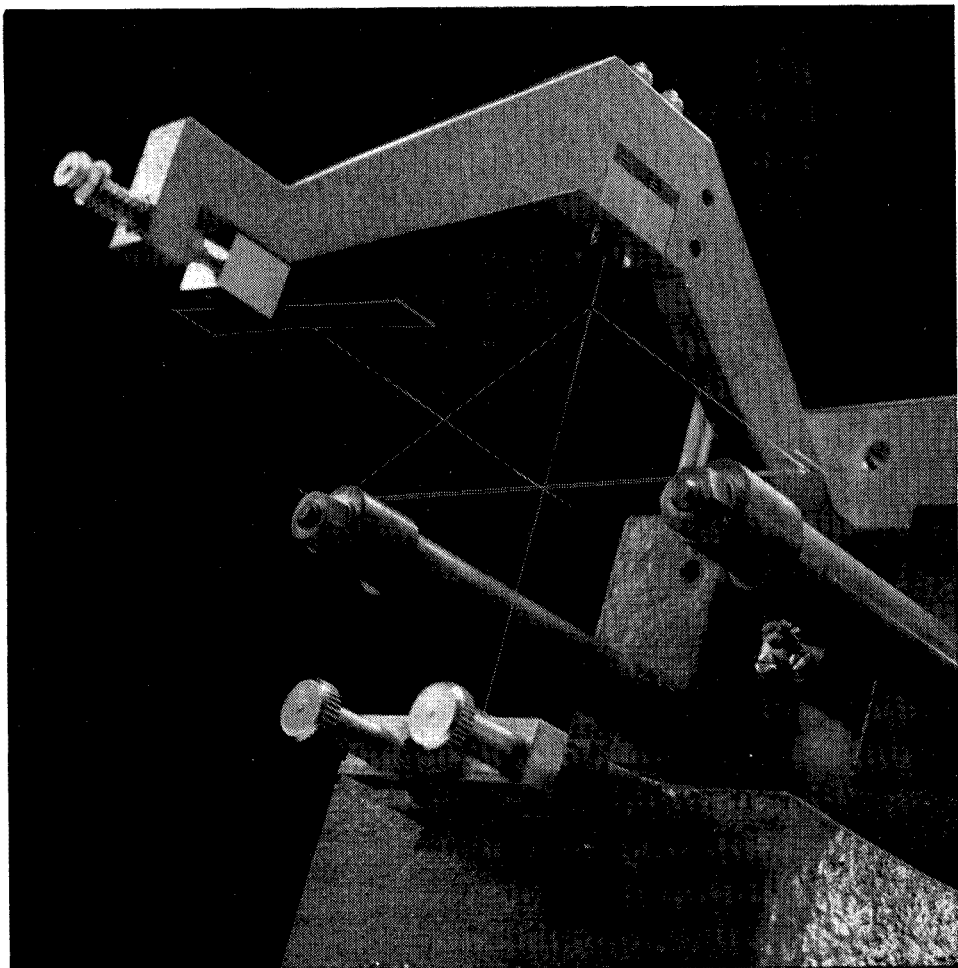
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SUMMARIES FOR CARD INDEXES

Determination of the methylol group in phenolic resins: N. YOSHIMI, M. YAMAO and S. TANAKA, *Talanta*, 1964, **11**, 901. (Fudow Chemical Co., Nishi-Rokugo, Ota-ku, Tokyo, Japan.)

Summary—An accurate and simple method for determination of the methylol group in phenolic resins is described. The phenolic hydroxyl group is determined by titration with sodium methoxide in non-aqueous solvent, and total hydroxyl group (phenolic hydroxyl plus alcoholic hydroxyl) is found by calculation of the integrated absorption intensity from the infrared spectrum observed between 3600 and 3000 cm^{-1} . The alcoholic hydroxyl group (methylol group) is calculated as the difference between the total and the phenolic hydroxyl group. In contrast to customary techniques, this method is simple, direct and provides a satisfactory precision ($\pm 8\%$).

Paper chromatography in inorganic qualitative analysis: A. SCHNEER-ERDEY and T. TÓTH, *Talanta*, 1964, **11**, 907. (Research Group for Inorganic Chemistry, Hungarian Academy of Sciences, Budapest VIII, Múzeum-körút 6-8, Hungary.)

Summary—A two-dimensional paper chromatographic method for the separation and identification of several metal ions is described. After preparation, the sample is run with an ethanol:hydrochloric acid:water (75:20:5) mixture, and later in a second dimension with a tetrahydrofuran: nitric acid:water (85:5:10) mixture. The chromatogram can be developed with a 0.2% ethanolic solution of Morin, and is examined both in sunlight and in ultraviolet light, in acidic conditions and after alkalisatation with ammonia vapour. Those metal ions which migrate together in the first solvent will be separated in the second one, and can be identified reliably. The composition of the original sample can be deduced from the R_f values, colours and fluorescences of the various spots.

Thermoanalytical properties of analytical-grade reagents: Ammonium salts: L. ERDEY, S. GÁL and G. LIPTAY, *Talanta*, 1964, **11**, 913. (Institute for General Chemistry, Technical University, Budapest XI, Gellért tér 4, Hungary.)

Summary—Twenty-six ammonium salts have been investigated derivatographically. The weight change, rate of weight change and enthalpy change of the salts have been measured as a function of temperature. From the results the temperatures at which the salts may be dried without decomposition are given.

**ОПРЕДЕЛЕНИЕ МЕТИЛОЛ-ГРУППЫ В
ФЕНОЛЬНЫХ СМОЛАХ:**

N. YOSHIMI, M. YAMAS и S. TANAKA, *Talanta*, 1964, 11, 901.

Резюме—Описан точный и несложный метод для определения метилол-группы в фенольных смолах. Фенольный гидроксил определяется титрованием метилатом натрия, а общее содержание гидроксила (фенольный + спиртовый гидроксил) вычисляется на основании интегрированного поглощения в инфракрасной области спектра между 3600 и 3000 см^{-1} . Спиртовый гидроксил получается из разницы между общим и фенольным гидроксилом. Этот метод отличается от обыкновенных методов с тем что он несложный, прямой и довольно точный ($\pm 8\%$).

**РАЗРАБОТКА МЕТОДА БУМАЖНОЙ
ХРОМАТОГРАФИИ ДЛЯ КАЧЕСТВЕННОГО
АНАЛИЗА:**

A. SCHNEER-ERDEY и T. TOTI, *Talanta*, 1964, 11, 907

Резюме—Представлен двухмерный метод бумажной хроматографии для разделения и отождествления некоторых ионов металлов. После соответствующей подготовки проба хроматографируется смесью этиловый спирт-соляная кислота-вода (75:20:5) в одном направлении, а затем смесью тетрагидрофуран-азотная кислота-вода (85:5:10) в другом направлении. Хроматограмма прыскается 0,2%-тным раствором морина в спирте и рассматривается в дневном и УФ-свете, в кислом состоянии, а потом изложена парам аммиака. Ионы которые двигаются вместе в первом растворителе, разделяются в другом и могут быть отождествлены. Состав пробы оценивается на основании числа R_f окраски и флуоресценции пятен.

**ТЕРМОАНАЛИТИЧЕСКИЕ СВОЙСТВА
АНАЛИТИЧЕСКИХ РЕАГЕНТОВ: СОЛЫ АММОНИЯ:**

L. ERDEY, S. GÁL и G. LIPTAJ, *Talanta*, 1964, 11, 913.

Резюме—Было изучено 26 солей аммония дериватогрaфическим методом: измерилась переменa веса, скорость перемены веса и переменa энтальпии в зависимости от температуры. На основании полученных данных приведены температуры, при которых могут сушиться соли без разложения.

Use of oxycellulose for collection of traces of metals—II: Application of oxycellulose in solvents and in solutions of different organic compounds: E. SCHULEK, Zs. REMPORT-HORVÁTH and A. LÁSZITTY, *Talanta*, 1964, **11**, 941. (Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary.)

Summary—Oxycellulose has been applied as a collector for the following metal-ion contaminants of organic solvents and of different organic compounds: Cu^{2+} , Fe^{3+} , Ni^{2+} , Pb^{2+} , Zn^{2+} . From 100 ml of solvent 1–20 μg of ions have been collected with 5 mg of oxycellulose. The solutions of the organic compounds were 1–3%. The water-content of the solvents has a marked effect on the collection. By repeated collection an ion can be removed quantitatively.

The chromatography of *p*'-substituted-*p*-hydroxyazobenzenes on alumina-impregnated papers: R. J. T. GRAHAM and C. W. STONE: *Talanta*, 1964, **11**, 947 (Department of Chemistry and Applied Chemistry, Royal College of Advanced Technology, Salford 5, Lancs., England.)

Summary— R_f values of *p*'-substituted-*p*-hydroxyazobenzenes on paper, glass-fibre "paper", and these papers impregnated with different amounts of alumina are given. Results indicate that the alumina is primarily responsible for sorption. The effect of the electrical nature of the *p*'-substituent on sorption is small. Sorption is considered to be a result of hydrogen bonding between oxygen centres in the sorbed molecule and active hydrogen centres on the hydroxylated alumina.

Ammonium hexanitratocerate(IV) as an oxidising agent—III: Photometric determination of manganese^{II} through oxidation to manganese^{VII}: G. GOPALA RAO, K. S. MURTY and P. V. KRISHNA RAO, *Talanta*, 1964, **11**, 955. (Department of Chemistry, Andhra University, Waltair, India.)

Summary—Manganese^{II} is oxidised to permanganic acid by treatment with a slight excess of ammonium hexanitratocerate(IV) in a 0.5–2*M* nitric acid medium at room temperature. The reaction is markedly catalysed by silver nitrate, so that quantitative oxidation is possible within 1 min. Conditions have been developed for utilising the catalysed reaction for the colorimetric determination of manganese over the range 0.33–19.93 mg/litre. The new method has the advantage over those currently available in that the oxidation to manganese^{VII} is stoichiometric at room temperature. Under the conditions prescribed the permanganic acid formed is stable for at least 24 hr. Interference from sulphate and from chloride, bromide and iodide can be eliminated by treating the test solution with barium nitrate or silver nitrate, respectively, before the oxidation with cerium^{IV}. Application of the method to the determination of manganese in steel is considered.

ПРИМЕНЕНИЕ ОКСИЦЕЛЛЮЛОЗА ДЛЯ КОНЦЕНТРИРОВАНИЯ СЛЕДОВ МЕТАЛЛОВ—II:

E. SCHULER, Zs. REMPÖRT-HORVÁTH и A. LÁSZTITY, *Talanta*, 1964, **11**, 941.

Резюме—Оксицеллюлоза была применена в качестве коллектора для концентрирования следующих металлических загрязнений в органических растворителях и органических соединениях (Cu^{2+} , Fe^{3+} , Ni^{2+} , Pb^{2+} , Zn^{2+}). При помощи 5 мг. оксицеллюлозы в качестве коллектора было выделено 1–20 микрограммов описанных металлов. Концентрация органических соединений была 1–3%. Количество воды в растворах имеет влияние на действительность выделения. Количественное разделение можно достигнуть повторением процесса.

**ХРОМАТОГРАФИЯ p'-ЗАМЕЩЕННЫХ
p-ГИДРОКСИАЗОБЕНЗОЛОВ:**

R. J. T. GRAHAM и C. W. STONE, *Talanta*, 1964, **11**, 947.

Резюме—Дано значение чисел R_f p'-замещенных p-гидроксиазобензолов на фильтровальной бумаге, на бумаге из стеклянных волокон и на этихже бумагах пропитанных различными количествами окиси алюминия. Из результатов видно, что за сорбцию в первую очередь отвечает окись алюминия. Эффект электрического характера p'-заместителя на сорбцию незначителен. Предполагается что сорбция появляется в результате образования связи водорода между центрами кислорода в сорбированной молекуле и активными центрами водорода на гидроксильной окиси алюминия.

Polarographic determination of dissolved oxygen in petrol: G. L. WOODROFFE, *Talanta*, 1964, **11**, 967. (Research Department, I.C.I. Ltd., Heavy Organic Chemicals Division, Organic House, Billingham, Co. Durham, England.)

Summary—A method is described for the determination of dissolved oxygen in petrol using a cathode ray polarograph. Oxygen produces two waves, with reduction potentials at -0.67 V and -1.25 V against a mercury pool anode, when an ethanolic solution of lithium chloride is used as supporting electrolyte. Calibrations are carried out using water of known oxygen content for the preparation of standards and the wave at -0.67 V is preferred for quantitative measurement.

New ideas on the reaction mechanism of determinations based on decolorisation: R. VALACH, *Talanta*, 1964, **11**, 973. (Central Geological Survey, Prague, Czechoslovakia.)

Summary—The existence of fluoride-metal-dye (FDM) ternary complexes which have a different colour from that of the MD chelate and of the free dye, as well as the existence of MD binary chelates with the same colour as the free dye, is known. By analogy, the existence of FDM ternary complexes with the same colour as MD or as D may be assumed. Such ternary complexes may be formed in some determinations based on "decolorisation", so that these determinations should not generally be considered as indirect methods.

The determination of chlorosuccinic acid in aqueous solutions: R. ANNINO and T. J. BERAS, *Talanta*, 1964, **11**, 975. (Department of Chemistry, Canisius College, Buffalo 8, New York, U.S.A.)

Summary—Chlorosuccinic acid is determined by dehydrohalogenation and polarographic determination of the fumaric acid formed.

Microtitration of plutonium^{III} and hydrogen peroxide present with plutonium^{IV} in hydrochloric acid solutions: P. V. BALAKRISHNAN, A. S. GHOSH MAZUMDAR and R. N. SINGH, *Talanta*, 1964, **11**, 977. (Radiochemistry and Isotope Division, Atomic Energy Establishment Trombay, Bombay, India.)

Summary—A method has been developed for the estimation of a few tens of micrograms of plutonium^{III} and hydrogen peroxide in hydrochloric acid solutions containing plutonium^{IV}. The sum of plutonium^{III} and hydrogen peroxide is obtained by successive addition, in excess, of known quantities of potassium dichromate and iron^{II} sulphate to one aliquot of the mixture, then titration with cerium^{IV} sulphate using ferroin as indicator. Their difference is obtained by adding the same quantities of the first two reagents in reverse order to another aliquot, then completing the titration as before.

НОВЫЕ ПРЕДСТАВЛЕНИЯ О РЕАКЦИЯХ,
ПРОТЕКАЮЩИХ ПРИ ОПРЕДЕЛЕНИЯХ,
ОСНОВЫВАЮЩИХСЯ НА ПОТЕРЕ ЦВЕТА:

R. VALACH, *Talanta*, 1964, **11**, 973.

Резюме—Известны тройные комплексы фторид-металл-краситель (FDM), цвет которых отличается от цвета MD-комплекса и цвета свободного красителя. Соответственно, можно предполагать существование FDM-тройных комплексов одинакового цвета как MD и D. Такие тройные комплексы могут образоваться при некоторых определениях, основывающихся на потере цвета; таким образом эти определения не нужно считать косвенными методами.

ОПРЕДЕЛЕНИЕ ХЛОРЯНТАРНОЙ КИСЛОТЫ В
ВОДНЫХ РАСТВОРАХ:

R. ANNINO и T. J. VERAS, *Talanta*, 1964, **11**, 975

Резюме—Хлорьянтарная кислота превращается отщеплением хлористого водорода в фумаровую кислоту, которая определяется полярографическим методом.

The response of cation-sensitive glass electrodes to alkali metal ions in partially aquated media: G. A. RECHNITZ and S. B. ZAMOCHNICK, *Talanta*, 1964 **11**, 979. (Department of Chemistry, University of Pennsylvania, Philadelphia 4, Pennsylvania, U.S.A.)

Summary—The response of cation-sensitive glass electrodes to alkali metal ions in ethanol-water and acetone-water mixtures has been evaluated. The increase in measured potential when water is replaced with organic solvent is proved to result from the changing liquid-junction potential of the reference electrode. The response of the glass electrode is essentially solvent-independent for a given concentration and type of solute.

Separation of commercial diphenylcarbazone into its components: J. J. R. F. DA SILVA, J. C. G. CALADO and M. L. DE MOURA, *Talanta*, 1964, **11**, 983. (Centro de Estudos de Química Nuclear (I.A.C.): Instituto Superior Técnico, Lisboa, Portugal.)

Summary—Confirming results of previous workers, it is shown that commercial AnalaR diphenylcarbazone can be separated into its components (diphenylcarbazide and pure diphenylcarbazone) by thin-layer chromatography or continuous liquid-liquid extraction, the latter method being preferred for preparative purposes. Some physical properties of pure diphenylcarbazone are reported.

**КАТИОНОЧУВСТВИТЕЛЬНЫЕ СТЕКЛЯНЫЕ
ЭЛЕКТРОДЫ: ОТВЕТ НА ИОНЫ ЩЕЛОЧНЫХ
МЕТАЛЛОВ ЧАСТЬЮ ГИДРАТИРОВАННЫХ СРЕДАХ.**

G. A. RESCHNITZ и S. B. ZAMOSCHNICK, *Talanta*, 1964, 11, 979.

Резюме—Был исследован ответ этих электродов на ионы щелочных металлов в смесях этиловый спирт—вода и ацетон—вода. Показано что повышение измеренного потенциала при замещении воды с органическим растворителем, вызвано переменной потенциала жидкой связи эталонного электрода. Ответ стеклянного электрода в сущности независимый от растворителя при данной концентрации и для данного типа растворенного вещества.

**РАЗДЕЛЕНИЕ ПРОДАЖНОГО ДИФЕНИЛКАРБА-
ЗОНА НА ЕГО КОМПОНЕНТЫ.**

J. J. R. F. DA SILVA, J. C. G. CALADO, и M. L. DE MOURA, *Talanta*, 1964, 11, 983.

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Publishing Offices: Headington Hill Hall, Oxford (Oxford 64881).

Published monthly - 1 Volume *per annum*

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- ³ A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.
- ⁴ W. Jones, *Brit. Pat.* 654321, 1959.

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DETERMINATION OF THE METHYLOL GROUP IN PHENOLIC RESINS

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(Received 4 October 1962. Accepted 15 February 1964)

Summary—An accurate and simple method for determination of the methylol group in phenolic resins is described. The phenolic hydroxyl group is determined by titration with sodium methoxide in non-aqueous solvent, and total hydroxyl group (phenolic hydroxyl plus alcoholic hydroxyl) is found by calculation of the integrated absorption intensity from the infrared spectrum observed between 3600 and 3000 cm^{-1} . The alcoholic hydroxyl group (methylol group) is calculated as the difference between the total and the phenolic hydroxyl group. In contrast to customary techniques, this method is simple, direct and provides a satisfactory precision ($\pm 8\%$).

INTRODUCTION

SEVERAL techniques have recently been described for determination of the methylol group in phenolic resins, but they have not been found generally satisfactory.

Stenmark and Weiss¹ reported an accurate and simple method for determination of the methylol group in resins. Methylol groups and phenol condense in the presence of acid catalyst to form water which is titrated directly with Karl Fischer reagent. This method provided an accurate value with small samples and thus facilitated experiments on laboratory scale preparations. However, the reaction is slow, requiring as long as 3 hr for completion.

Motoyoshi² reported the determination of methylol groups in resins by the following method. The resin, dried in vacuum at 50°, is extracted by methanol, the phenolic hydroxyl group in the extracted resin methylated by methyl iodide-potassium hydroxide solution, and the alcoholic hydroxyl group determined by phthalic anhydride. The precision of this method was not quoted.

Somiya *et al.*³ measured the infrared spectra of methylol derivatives of phenol, *o*-, *m*- and *p*-cresol, 2,4-dimethylphenol and 2,4-dibromophenol, and determined the intensity of the methylol group absorption at 10 μ by the potassium bromide disc process. They proved that methylol groups in novolaks can be determined with satisfactory precision by their method. However, methylol groups of phenolic alcohols absorb between 9.5 and 10.5 μ and these absorptions are not always constant in position. For this reason, methylol groups of resoles are difficult to determine with sufficient precision.

In this paper, a comparatively accurate, rapid and simple method for the determination of methylol groups in phenol-formaldehyde resins is proposed. Phenolic hydroxyl groups are titrated directly with sodium methoxide, and total hydroxyl group (phenolic hydroxyl group plus alcoholic hydroxyl group) is determined from

infrared absorption spectrum between 3600 and 3000 cm^{-1} . The methylol group is calculated as the difference between the total and phenolic hydroxyl groups.

EXPERIMENTAL

Determination of Phenolic Hydroxyl Group

In 1948, Moss, Elliott and Hall⁴ pointed out that phenols behave as moderately strong acids in anhydrous ethylenediamine. They were unable to find a satisfactory visual indicator, but carried out potentiometric titrations successfully using sodium aminoethoxide in ethylenediamine-ethanolamine as the titrant.

Fritz and Lisicki⁵ titrated phenols potentiometrically in butylamine with sodium methoxide, but found no successful visual indicator. Later, Fritz and Keen⁶ reported that phenol and alkyl-substituted phenols were somewhat weaker acids but could be titrated in ethylenediamine using *o*-nitroaniline as the indicator.

In the present work, essentially the same procedure as that of Fritz and Keen was used.

Reagents

Benzene. Extra pure (Kanto Chemical Co., Japan)

Methanol. Extra pure (Kanto Chemical Co., Japan)

Ethylenediamine (anhydrous). Guaranteed reagent (Kanto Chemical Co., Japan)

Phenol samples. Commercial samples (98–100% purity)

Benzyl alcohol. Guaranteed reagent (Daiichi Pure Chemicals Co., Japan)

o-Hydroxybenzyl alcohol (*saligenine*). Guaranteed reagent (Tokyo Kasei Kogyo Co., Japan)

p-Hydroxybenzyl alcohol. Prepared by hydrogenation of *p*-hydroxybenzaldehyde (Tokyo Kasei Kogyo Co., Japan) and recrystallised from water, m.p. 123°

p-Cresol dialcohol. Prepared by Auwer's Method,⁹ m.p. 128.5°

o-Cresol dialcohol. Prepared by Hanus's Method,¹⁰ m.p. 92.5°

o-Nitroaniline. Guaranteed reagent, 0.15 g dissolved in 100 ml of benzene.

Benzoic acid. Guaranteed reagent (Kanto Chemical Co., Japan)

Sodium methoxide (0.1–0.2 *M*). About 0.6 g of freshly cut sodium metal is added to 10 ml of methanol in a loosely covered flask. When the reaction is complete, 15 ml of methanol and 150 ml of benzene are added with stirring until the solution becomes homogeneous and clear. This is stored in a glass bottle protected from moisture and carbon dioxide. The titrant solution is standardised against benzoic acid.

Apparatus

The titration assembly consists of a 10-ml burette, a 50 to 100-ml titration vessel (covered to prevent absorption of carbon dioxide from the air), and a magnetic stirrer (equipped with a small stirring bar sealed in glass).

Procedure

About 25 ml of ethylenediamine, with 3–4 drops of *o*-nitroaniline as the indicator, is titrated with sodium methoxide to a red colour. The neutralised solvent is combined with the sample solution and titrated with sodium methoxide, the end-point being the change from clear yellow to orange-red. The weight of sample taken is so selected that 1–5 ml of the methoxide will be consumed.

Determination of Phenolic and Alcoholic Hydroxyl Group

From infrared studies on the association of phenol with several ketones Widom *et al.*⁷ reported that the phenol-acetone complex has a great association effect. In general,⁸ the intensity is greatly increased in solvents in which the association effect occurs.

In the present work, acetone was used as a solvent that not only dissolves phenols and resins but also increases the association effect, and the total hydroxyl group (phenolic hydroxyl plus alcoholic hydroxyl) was determined quantitatively by infrared absorption spectra between 3600 and 3000 cm^{-1} .

Reagents

Acetone. Extra pure (Kanto Chemical Co., Japan) distilled in an all-glass apparatus from phosphorus pentoxide immediately before use.

Phenols and phenolic alcohols. As above.

Apparatus

The absorption was measured using a Nihon Bunko Model 301 infrared spectrophotometer. Two 0.100-mm cells having sodium chloride plates were used.

Procedure

In actual measurements, a solution in which 5–30 mg of sample is dissolved in 1 ml of acetone is placed in the sample beam and acetone in the reference beam of the instrument. Examples of the spectra obtained are given for the phenol-acetone solution in Fig. 1.

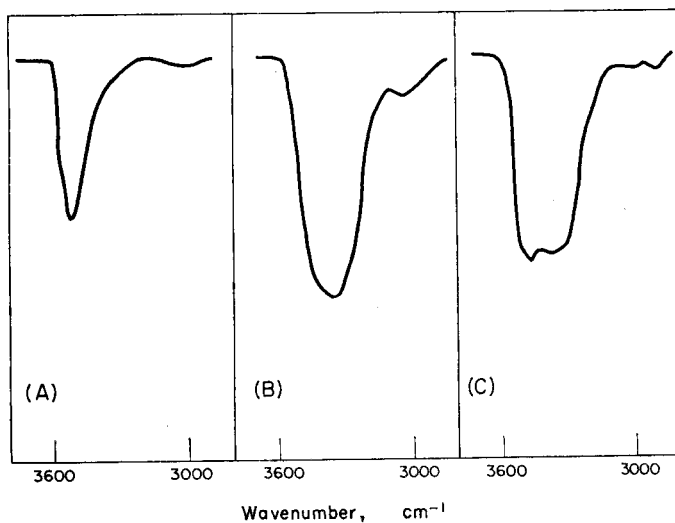


FIG. 1.—Infrared spectra of samples:
 (A) benzyl alcohol,
 (B) phenol,
 (C) *p*-methylol phenol.

Because the phenolic and alcoholic hydroxyl absorptions occur at somewhat different wavelengths, integrated absorption intensities were calculated by dividing the range 3000 to 3600 cm^{-1} into fifteen equal parts using the following equation

$$A = 1/c, l \left(\sum_{n=1}^{15} \log (T_0/T) \Delta\nu \right)$$

where c is the concentration (mole/l.), l is the cell length (cm) and $\Delta\nu$ is the width of each part (40 cm^{-1}).

Determination of Methylol Group

The methylol content (mole/g) of the samples was calculated from the expression

$$\frac{A' - B \times D}{C}$$

- where A' = the integrated absorption intensity of total hydroxyl group/g ($1/\text{g} \cdot \text{cm}^2$),
 B = the mean integrated absorption intensity of phenolic hydroxyl group/molecule ($1/\text{mole} \cdot \text{cm}^2$),
 C = the mean integrated absorption intensity of alcoholic hydroxyl group/molecule ($1/\text{mole} \cdot \text{cm}^2$),
 D = phenolic hydroxyl group (mole/g).

RESULTS AND DISCUSSION

Data for determination of phenolic hydroxyl groups are given in Table I.

TABLE I.—TITRATION OF PHENOLS IN ETHYLENEDIAMINE
(Indicator: *o*-nitroaniline)

Compound	Taken, mg	MeONa, ml	MeONa, M	Found, %
Phenol	53.98	4.79	0.1206	100.5
<i>o</i> -Hydroxybenzyl alcohol	20.36	1.23	0.1331	100.0
<i>p</i> -Hydroxybenzyl alcohol	28.18	1.81	0.1231	97.5
<i>p</i> -Cresol dialcohol	23.33	1.23	0.1124	100.0
<i>o</i> -Cresol dialcohol	22.97	1.22	0.1124	98.5
2,6-Xylenol	40.19	2.91	0.1124	99.5
	36.16)			
Phenol + benzyl alcohol	37.94)	3.12	0.1212	98.5
Phenol + water	54.73)			
	14.25)	4.78	0.1218	100.0

This method gave satisfactory results for the titration of this type of phenolic hydroxyl group. The precision was within $\pm 1\%$ and the bias was not significant. However, this method possessed the defect that high molecular weight substances precipitated in the course of titration, obscuring the end-point. The presence of a small amount of water in the sample did not interfere.

The integrated absorption intensities of phenols and phenolic alcohols are given in Table II. The intensity of aromatic CH was neglected because it was less than 1% of the intensity of phenolic hydroxyl group in the samples.

TABLE II.—INTEGRATED ABSORPTION INTENSITY OF PHENOLIC
AND ALCOHOLIC HYDROXYL GROUPS

Compound	Integrated absorption intensity, $\times 10^4$ litre. mole ⁻¹ . cm ⁻²
Phenol	3.35
<i>o</i> -Cresol	3.37
<i>p</i> -Cresol	3.34
2,4-Xylenol	3.35
2,6-Xylenol	2.37
Benzyl alcohol	1.35
<i>o</i> -Hydroxybenzyl alcohol	4.69
<i>p</i> -Hydroxybenzyl alcohol	4.62
<i>o</i> -Cresol dialcohol	5.66
<i>p</i> -Cresol dialcohol	6.10

The data were arranged by least squares, supposing that the following equation was applicable to them

$$A_{\text{total}} = mB + nC$$

where A_{total} is the integrated absorption intensity of total hydroxyl/mole, B and C are as before, m is the number of phenolic hydroxyl groups/molecule, and n is the number of alcoholic hydroxyl groups/molecule.

The results were as follows: $B = 3.35 \times 10^4$, $C = 1.29 \times 10^4$, standard deviation $\sigma = 0.11 \times 10^4$.

Because the hydroxyl absorption of water and alcohol occurs in the same region, the presence of small amounts of water and alcohol in the sample interferes. While the presence of lower polyoxymethylene glycols (formaldehyde polymers) is to be avoided, small amounts do not interfere.

Data of determination of methylol groups in phenolic alcohols are shown in Table III.

The precision of the method is about 8%, with a daily error of determination of about 4%. This is considered to be satisfactory.

Analysis of Phenol-Formaldehyde Resins

The method was applied to three phenolic resins of the resol type with the results shown in Table IV. These resins were prepared with varied concentrations of formaldehyde under alkaline conditions and were freeze-dried two or three times from benzene-methanol to eliminate water.

TABLE III.—DETERMINATION OF METHYLOL GROUPS IN PHENOLIC ALCOHOL

Compound	A', 1/g. cm ²	D, × 10 ⁻³ mole/g	Alcoholic OH, × 10 ⁻³ mole/g	
			Found	Theoretical
<i>o</i> -Hydroxybenzyl alcohol	378	8.01	8.5	8.1
<i>p</i> -Hydroxybenzyl alcohol	372	7.87	8.4	8.1
<i>o</i> -Cresol dialcohol	362	5.95	10.7	11.9
<i>p</i> -Cresol dialcohol	337	5.85	12.9	11.9

TABLE IV.—DETERMINATION OF METHYLOL GROUPS IN PHENOLIC RESINS

Resin	A', 1/g. cm ²	D, × 10 ⁻³ mole/g	Alcoholic OH, × 10 ⁻³ mole/g
1	351	7.13	8.7
2	321	5.98	9.4
3	385	5.44	15.7

The methylol content was determined under the conditions outlined above; satisfactory results were obtained.

Acknowledgement—The authors thank Professor H. Kamada of Tokyo University for advice and Vice-President T. Kikuchi of Fudow Chemical Company for permission to publish this paper.

Zusammenfassung—Eine genaue und einfache Methode zur Bestimmung der Methylolgruppe in Phenolharzen wird beschrieben. Die phenolische Hydroxylgruppe wird durch Titration mit Natriummethylat in einem nichtwässrigen Lösungsmittel bestimmt, die Gesamtmenge an OH-Gruppen (phenolische und alkoholische) findet man aus der integrierten Absorptionsintensität im Infrarotspektrum zwischen 3600 und 3000 cm⁻¹. Der Gehalt an alkoholischen (Methylol-) Hydroxylgruppen wird als Differenz zwischen Gesamt- und phenolischen Hydroxylgruppen berechnet. Im Gegensatz zu herkömmlichen Vorschriften ist die Methode einfach und direkt und liefert zufriedenstellende Genauigkeit (±8%).

Résumé—On décrit une méthode précise et simple de dosage du groupe méthylol dans les résines phénoliques. Le groupe hydroxyle phénolique est dosé volumétriquement au moyen de méthylate de sodium en solvant non aqueux, et l'hydroxyle total (hydroxyle phénolique plus hydroxyle alcoolique) est trouvé par calcul de l'intensité d'absorption intégrée à partir du spectre infra-rouge observé entre 3600 et 3000 cm⁻¹. Le groupe hydroxyle alcoolique (groupe méthylol) est calculé en tant que différence entre l'hydroxyle total et l'hydroxyle phénolique. Par opposition à la technique usuelle, cette méthode est simple, directe, et fournit une précision satisfaisante (±8%).

REFERENCES

- G. A. Stenmark and F. T. Weiss, *Analyt. Chem.*, 1956, **28**, 260.
- M. Motoyoshi, Japan Patent No. 33-1143, 1958.
- T. Somiya, S. Hirano, S. Tanaka and T. Kurachi, *Ann. Report Eng. Res. Inst., Fac. Eng., Univ. Tokyo*, 1960, **18-2**, 130.
- M. L. Moss, J. H. Elliott and R. T. Hall, *Analyt. Chem.*, 1948, **20**, 784.
- J. S. Fritz and N. M. Lisicki, *ibid.*, 1951, **23**, 589.
- J. S. Fritz and R. T. Keen, *ibid.*, 1953, **25**, 179.
- J. M. Widom, R. J. Philippe and M. E. Hobbs, *J. Amer. Chem. Soc.*, Methuen, London, 1957, **79**, 1383.
- L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 1958, p. 107.
- K. V. Auwers, *Ber.*, 1907, **40**, 2531.
- F. Hanus, *J. prakt. Chem.*, 1940, **155**, 317.

PAPER CHROMATOGRAPHY IN INORGANIC QUALITATIVE ANALYSIS

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(Received 8 July 1963. Accepted 1 March 1964)

Summary—A two-dimensional paper chromatographic method for the separation and identification of several metal ions is described. After preparation, the sample is run with an ethanol:hydrochloric acid:water (75:20:5) mixture, and later in a second dimension with a tetrahydrofuran:nitric acid:water (85:5:10) mixture. The chromatogram can be developed with a 0.2% ethanolic solution of Morin, and is examined both in sunlight and in ultraviolet light, in acidic conditions and after alkalislation with ammonia vapour. Those metal ions which migrate together in the first solvent will be separated in the second one, and can be identified reliably. The composition of the original sample can be deduced from the R_f values, colours and fluorescences of the various spots.

In a previous paper a general method for orientative qualitative analysis has been described.¹ This was not suitable for the simultaneous detection of the following combinations: Zr-Th, Sc-Al, Co-V-Ti, Cu-U, Bi-Pd, Zn, and Sn. A further development of the method, by which any of these ions in admixture can be detected reliably, is based on the use of a solvent in a second dimension, with an appreciably lower dielectric constant than the first. Tetrahydrofuran (THF) was found to be suitable. THF has already been used chromatographically by Specker and Hartkamp.²

Pure THF is generally unsuitable as a chromatographic solvent, because the cations, used in the form of chlorides, sulphates or nitrates, remain at the starting point of the chromatogram. If, however, inorganic acids and water are added to the solvent, migration of the ions takes place. To find the optimal composition of the solvent mixture, thorium and zirconium, which generally show a marked difference in behaviour in this type of chromatography, were examined. If the amount of electrolyte in the solvent is increased, thorium migrates with the front, and even zirconium moves from the origin. Both ions, however, form extended spots. If the composition of the solvent is within the limits by volume of 80–85% of THF, 5–10% of nitric acid and 10–15% of water, thorium migrates exactly along with the front. In those cases where the solvent forms two fronts in the chromatographic process, thorium is found in the second front. Zirconium migrates only slightly, and although its spot may extend up to an R_f value of 0.5, it can be reliably distinguished from thorium. In addition, other metal ions, which cannot be separated with an ethanol-hydrochloric acid solvent, are separated with this solvent to such an extent that individual qualitative test can be carried out without difficulty.

Specker and Hartkamp² investigated the dependence of R_f values of cations on the composition of solvent mixtures. Burstall and co-workers³ separated thorium from rare earths with 2-methyltetrahydrofuran (tetrahydrofuran), containing 10%

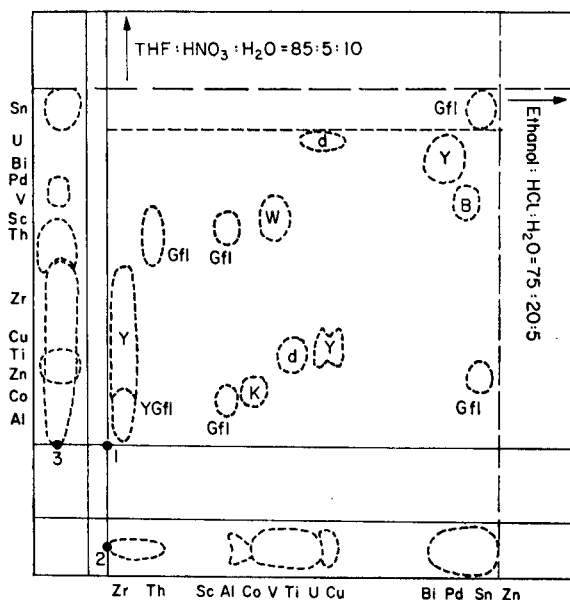


FIG. 1

by volume of nitric acid and 5% of water. For the present purpose a mixture of THF: nitric acid:water (85:5:10) is the most suitable one. Using this solvent in a second dimension, after a run with a hydrochloric acid-ethanol solvent, and drying, all those ions which were not separated by the first solvent will form clearly discernable spots in the chromatogram.

TABLE I.— R_f VALUES IN THE SOLVENT THF:HNO₃:H₂O (85:5:10)

Element	R_f value
Zr	Yellow strip extending from the origin to approximately R_f 0.5; green fluorescence at the origin.
Th	In Front 2 (R_f value in relation to Front is 1:0.9)
Al	0.14
Sc	0.65
Co	0.14
V	0.65
Ti	0.23
U	In Front 2 (R_f related to Front is 1:0.9)
Cu	0.25
Bi	0.88
Pd	0.72
Zn	0.20
Sn	0.94

If, after drying, the chromatogram is sprayed with a 0.2% ethanolic solution of Morin, the spots will appear as indicated in Fig. 1. The R_f values in the solvent mixture of the pairs and the triplet are presented in Table I.

In Table I the R_f values are related to the first Front. The distance of the two Fronts, if the first Front has migrated approximately 20 cm from the origin, is about 20 mm; the R_f value of the second Front therefore is about 0.90.

EXPERIMENTAL

*Reagents**Tetrahydrofuran (THF): Puriss**Ethanol: 96%**Hydrochloric acid: S.g. = 1.19**Nitric acid: S.g. = 1.42**Morin (3,5,7,2',4'-pentahydroxyflavone): 0.2% in ethanol**Solvent I (ethanol:HCl:H₂O = 75:20:5):* Mix 5 ml of water with 20 ml of concentrated hydrochloric acid, and pour this solution into 75 ml of ethanol.*Solvent II (THF:HNO₃:H₂O = 85:5:10):* Mix 5 ml of concentrated nitric acid with 10 ml of water and pour this with constant stirring into 85 ml of THF.*Paper: Schleicher and Schull No. 2043/A, size 58 × 60 cm.**Procedure*

Prepare the solution to be analysed, using the procedure described elsewhere,¹ by boiling with H₂O₂ and HCl. Place a drop of the solution on a 29 × 30 cm (quarter) sheet of Schleicher-Schüll No. 2043/A paper. The origin must be chosen as follows (see Fig. 2). First draw two base-lines at right angles to each other, 30 mm from the original (machine-cut) edges of the paper. These lines

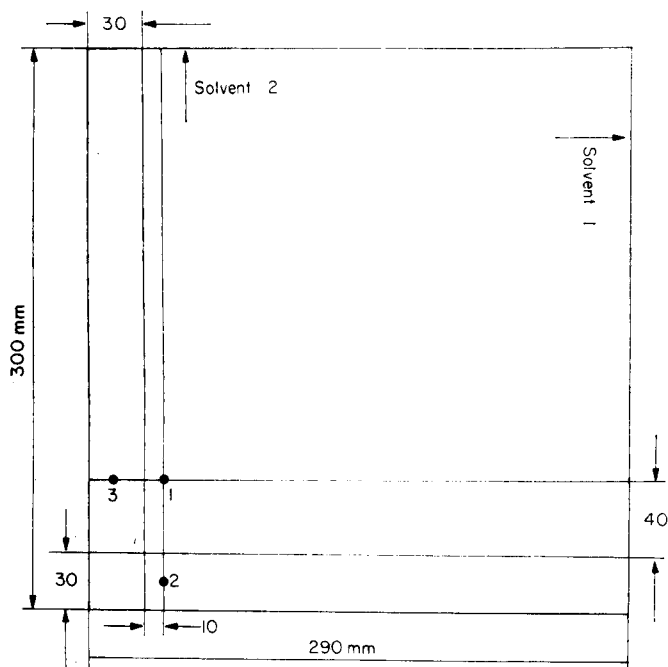


FIG. 2

act as the boundaries of the two test-strips which will later be cut from the chromatogram. Now ascertain the direction of the fibres of the paper; they appear in normal cases to be parallel to the longer side. Draw two starting lines at distances of 10 and 30 mm from the base-lines, one parallel and one perpendicular to the fibres. The origin is the point of intersection of these last lines (Point 1 on Fig. 2). Place a further drop of the sample at Point 2 (15 mm from the edge of the paper). Dip the paper, at right angles to the fibres, in Solvent I, and let the solvent run overnight, using ascending technique. During this time the front travels about 20 cm from the start. Dry the chromatogram under an infrared lamp, and remove traces of hydrochloric acid as completely as possible by an air stream. Cut off the 30-mm test strip (which is parallel to the shorter edge of the paper), and store for further experiments (Test strip of Solvent I).

Place a further drop of the original solution on Point 3 (see Fig. 3), 40 mm from the freshly-cut edge and 15 mm from the original edge of the paper. (Test strip of Solvent II). Dip the freshly-cut

edge of the paper in Solvent II and let the solvent run for 4–5 hr, during which time the front migrates about 20 cm from the start. (This distance can be marked on the paper previously.) Dry the paper, remove the traces of nitric acid by an air stream, and spray the paper with a 0.2% ethanolic Morin solution.

Examine the paper in sunlight, and in transparent and reflected ultraviolet light. Mark the coloured spots and the green or yellow fluorescent ones on one side of the paper. Hold the paper over ammonia vapour and examine once more. Mark any spots on the other side of the paper. This examination shows whether spots corresponding to ions which are not separated by Solvent I contain one or more components. R_f values for Solvent II are presented in Table I, and a typical chromatogram is shown in Fig. 1. The notations are those used in an earlier paper.¹

It is very important to remove hydrochloric acid as completely as possible from the paper after the first run by thorough drying and ventilation. Otherwise the formation of the thorium-nitrate complex (which is soluble in THF) will not be achieved. If it is not, thorium shows an R_f value of about 0.5–0.6. If the chromatographic separation is interrupted after the run with Solvent I, and the dry paper is placed over ammonia vapour, thorium will then have an R_f value higher than 0.5 in Solvent II, but it does not reach the second front. It can still, however, be reliably identified in the presence of zirconium. If only THF is used, thorium migrates along with the second front. The R_f values for the other metal ions are not affected by previous treatment with the hydrochloric acid solvent, and therefore the same results will be obtained if only Solvent II is used for the chromatographic separation. Uranium, as opposed to thorium, will be found in either case in the second front.

There are difficulties in identifying those ions which have high R_f values in both solvent systems (0.9 to 1.0); these will be concentrated on the diagonally opposite corner of the chromatogram from the origin. The difficulties occur because impurities dissolved from the paper (particularly iron) are concentrated on this part of the chromatogram, and the resulting dark spot will hide the spots being sought, both in sunlight and in ultraviolet radiation. However, most of these ions, e.g., antimony, tin and gallium, can be identified easily in Solvent I, and of the unresolved zinc-tin pair, zinc migrates more slowly in Solvent II than does tin.

Sensitivities for the qualitative tests on the single ions are about the same as described previously;¹ if the ions are in mixtures, the sensitivities are generally lower by 1–2 magnitudes. Morin is not a very sensitive reagent for most of the metal ions. The sensitivities can be increased as follows: examine the chromatogram after the run with Solvent I, and then from the information gained in this way, apply specific reagents, after the run with Solvent II, on the spots in which any given ion is suspected.

Acknowledgement—The authors wish to express their thanks to Prof. B. Lengyel, Head of the Research Group, for having kindly permitted this work to be carried out in his Institute.

Zusammenfassung—Eine zweidimensionale papierchromatographische Methode zur Trennung und Identifikation mehrerer Metallionen wird vorgeschlagen. Nach geeigneter Vorbereitung lässt man die Probe mit einem Äthanol-Salzsäure-Wasser-Gemisch 75:20:5 laufen, anschließend in der zweiten Dimension mit Tetrahydrofuran-Salpetersäure-Wasser 85:5:10. Das Chromatogramm kann mit einer 0.2% igen alkoholischen Morinlösung entwickelt werden und wird im Tageslicht und unter einer Ultraviolettlampe betrachtet, sowohl im sauren Zustand als auch nach Behandlung mit Ammoniakgas. Die Metallionen, die im ersten Laufmittel zusammen wandern, werden im zweiten getrennt und können zuverlässig identifiziert werden. Die Zusammensetzung der Probe kann aus R_f -Wert, Farbe und Fluoreszenz der einzelnen Flecke ermittelt werden.

Résumé—On présente une méthode de chromatographie sur papier à deux dimensions pour séparer et identifier plusieurs ions métalliques. Après une préparation convenable, l'échantillon est entraîné par un mélange éthanol—acide chlorhydrique—eau (75:20:5) puis, dans la seconde dimension, par un mélange tétrahydrofuran—acide nitrique—eau (85:5:10). Le chromatogramme peut être révélé par une solution alcoolique à 0.2% de morin, et doit être examiné à la lumière solaire et en lumière ultra-violette, tant à l'état acide qu'après alcalinisation aux vapeurs d'ammoniac. Les ions métalliques qui migrent ensemble dans le premier solvant seront séparés dans le second, et peuvent être identifiés de façon certaine. On peut estimer la composition de l'échantillon original à partir des valeurs des R_f , des couleurs et de la fluorescence des diverses taches.

REFERENCES

- ¹ A. Schneer-Erdey, *Talanta*, 1963, **10**, 591.
- ² H. Specker and H. Hartkamp, *Naturwiss.*, 1955, **42**, 535; *Z. analyt. Chem.*, 1956, **152**, 107; 1957, **158**, 92, 161.
- ³ T. V. Arden and F. Burstall, *Nature*, 1948, **162**, 691; T. V. Arden, F. H. Burstall and R. P. Linstead, *J. Chem. Soc.*, 1949, 311; F. H. Burstall, R. A. Wells and R. P. Linstead, *ibid.*, 1950, 516.
- ⁴ G. Sommer, *Z. analyt. Chem.*, 1955, **147**, 241; 1956, **151**, 336.

THERMOANALYTICAL PROPERTIES OF ANALYTICAL- GRADE REAGENTS AMMONIUM SALTS

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(Received 7 October 1963. Accepted 13 January 1964)

Summary—Twenty-six ammonium salts have been investigated derivatographically. The weight change, rate of weight change and enthalpy change of the salts have been measured as a function of temperature. From the results the temperatures at which the salts may be dried without decomposition are given.

DUVAL and his coworkers¹ studied nearly one thousand analytical precipitates by the method of thermal gravimetry. The intention was to establish the temperature at which the analytical precipitate is of stoichiometric composition and the temperature interval over which the precipitate is suitable for weighing. Berg² and Smothers and Chiang³ introduced the method of differential thermal analysis in their books and treated in detail its most important fields of application. Few workers have used the two methods in conjunction with each other. Erdey, Paulik and Paulik combined the methods of thermal gravimetry (TG) and differential thermal analysis (DTA) with the method of derivative thermal gravimetry (DTG) elaborated by themselves.⁴ TG, DTA and DTG curves were recorded automatically on an apparatus designated a derivatograph.^{5,6} The derivatograph can measure simultaneously, for a single sample, change of weight (TG), rate of change of weight (DTA) and enthalpy change (DTG), as a function of temperature, at a heating rate of 1–20°/min.

Twenty-six ammonium salts have now been investigated derivatographically (Table I). We have attempted to explain the results in terms of the Lewis electron theory previously applied to acid-base reactions.^{7,8} The various decomposition processes can be interpreted satisfactorily on the basis of the derivatograms. Where intermediate plateaux occur on the TG curves, they correspond to the formation of definite compounds, the formulae of which have been marked on the appropriate figures. Experimental weight losses agree well in most cases with the theoretical losses expected for the formation of such compounds. In those cases where agreement was not so good, the deviation could be attributed to two processes occurring at about the same temperature. Not all of the decomposition products were examined.

EXPERIMENTAL

The studies were carried out using a Paulik-Paulik-Erdey type 676 derivatograph manufactured by Orion-Gyem, Budapest, Hungary. The sample (100–200 mg) was weighed in the platinum crucible of the instrument. Gaseous decomposition products were pumped off from the air space of the furnace. A heating rate of 5°/min was employed. Samples were pulverised in a porcelain mortar and passed through a sieve of the same mesh-size in every case before being weighed.

The reagents used in the experiments were made available to us by E. Merck (Darmstadt, Germany), for which we would like to express our thanks.

TABLE I

Figure	Ammonium salt	Formula	DTA peaks, °C	DTG peaks, °C	Temperature of drying, ^a °C
1	Fluoride	NH ₄ F	Endothermic: 145, 220	145, 225	<50
2	Hydrogen fluoride	NH ₄ F·HF	Endothermic: 125, 240	235	<60
3	Chloride	NH ₄ Cl	Endothermic: 185, 345	345	110–120
4	Bromide	NH ₄ Br	Endothermic: 150, 415	410	<200
5	Iodide	NH ₄ I	Endothermic: 390	400	<200 ^b
6	Perchlorate	NH ₄ ClO ₄	Endothermic: 250;	400	<200 ^c
7	Sulphate	(NH ₄) ₂ SO ₄	Endothermic: 330, 410	410	<200
8	Thiosulphate	(NH ₄) ₂ S ₂ O ₃	Endothermic: 140, 225, 400;	220, 245, 350, 400	<80
9	Persulphate	(NH ₄) ₂ S ₈ O ₈	Endothermic: 370;	180, 365	<100 ^c
10	Thiocyanate	NH ₄ SCN	Endothermic: 90, 115, 150, 245;	245, 290, 515	<100 ^c
11	Nitrate	NH ₄ NO ₃	Endothermic: 45, 84, 130, 166;	285	100–110
12	Molybdate	(NH ₄) ₆ Mo ₇ O ₃₄ ·4H ₂ O	Endothermic: 120, 235, 350	110, 230, 350	<100
13	Metavanadate	NH ₄ VO ₃	Endothermic: 240, 375	230, 375	<100
14	Monohydrogen phosphate	(NH ₄) ₂ HPO ₄	Endothermic: 170;	150, 170, 260, 760	<100
15	Dihydrogen phosphate	NH ₄ H ₂ PO ₄	Endothermic: 200	230, 730	<150
16	Chromate	(NH ₄) ₂ CrO ₄	Endothermic: 130;	125, 236, 405	<40
17	Dichromate	(NH ₄) ₂ Cr ₂ O ₇	Endothermic: 245, 405	230, 395	<200
18	Pentaborate	NH ₄ B ₅ O ₈ ·4H ₂ O	Endothermic: 160, 280, 400	160, 280, 400, 430	—
19	Sulphamate	NH ₄ SO ₃ NH ₂	Endothermic: 135, 475	225, 290, 465	—
20	Carbonate	(NH ₄) ₂ CO ₃	Endothermic: 80	75	—
21	Acetate	NH ₄ OOCCH ₃	Endothermic: 100, 115, 155	150	30–40
22	Oxalate	(NH ₄) ₂ (COO) ₂ ·H ₂ O	Endothermic: 115, 235	115, 235, 300	<150 ^d
23	Citrate	(NH ₄) ₃ C ₆ H ₅ O ₇	Endothermic: 195	195	<100
24	Benzoate	NH ₄ C ₇ H ₅ O ₂	Endothermic: 195, 250	235	<50
25	Salicylate	NH ₄ C ₇ H ₅ O ₃	Endothermic: 200	190	<100
26	Tartrate	(NH ₄) ₂ C ₄ H ₄ O ₆	Endothermic: 185, 245	180, 245	<100

^a Without decomposition.^b Sample is hygroscopic.^c If pure.^d This temperature is for anhydrous ammonium oxalate. The monohydrate can be dried at 30–40°.

RESULTS AND DISCUSSION

Ammonium fluoride

It can be seen from the derivatogram (Fig. 1) that the mechanically bound water content of the sample is lost at about 50°. The peak on the DTA and DTG curves at 145° indicates a maximal rate of removal of ammonia according to

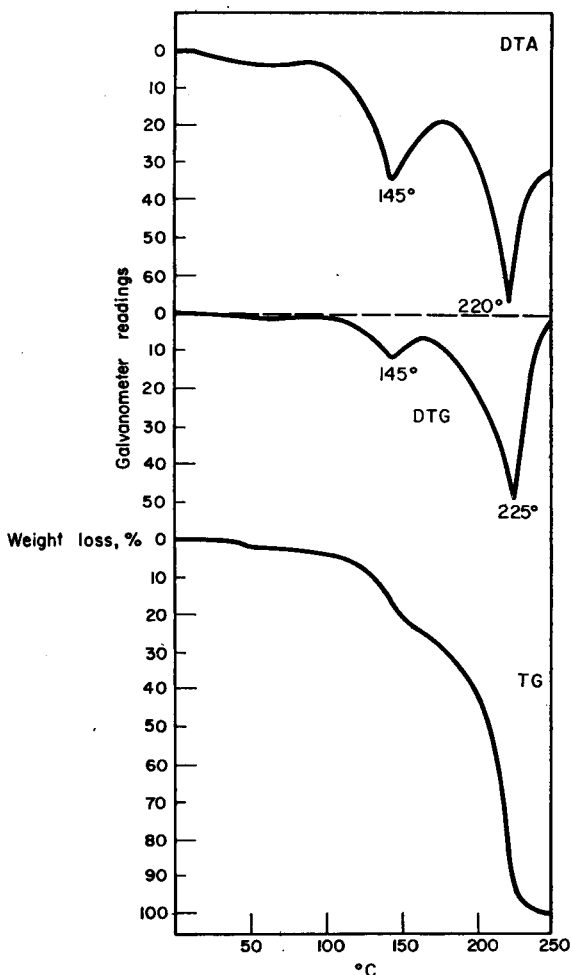


FIG. 1.—Ammonium fluoride.

The ammonium hydrogen fluoride formed begins to decompose to a small degree at this temperature. This decomposition proceeds at a maximal rate at 225°, ammonia and hydrogen fluoride being obtained.

Ammonium hydrogen fluoride

The sample melts at 125° (DTA curve in Fig. 2). The rate of decomposition—beginning at 80°—increases and the rate of weight decrease is maximal at 235°. Ammonium hydrogen fluoride is more stable than the neutral salt.

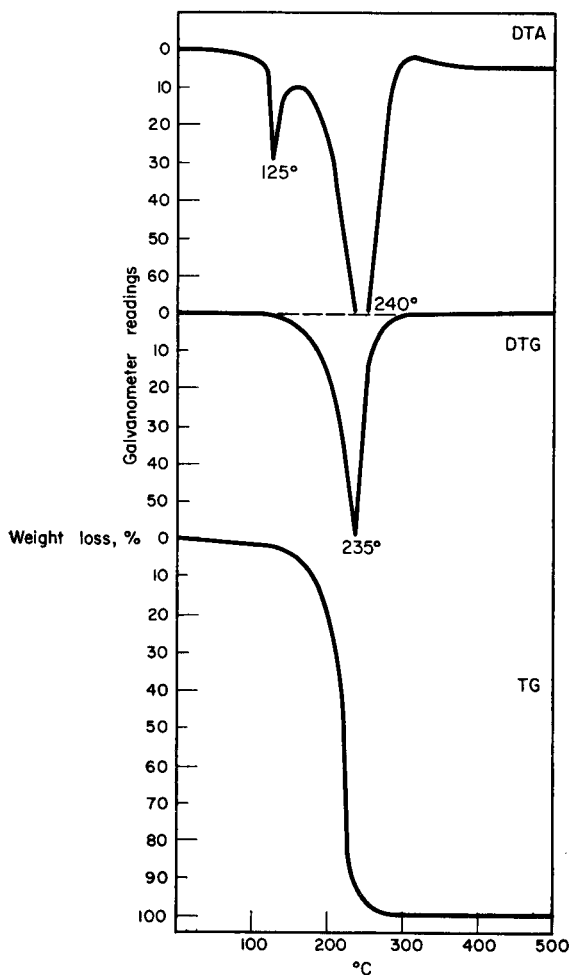


FIG. 2.—Ammonium hydrogen fluoride.

Ammonium chloride

Ammonium chloride shows little change in weight up to 200° (Fig. 3). The endothermic DTA peak at 185° indicates a change of crystal structure of ammonium chloride. Above 200° the substance sublimes, the sublimation rate being maximal at 345°. After sublimation it dissociates completely in the gaseous phase into ammonia and hydrochloric acid



On cooling, the reaction is reversed and ammonium chloride condenses from the gaseous phase.

Hydrochloric acid formed during the decomposition is very active and reacts with various metal oxides or carbonates at a temperature above 300° to form chlorides, water and carbon dioxide. Thus, aluminium oxide can be fused in this way.

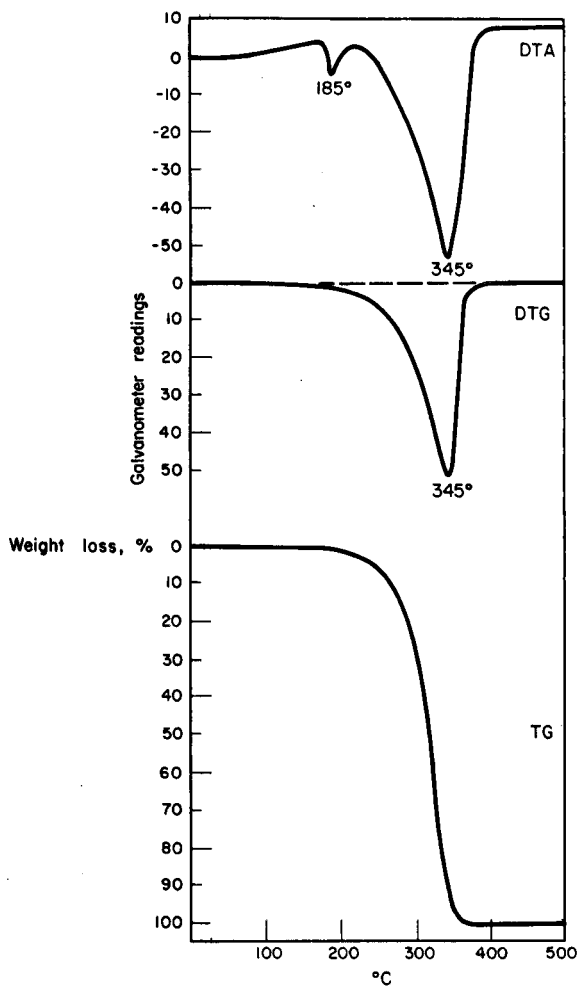


FIG. 3.—Ammonium chloride.

Ammonium bromide

Ammonium bromide shows a change in crystal structure at 150° (DTA curve in Fig. 4). Decomposition only begins to any marked extent above 250°. The salt does not melt at atmospheric pressure, but sublimes and decomposes completely in the gaseous phase to form ammonia and hydrogen bromide



On cooling, ammonium bromide condenses, *i.e.*, the reaction is reversible. Sublimation proceeds at the highest rate at 410°.

Ammonium iodide

Sublimation of ammonium iodide proceeds over nearly the same temperature interval as that of ammonium bromide (Fig. 5). Also, the ammonium iodide sublimes

and decomposes in the gaseous phase to ammonia and hydrogen iodide



On cooling, ammonium iodide condenses.

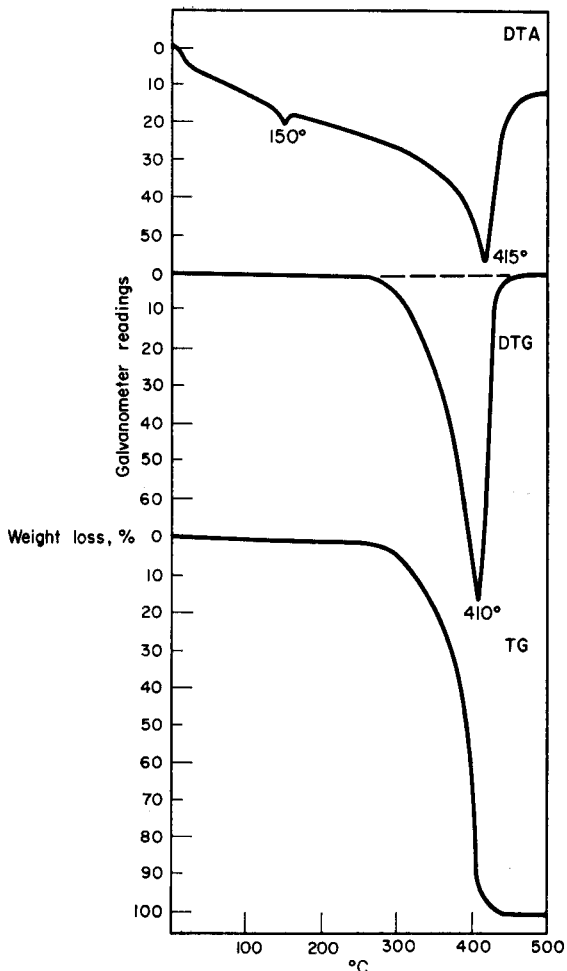


FIG. 4.—Ammonium bromide.

Ammonium perchlorate

An endothermic process can be observed on the DTA curve at 250° (Fig. 6), which accompanies a change in crystal structure of the ammonium perchlorate. Thereafter a decrease of weight begins. This decrease of weight is caused by decomposition and sublimation of the salt. Decomposition begins at a much lower temperature if there are small amounts of metal oxide or organic substance contamination. The sample studied is of analytical-grade material and is, therefore, very stable. The decomposition beginning above 250° is an exothermic process, as shown by the DTA peak at 400°. As the temperature of the sample reaches 400° decomposition proceeds explosively.

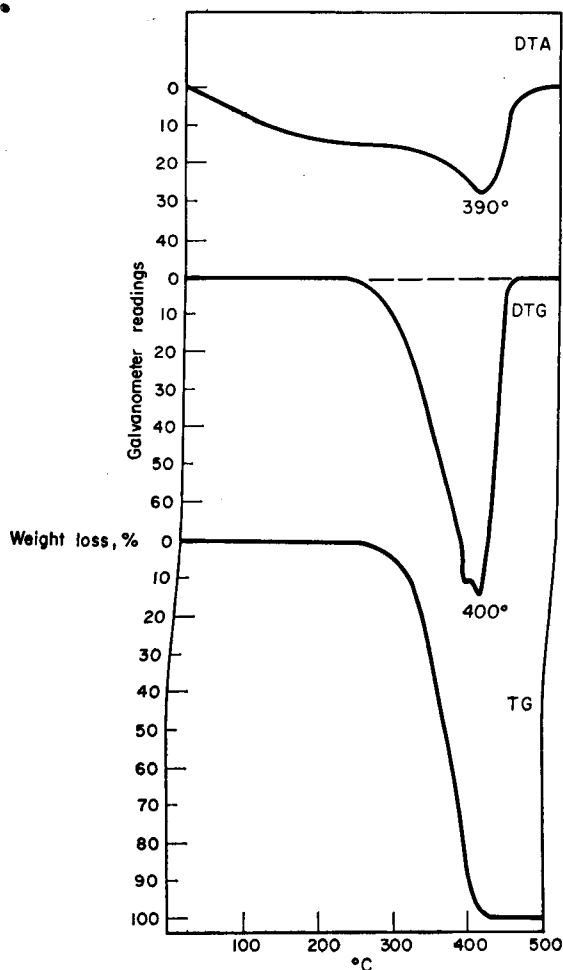
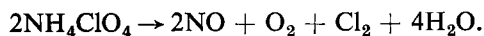


FIG. 5.—Ammonium iodide.

In the gaseous phase quite different reaction products are present depending on the temperature of decomposition. Below 300°, the reaction products are gaseous nitrogen, oxygen, chlorine and water vapour. Above 300°, various nitrogen oxides are also present besides gaseous nitrogen



At the temperature of the reaction the nitrogen monoxide reacts with oxygen and chlorine to form nitrogen dioxide (NO_2), dinitrogen trioxide (N_2O_3) and nitrosyl chloride (NOCl). The temperature of decomposition and composition of decomposition products varies according to the nature and amount of contaminants.

Ammonium sulphate

The ammonium sulphate sample contains neither mechanically bound nor water of crystallisation. The substance begins to decompose above 250° (Fig. 7). In the

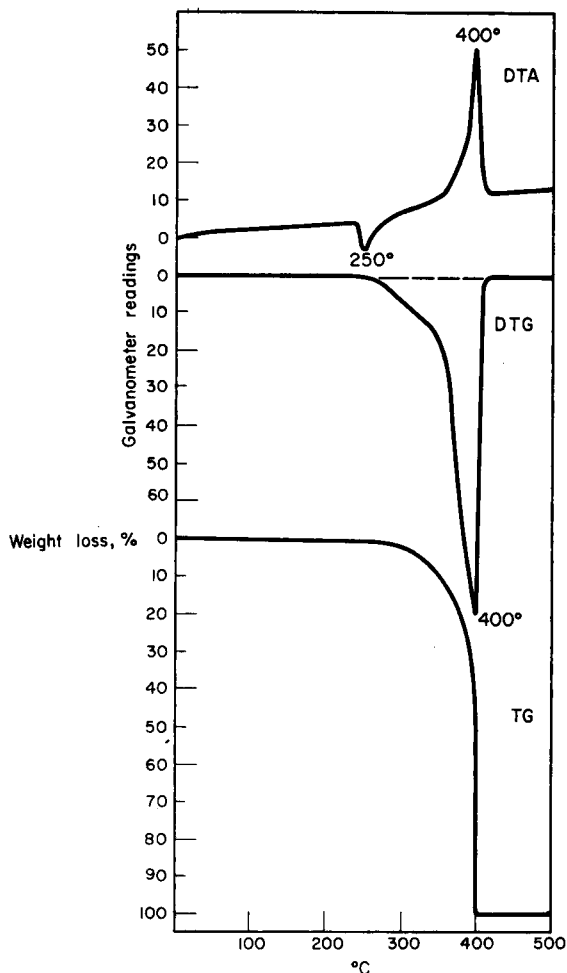
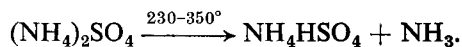
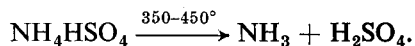


FIG. 6.—Ammonium perchlorate.

first step of the decomposition the molecule loses ammonia and ammonium hydrogen sulphate is formed



This reaction seems to be quantitative according to the derivatogram. The reaction is indicated by the endothermic DTA peak at 330°. Ammonium sulphate itself does not melt, although the ammonium hydrogen sulphate formed during the decomposition does. The ammonium hydrogen sulphate decomposes at 410° at a maximal rate and the process is completed at 450°



Sulphuric acid formed during the decomposition is very active and fuses various metal oxides.

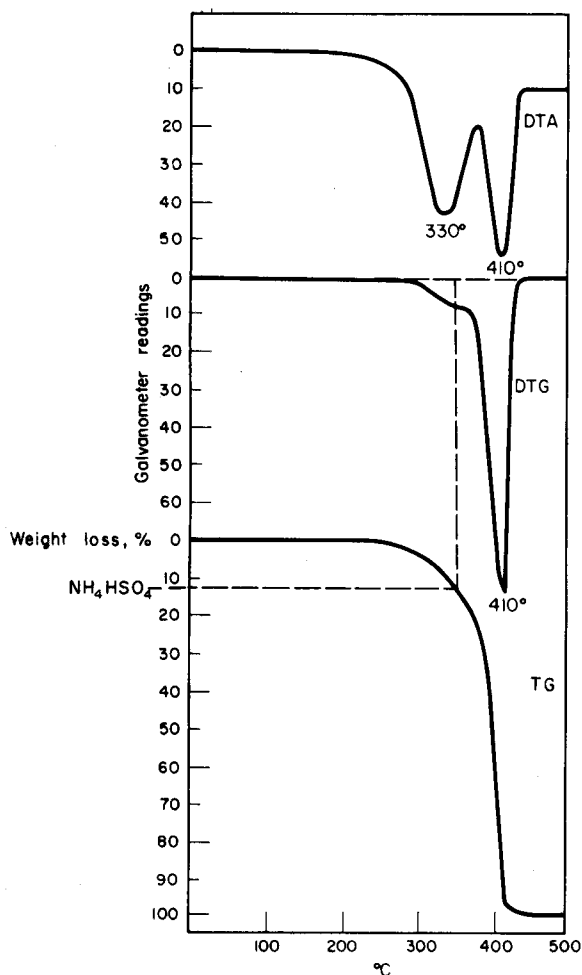
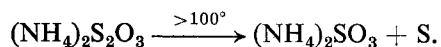


FIG. 7.—Ammonium sulphate.

Ammonium thiosulphate

The thermal decomposition of ammonium thiosulphate is complicated (Fig. 8). Up to 100° neither weight nor enthalpy change can be observed. The endothermic DTA peak at 140° indicates a change of crystal structure. Above 100° decomposition begins, ammonium sulphite and sulphur being formed



Part of the ammonium sulphite immediately decomposes, the maximal rate being at 230–245°



The rest of the ammonium sulphite is oxidised to ammonium sulphate. The net effect of the enthalpy changes of the two processes is endothermic. Above 275° the sulphur burns exothermically and ammonium hydrogen sulphate is formed from the

ammonium sulphate. Above 360° the ammonium hydrogen sulphate decomposes, the rate being maximal at 400°.

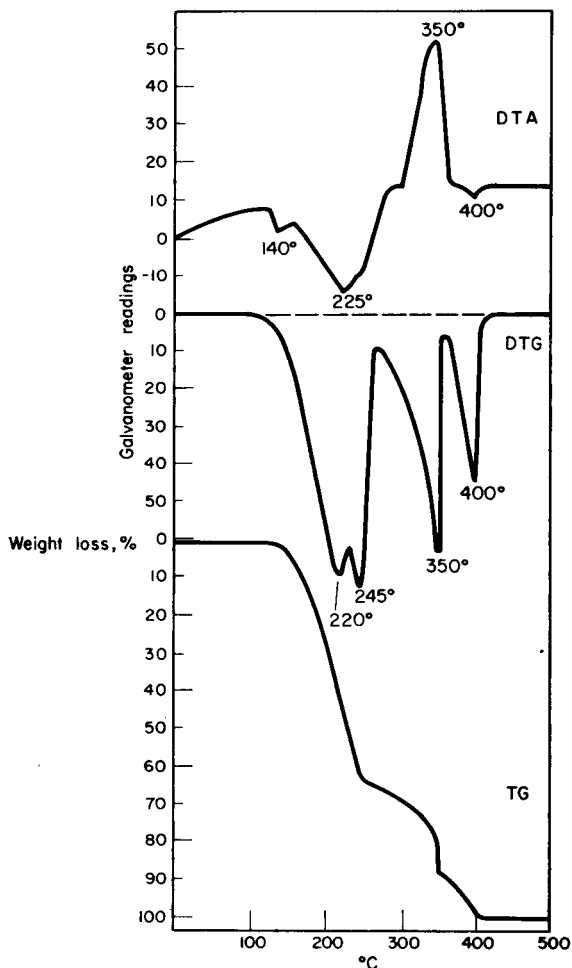
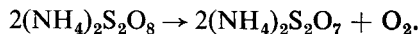


FIG. 8.—Ammonium thiosulphate.

Ammonium persulphate

Pure ammonium persulphate decomposes explosively at 180° according to the derivatographic curves (Fig. 9), ammonium pyrosulphate being formed and oxygen liberated



As shown by the TG curve, the exothermic reaction proceeds quantitatively. If water vapour is present in the furnace air space or the sample contains any organic matter, this reaction proceeds at a lower temperature. Ammonium pyrosulphate begins to decompose above 250°, sulphur trioxide being lost and ammonium sulphate remaining



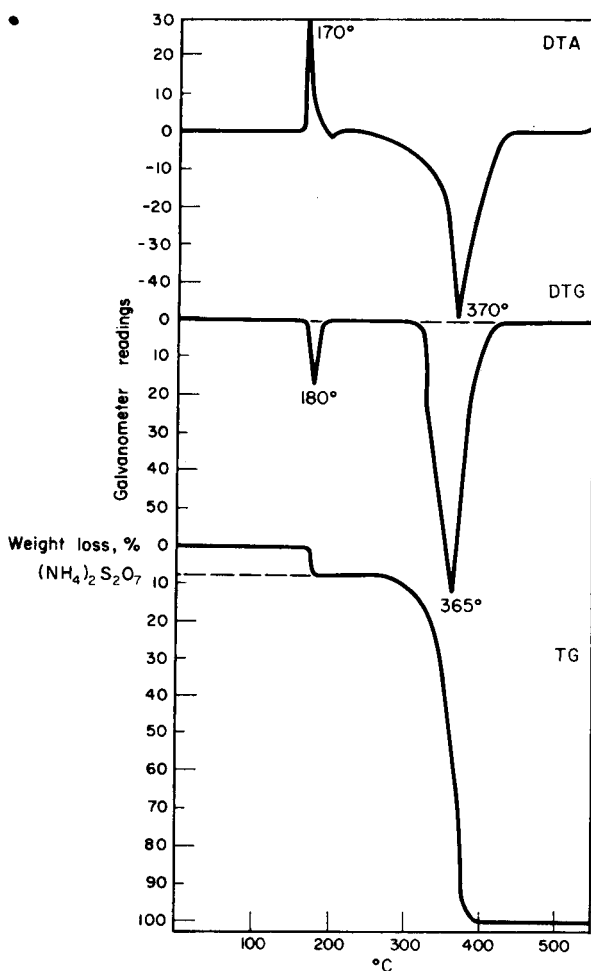


FIG. 9.—Ammonium persulphate.

This process is, however, very slow and not quantitative, because at the same time the ammonium sulphate formed decomposes to ammonium hydrogen sulphate, which in turn decomposes to ammonia and sulphuric acid



The above three decomposition processes proceed between 300 and 400° and are maximal in rate at 365°. All three decomposition processes are endothermic. Pure ammonium persulphate can be dried to about 100° without decomposition and heating it to 200° ammonium pyrosulphate can be obtained.

Ammonium thiocyanate

The endothermic peaks on the DTA curve (Fig. 10) of ammonium thiocyanate at 90 and 115° are characteristic of changes of crystal structure of the sample. These

changes are reversible. The endothermic DTA peak at 150° is characteristic of melting of the sample; the break in the curve at about 170° shows that after the melting another process accompanied by an enthalpy change proceeds. This region of the

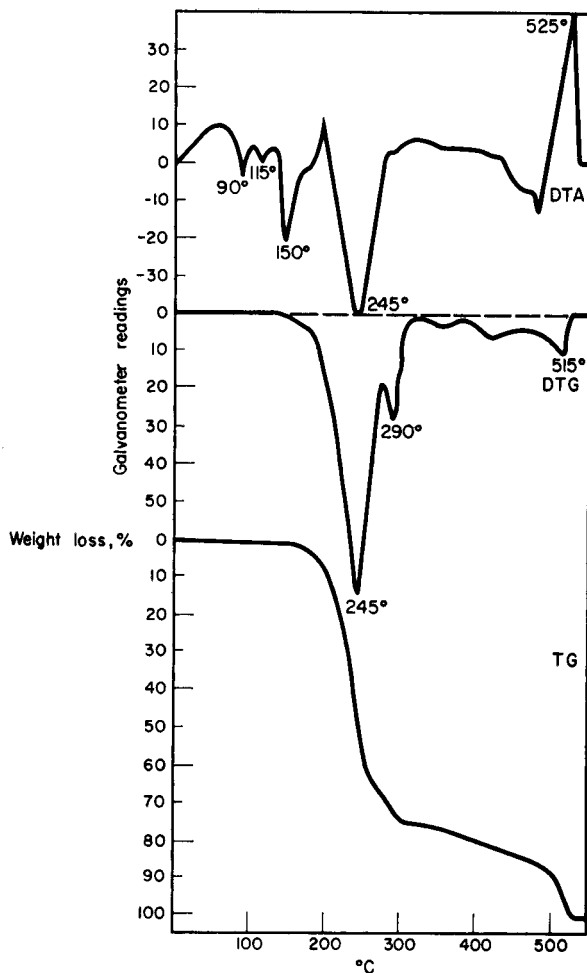
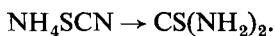


FIG. 10.—Ammonium thiocyanate.

DTA curve shows the transformation of the ammonium thiocyanate into thiourea



The transformation proceeds only partially and on further increase of temperature the amount of the thiourea formed decreases. After melting and partial transformation the substance decomposes, ammonia, carbon disulphide and hydrogen sulphide being removed, while guanidine thiocyanate and melamine thiocyanate remain. The first decomposition process is complete at about 300°, while the thiocyanates formed, having a higher decomposition temperature, are removed at a maximal rate only at 515°. This process is exothermic.

Ammonium nitrate

The derivatographic curve (Fig. 11) of ammonium nitrate provides a good illustration of the advantage of a multifunctional apparatus (TG, DTG and DTA).

Ammonium nitrate has three transformation points above room temperature.

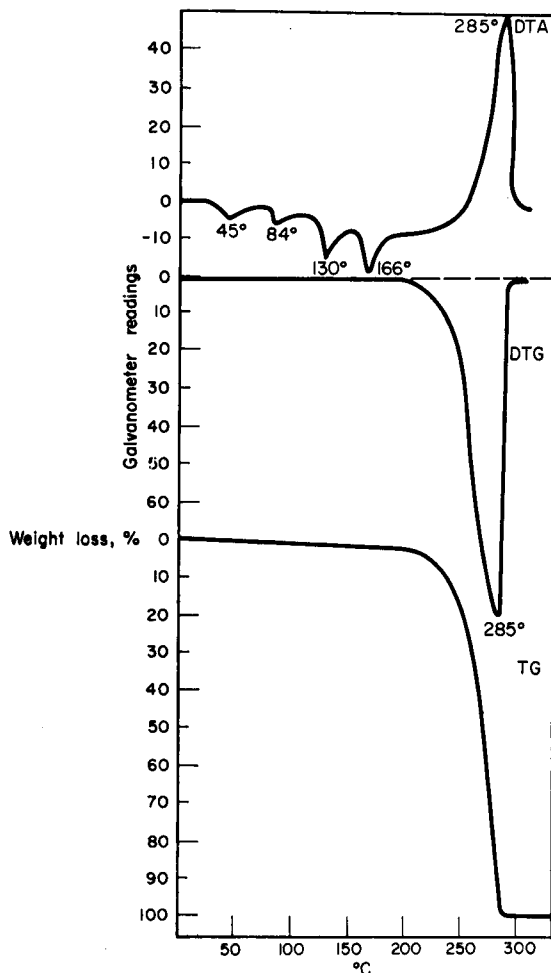
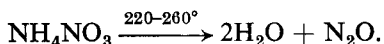


FIG. 11.—Ammonium nitrate.

The three changes of crystal structure are well shown on the DTA curve by the endothermic peaks at 45, 84 and 130°. The sample melts at 166° (DTA curve). Decomposition and decrease in weight of ammonium nitrate begin above 150°. Up to 200° the decomposition is of small extent, and above 220° it becomes exothermic. Between 220 and 260° dinitrogen oxide (N_2O) is formed in 98% yield:

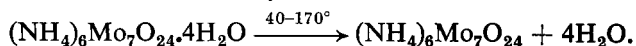


The decomposition proceeds explosively between 260 and 290° and on further rise in temperature the amount (previously very small) of poisonous nitrogen monoxide (NO) and nitrogen dioxide (NO_2) increases. Care should be taken in drying large

amounts of ammonium nitrate not to raise the temperature above 100–110° because explosion then becomes possible.

Ammonium molybdate tetrahydrate

The sample weight begins to decrease above 40°. In the first step (Fig. 12) it loses its four molecules of water of crystallisation



This process is shown by the DTG peak at 110° and the endothermic DTA peak at 120°.

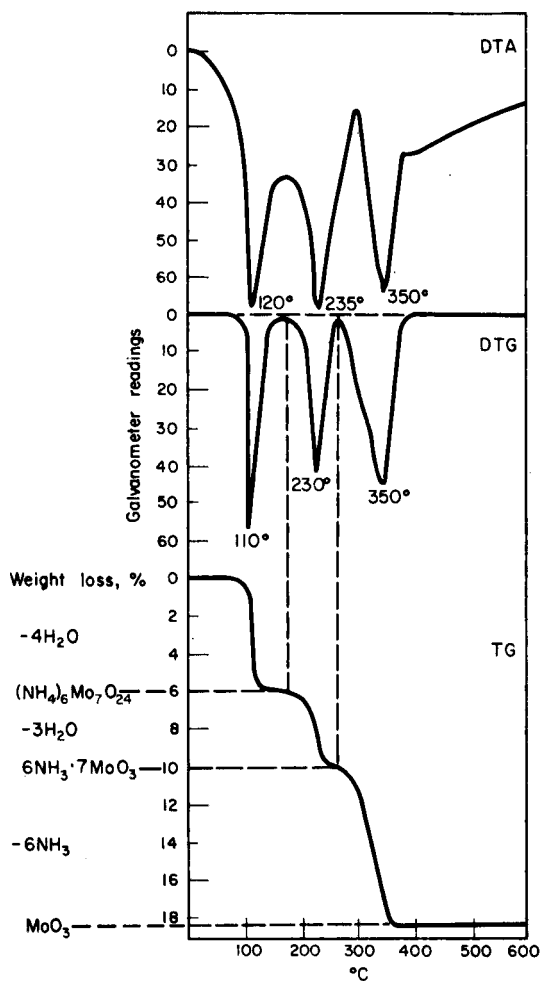
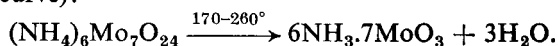
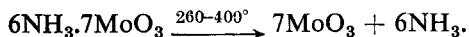


FIG. 12.—Ammonium molybdate tetrahydrate.

The sample weight then decreases further, the rate of decrease being a minimum at 170°. Above 170° the weight of the sample decreases more quickly, the weight decrease, corresponding to the removal of three molecules of water, being at a maximal rate at 230° (TG curve):



The next decomposition process lasts from 260 to 400°, while six molecules of ammonia are removed and a residue of molybdenum trioxide remains



The composition of the sample, calculated on the basis of the TG curve, is exactly identical with the above formula. The weight of the molybdenum trioxide residue slowly decreased above 600°, because at this temperature molybdenum trioxide sublimates. Material free from water of crystallisation can be produced by careful drying below 100°.

Ammonium metavanadate

The sample begins to decompose above 130° (Fig. 13), the decomposition proceeding in two well separated steps. In the first step, which is indicated by the endothermic DTA peak at 240° and the DTG peak at 230°, ammonia splits off

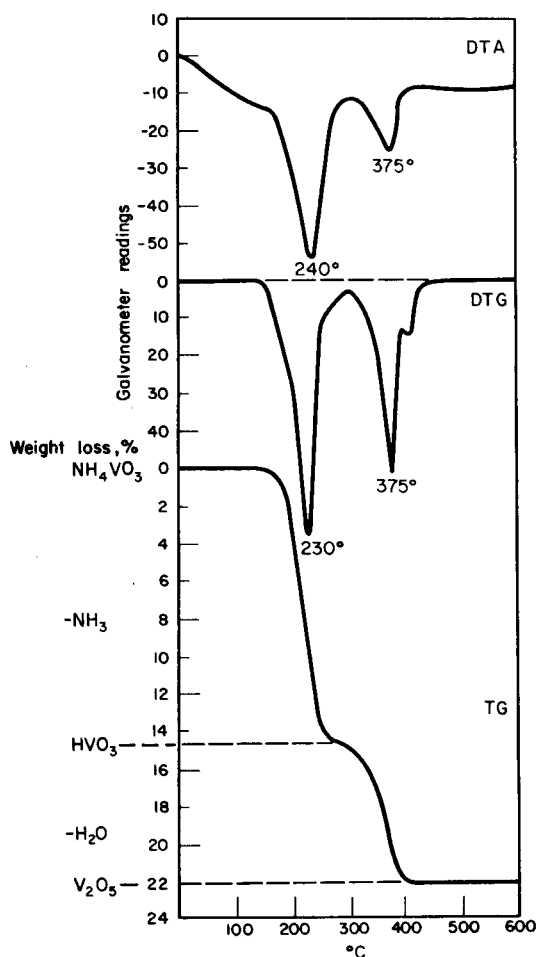
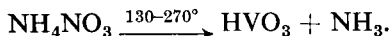
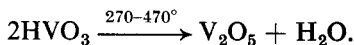


FIG. 13.—Ammonium metavanadate.

After the removal of ammonia, water starts to be lost, and above 470° only vanadium pentoxide remains



Diammonium monohydrogen phosphate

There is no weight change up to 100° (Fig. 14). Above this temperature loss of weight begins, proceeding at 150, 170 and 260° at a maximal rate. The three peaks

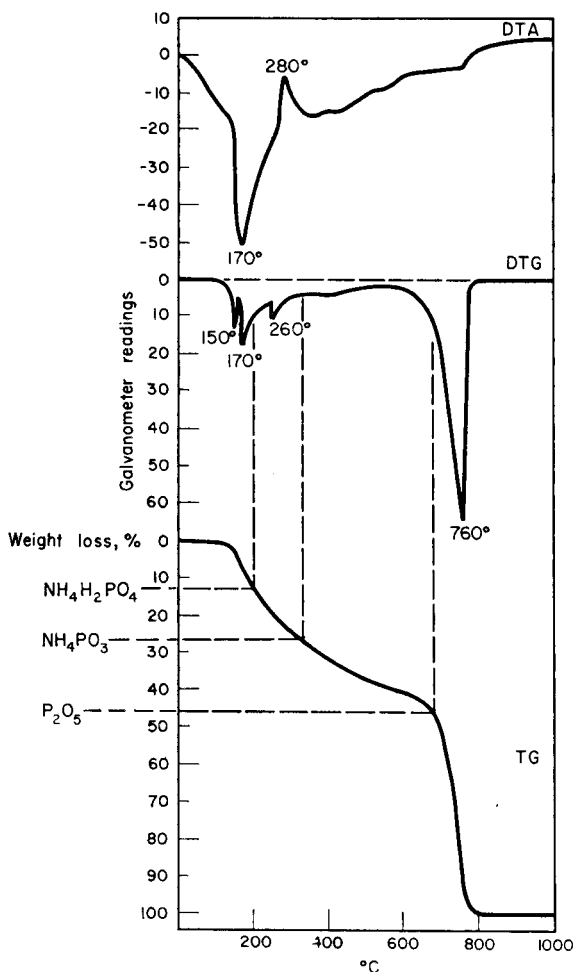


FIG. 14.—Diammonium monohydrogen phosphate.

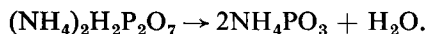
observed on the DTG curve indicate that several decomposition processes proceed simultaneously. In the first step ammonium dihydrogen phosphate is formed by removal of one mole of ammonia



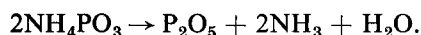
After this loss of ammonia (at about 150°), the sample melts and diammonium dihydrogen pyrophosphate is formed by removal of one mole of water



On further heating the pyrophosphate loses a further molecule of water and ammonium metaphosphate is formed



This ammonium metaphosphate melt is water-soluble up to 280°, then an exothermic transformation takes place and a glassy metaphosphate melt, insoluble in water, remains. Further ammonia and water are removed from the ammonium metaphosphate between 600 and 800° (maximal rate at 760°), leaving a residue of phosphorus pentoxide



During the experiment the various decomposition processes proceed simultaneously and may not be distinguished from each other. However, levels corresponding to the various compositions are drawn on Fig. 14, calculated on the basis of the weight of the sample, in order to make the decomposition processes clear. The various acidic pyro and metaphosphates formed from diammonium monohydrogen phosphate are very active and fuse different metal oxides, the phosphates of the metals being formed.

Monoammonium dihydrogen phosphate

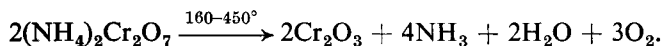
It can be seen in Fig. 15 that weight loss only starts above 150°. The sample melts at 200°, which is indicated by an endothermic DTA peak. Above 200° decomposition proceeds in the same way as was described in Fig. 14 for diammonium monohydrogen phosphate. The individual decomposition processes also cannot be separated from each other here.

Ammonium chromate

The weight of the sample decreases above 50° (Fig. 16), the first decomposition process having a maximal rate at 125°. Ammonia and water are released and ammonium dichromate is formed



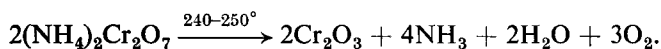
At this temperature, however, the ammonium dichromate is unstable and it slowly decomposes above 160°. The exothermic decomposition process proceeding at about 230–240° indicates the simultaneous splitting off of water, ammonia and oxygen



The decomposition finishes at about 405°, oxygen being lost in an exothermic process. The various stages show that the decomposition proceeds explosively and this fact causes a weight loss 2% more than the theoretical value, because the gaseous decomposition products carry away solid particles.

Ammonium dichromate

Ammonium dichromate is of constant weight up to 200° in air. Above this temperature the weight of the sample slowly begins to decrease, and between 240 and 250° decomposition proceeds explosively (Fig. 17)



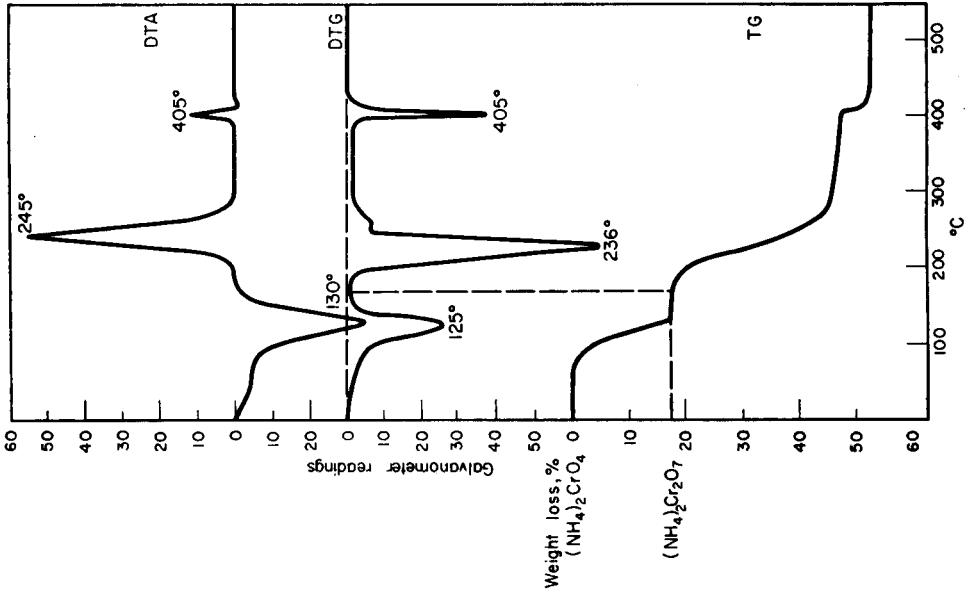


Fig. 16.—Ammonium chromate.

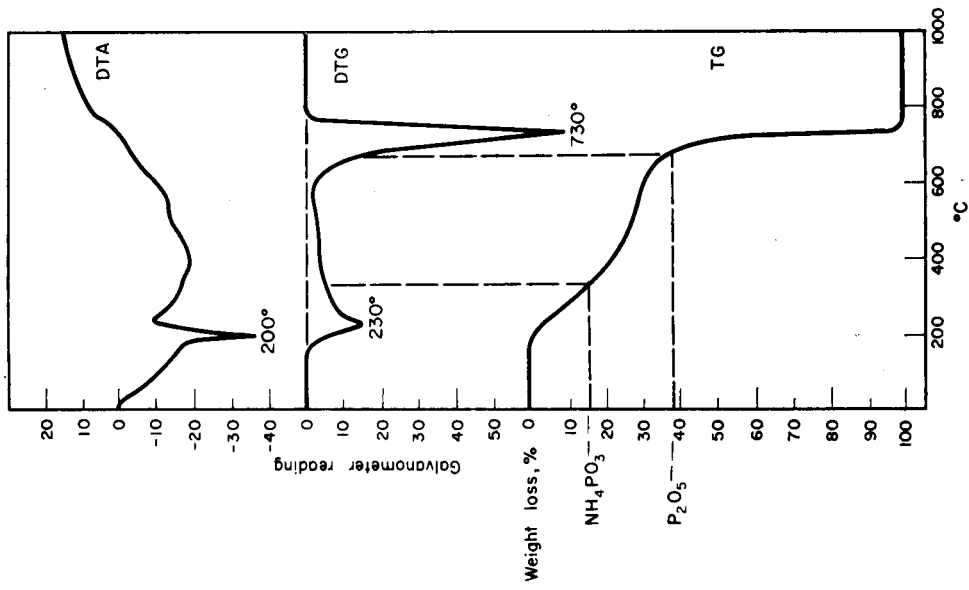


Fig. 15.—Monoammonium dihydrogen phosphate.

The decomposition proceeds in a single step when more than 100 mg of ammonium dichromate are involved (curve 1, Fig. 17). If the amount involved is decreased, decomposition proceeds in three steps. Curves 2 and 3 (Fig. 17) are thermograms of initial sample weights of 60 and 30 mg, respectively. The heating rate and other

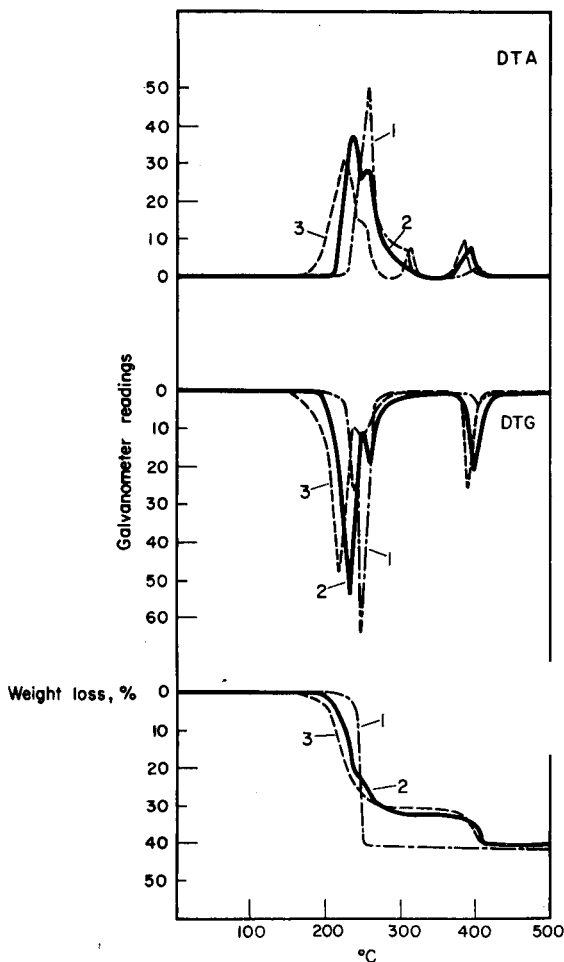
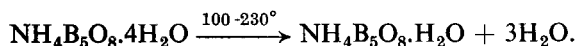


FIG. 17.—Ammonium dichromate.

experimental conditions were the same for all three measurements. The shape of curve 1 (TG curve) agrees well with that published by Duval,⁹ that of curves 2 and 3 is, however, markedly different.

Ammonium pentaborate tetrahydrate

Ammonium pentaborate tetrahydrate begins to lose weight above 100° (Fig. 18). The DTG maximum at 160° indicates a maximal rate of removal of three moles of water of crystallisation



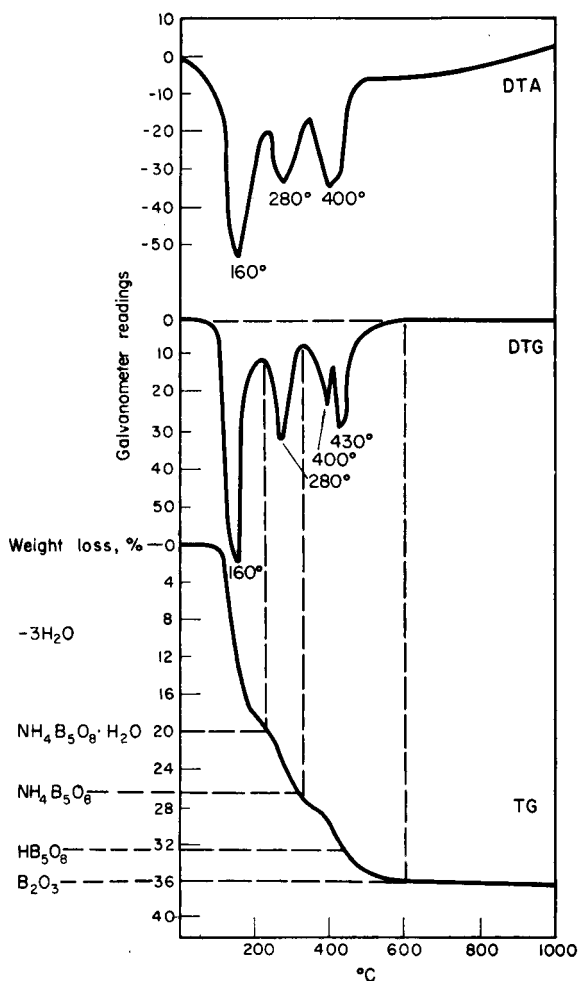
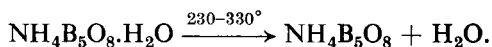
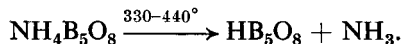


FIG. 18.—Ammonium pentaborate tetrahydrate.

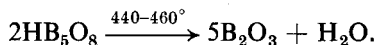
Above 230° the fourth water molecule begins to be lost, the rate being maximal at 280°



The fourth water molecule is bound more strongly than are the other three. After removal of the fourth molecule, ammonia splits off and pentaboric acid is formed



The pentaboric acid is, however, unstable at this temperature, immediately losing water to yield boric oxide



On the DTG and DTA curves a peak corresponds to each of the described processes. The individual decomposition processes are more separated at a lower heating rate.

Water-free ammonium pentaborate cannot be produced by drying because loss of the fourth water molecule proceeds simultaneously with decomposition of the substance.

Ammonium sulphamate

The sample melts at 135°, as indicated by the endothermic peak on the DTA curve (Fig. 19). The weight of the sample does not change until 200°, then

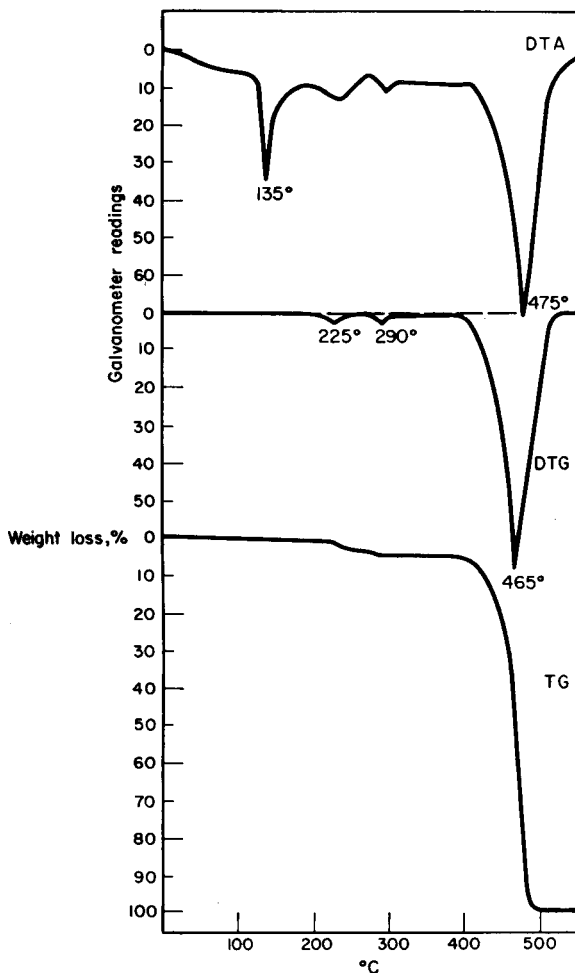


FIG. 19.—Ammonium sulphamate.

decomposition begins and is a maximum at 225 and 290°. Ammonia is removed and ammonium sulphamate is formed



According to our experimental conditions the reaction is not quantitative, because on raising the temperature decomposition of the ammonium sulphamate also starts. This decomposition is maximal in rate at 465° and is an endothermic process.

Ammonium carbonate

Decomposition of the sample has already begun at 20° and reaches its maximal rate at 75° (Fig. 20). Ammonia, carbon dioxide and water are formed



The sample does not melt, but sublimes, and in the meantime decomposes. The endothermic peak at 80° is the enthalpy change of the decomposition. The DTG peak at 105° indicates that water remaining in the crucible during the decomposition is a little overheated and evaporated quickly. The decomposition is practically finished at 100°. By decreasing the partial pressure of the decomposition products, the decomposition can be completed at lower temperatures. According to our measurements ammonium carbonate cannot be dried without decomposition.

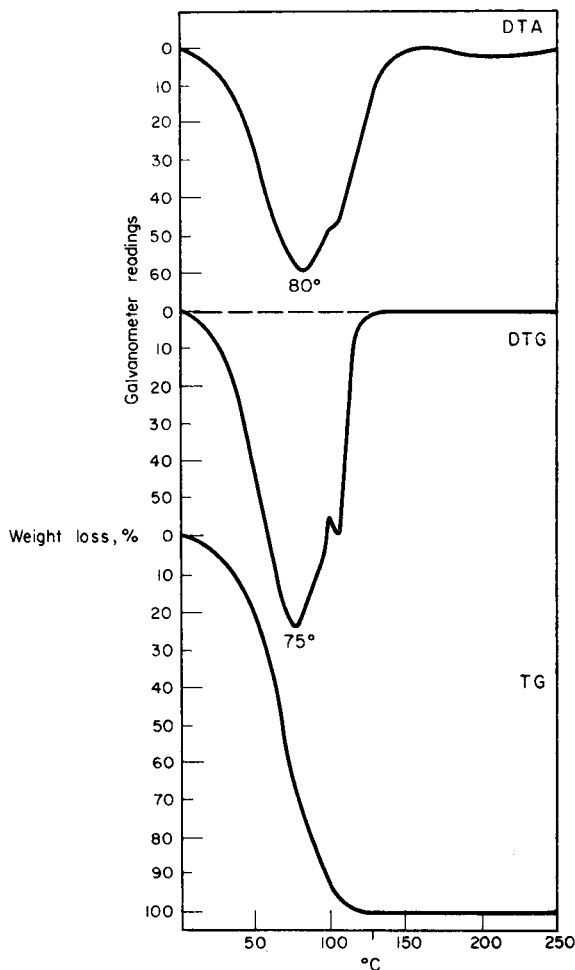


FIG. 20.—Ammonium carbonate.

Ammonium acetate

The decomposition of ammonium acetate starts above 60° (Fig. 21). The maximum on the DTA curve at 100° shows partly the decomposition and partly the onset

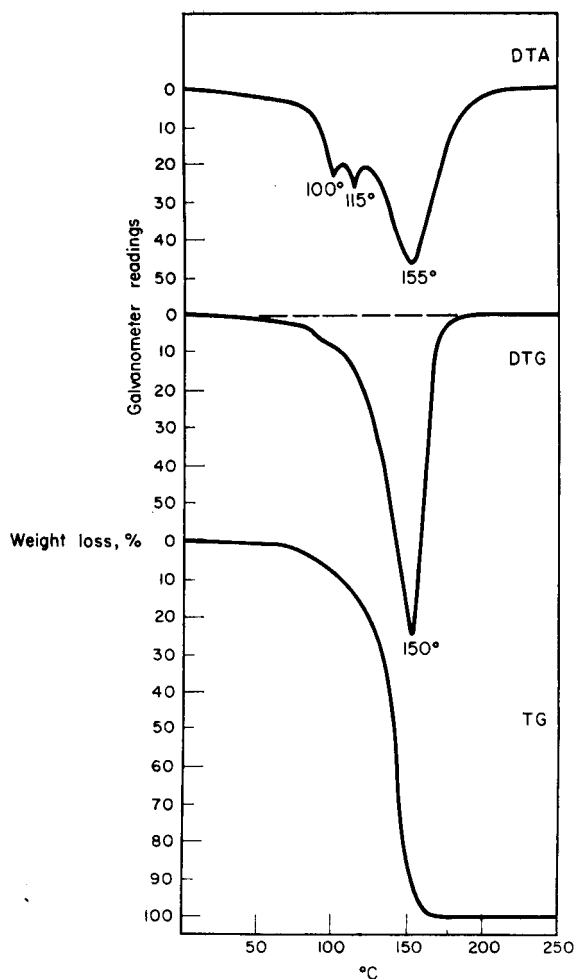
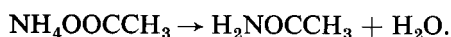


FIG. 21.—Ammonium acetate.

of melting. The sample melts at 115° (DTA curve). Ammonia is lost first during the decomposition and acetic acid is formed. On raising the temperature acetamide results and water splits off



The acetamide distils at about 150°. The decomposition is an endothermic process.

Ammonium oxalate monohydrate

Ammonium oxalate begins to decompose above 70° (Fig. 22). In the first stage it loses its molecule of water of crystallisation (maximal rate at 115°). The anhydrous ammonium oxalate is of constant weight between 120 and 200°, then decomposes above 200°. Decomposition proceeds in two stages. The first process is at a maximal

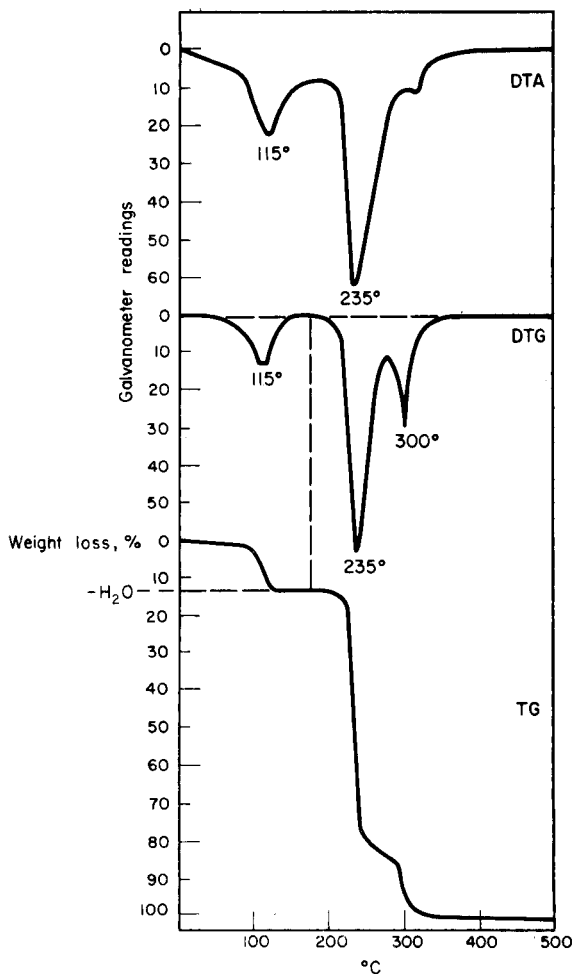
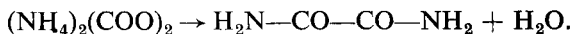


FIG. 22.—Ammonium oxalate monohydrate.

rate at 235° and the second one at 300°. The DTG peak at 235° indicates decomposition of oxalate. Carbon monoxide, carbon dioxide, ammonia, formic acid and oxamide are formed during the decomposition



The decomposition products are in the gaseous state at this temperature, except for oxamide, the composition varying according to the experimental conditions.

Ammonium citrate

The weight of the sample begins to decrease at about 150° (Fig. 23) in an endothermic process, the maximal rate being at 195°. Meanwhile, the sample cracked; the carbon residue was oxidised quantitatively only above 800°.

Ammonium benzoate

The weight of the sample scarcely changes before 100°, then it decreases and the substance sublimes. The endothermic DTA peak at 195° (Fig. 24) shows the melting

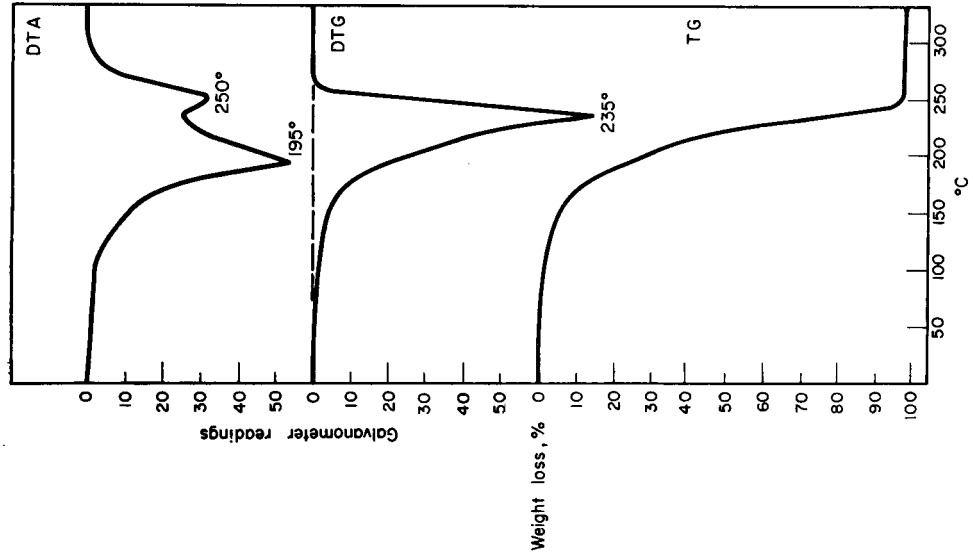


Fig. 24.—Ammonium benzoate.

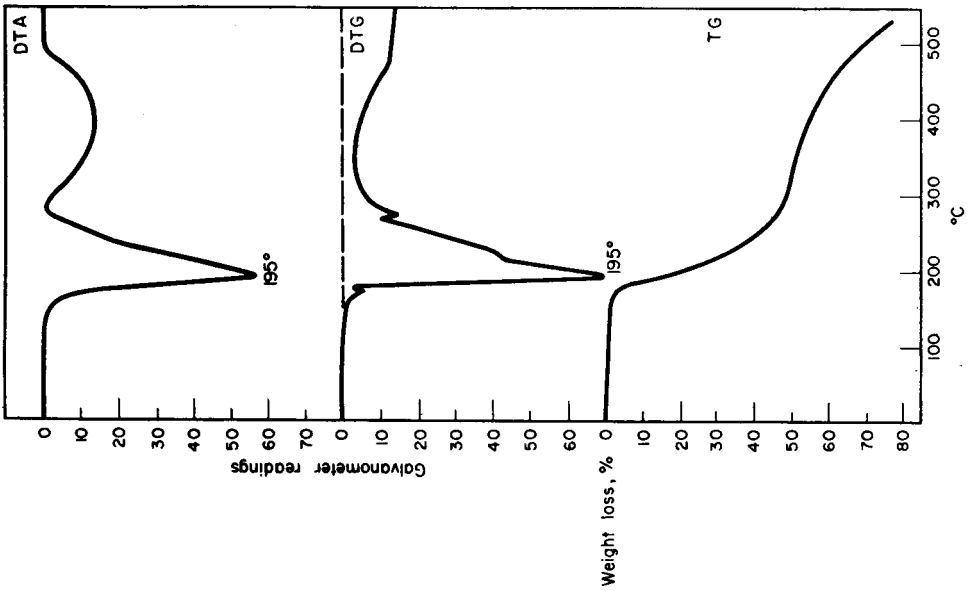


Fig. 23.—Ammonium citrate.

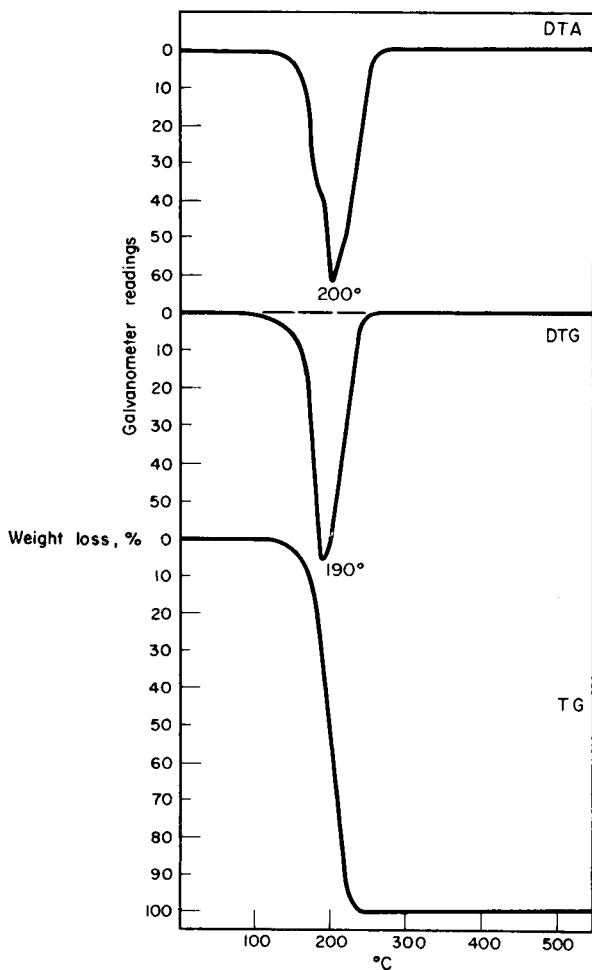


FIG. 25.—Ammonium salicylate.

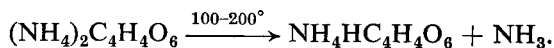
of the sample (m.p.:¹⁰ 190°). The rate of weight decrease is a maximum at 235° after the melting (DTG curve). The substance left the crucible without any change in composition. This was confirmed by the absence of any carbon residue.

Ammonium salicylate

There is no change in weight of the sample until 100°, when sublimation starts, its rate being maximal at 190°. Sublimation was complete at 250° and the crucible was empty.

Ammonium tartrate

Ammonium tartrate is of constant weight up to 100°, above which decomposition slowly starts. Ammonia is lost and ammonium hydrogen tartrate formed [maximal rate at 180° (Fig. 26)]¹¹



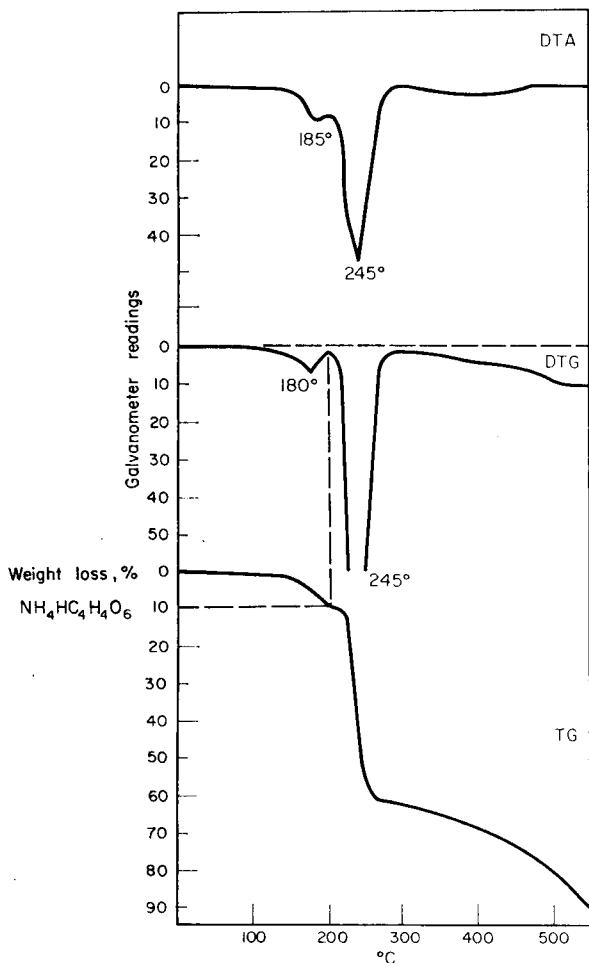


FIG. 26.—Ammonium tartrate.

The ammonium hydrogen tartrate begins to decompose above 200°, the decomposition products varying according to the experimental conditions. They may include water, ammonium carbonate, ammonium acetate, formamide, *etc.* This process is maximal in rate at 245°. Above 300° there was a residue of decomposition products from the sample (about 30% of it).

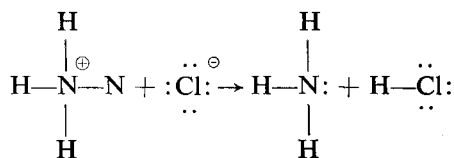
CONCLUSIONS

It is important to follow exactly the prescribed experimental conditions. Thus, in the case of ammonium dichromate it was possible by decreasing the amount of the substance to avoid an explosive decomposition (Fig. 17). For initial amounts of 30 and 60 mg of material, the decomposition products do not carry away solid particles, so the amount of the residue is equal to the theoretical value; for 120 mg of material, however, the decomposition proceeds explosively and the weight of the residue is 2% less than the theoretical value.

The decomposition curves of ammonium salts of organic acids show well that

the decomposition temperature increases with increasing molecular weight.⁹ Ammonium salicylate (Fig. 25) and ammonium benzoate (Fig. 26) sublime without decomposition.

On the basis of the high temperature acid-base theory, the decomposition of ammonium salts can be explained by the fact that the base strength of the anion increases with rise in temperature until it reaches the base strength of the ammonia molecule. At this temperature the anion base removes the proton from the ammonia.



The weaker the anion base, the higher the temperature of the decomposition. Comparison of decomposition curves of the various ammonium salts gives information on the base strength of the anions. According to the measurements—in agreement with the known facts—the strongest anion base is the oxygen ion. The strongly basic character of the oxygen ion is shown by the fact that ammonium oxide $[(\text{NH}_4)_2\text{O}]$ has never been made because of its instability. After the oxygen ion the halide ions follow in the order of decreasing base strength: F^- , Cl^- , I^- , Br^- . Under the given conditions iodide ion is a stronger base than bromide, which is connected with its higher deformability. On the DTA curves of ammonium salts temperatures of interconversion of different crystal modifications appear. During such conversions the more closely packed crystal structure is always formed on the higher temperature side, which is in agreement with the known fact that at higher temperatures the co-ordination number generally increases.

Zusammenfassung—26 Ammoniumsalze wurden derivatographisch untersucht. Gewichtsänderung und ihre Geschwindigkeit sowie die Enthalpieänderung der Salze wurden in Abhängigkeit von der Temperatur gemessen. An Hand der Ergebnisse werden die Temperaturen angegeben, bei denen die Salze unzersetzt getrocknet werden können.

Résumé—On a étudié vingt six sels d'ammonium par derivatographie. La variation de poids, la vitesse de variation de poids et la variation d'enthalpie ont été mesurées en fonction de la température. A partir de ces résultats, on donne les températures auxquelles les sels peuvent être séchés sans décomposition.

REFERENCES

- ¹ C. Duval, *Inorganic Thermogravimetric Analysis*. Elsevier Publishing Company, Amsterdam, 1953.
- ² L. G. Berg, *An Introduction to Thermogravimetry* (in Russian). Publishing House of Academy of Sciences, U.S.S.R.
- ³ W. J. Smothers and Y. Chiang, *Differential Thermal Analysis*. Chemical Publishing Corporation, New York, 1958.
- ⁴ F. Paulik, J. Paulik and L. Erdey, *Acta Chim. Hung.*, 1956, **10**, 61.
- ⁵ *Idem*, *Z. analyt. Chem.*, 1958, **160**, 241.
- ⁶ *Idem*, *Bergakademie*, 1960, **12**, 413.
- ⁷ L. Erdey, *Periodica Polytech.*, 1957, **1**, 91.
- ⁸ L. Erdey and S. Gál, *Talanta*, 1963, **10**, 23.
- ⁹ C. Duval, *Mikrochim. Acta*, 1962, 268.
- ¹⁰ R. C. Farmer, *J. Chem. Soc.*, 1903, **83**, 1442.
- ¹¹ S. Sonnetal, *Monatsh.*, 1891, **12**, 613.

USE OF OXYCELLULOSE FOR COLLECTION OF TRACES OF METALS—II*

APPLICATION OF OXYCELLULOSE IN SOLVENTS AND IN SOLUTIONS OF DIFFERENT ORGANIC COMPOUNDS

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(Received 28 October 1963. Accepted 12 February 1964)

Summary—Oxycellulose has been applied as a collector for the following metal-ion contaminants of organic solvents and of different organic compounds: Cu^{2+} , Fe^{3+} , Ni^{2+} , Pb^{2+} , Zn^{2+} . From 100 ml of solvent 1–20 μg of ions have been collected with 5 mg of oxycellulose. The solutions of the organic compounds were 1–3%. The water content of the solvents has a marked effect on the collection. By repeated collection an ion can be removed quantitatively.

INTRODUCTION

EARLIER investigations¹ showed that oxycellulose is a very suitable material for the collection and removal of traces of metals from distilled water and from highly diluted inorganic salt solutions. After collection, the metal ions are identified directly on the oxycellulose. The ionic strength of the solution has a marked effect on the metal-binding capacity of oxycellulose.

The detection and the quantitative determination of the metal contaminants of organic compounds is a frequent and an important task in analysis. The metal-binding capacity of oxycellulose in the presence of organic solvents and of different organic compounds has therefore been investigated. The collection of the following metal ions was studied: Cu^{2+} , Fe^{3+} , Ni^{2+} , Pb^{2+} and Zn^{2+} . For the collection of these ions the method described previously was used.¹ The fixation of lead ion on oxycellulose was followed quantitatively by the dithizone method.²

EXPERIMENTAL AND RESULTS

Qualitative investigations

Table I gives the minimum detectable quantity of the ions Cu^{2+} , Fe^{3+} , Ni^{2+} , Pb^{2+} and Zn^{2+} on oxycellulose, collected from water and from different solvents. The ions were added to the purified solvent in increasing quantity, and were tested for after collection on the oxycellulose disc. In most of the organic solvents the minimum detectable quantity of the ions was greater than in water. The greater the water content of the solution, the smaller was the quantity of metal ion that could be detected. With water-immiscible solvents, *e.g.*, chloroform, carbon tetrachloride, benzene, fatty acid salts of the metals were used.

* Part I—See ref. 1.

TABLE I.—IONS COLLECTED ON OXYCELLULOSE FROM SOLVENTS

Solvent	Ion, μg				
	Cu ²⁺	Fe ³⁺	Ni ²⁺	Pb ²⁺	Zn ²⁺
Acetone	5	5	5	10	10
Methyl alcohol	1	1	1	10	1
Ethyl alcohol	1	1	1	10	1
n-Propyl alcohol	15	10	5	20	5
n-Butyl alcohol	10	5	1	20	5
Isobutyl alcohol	5	5	1	10	5
Dioxan	15	5	5	20	20
Dimethylformamide	1	1	5	10	10
Chloroform	2	1	2	10	5
Carbon tetrachloride	2	1	2	10	5
Benzene	10	2	10	10	5
Water	1	1	1	1	1

The following list includes the various organic compounds from which more than 50% of the Cu²⁺, Fe³⁺, Ni²⁺, Pb²⁺ and Zn²⁺ ion (up to 10 μg) could be collected on oxycellulose:

Acetamide	Hyoscine hydrobromide
Acetanilide	Lactose
Antipyrine	Mannite
Aspirin	2-Naphthol
Benzoic acid	Phenacetin
Bromacetocarbamide	Phenol
Bromovalerocarbamide	2-Phenylcinchoninic acid
Caffeine	Pyrogallol
Carbamide	Raffinose
Chloral hydrate	Phenyl salicylate
Cholesterol	Santonin
5,5-Diethylbarbituric acid	Terpinal hydrate
5-Ethyl-5-butylbarbituric acid	Theophylline
Glucose	Thymol
Methyl <i>p</i> -hydroxybenzoate	Urethane

All the commercially available materials were contaminated with heavy metals. Therefore, before the experiments, these materials were purified with oxycellulose. In the case of complex-forming compounds (citric, oxalic, succinic, thiobarbituric acids, *etc.*) oxycellulose could not remove the metal ion. With alkaloid salts the collection is effective only in dilute solution. The detection of the ion is not influenced by the colour of the sample, because the organic compounds can be washed out from the oxycellulose disc by water or by another solvent. The bound metal ion is not removed by this procedure.

For an indication of the metal ions likely to be present in various solutions or solvents this qualitative process, using oxycellulose, is a very suitable rapid method. By dividing the oxycellulose disc into pieces, more than one ion can be tested for without using the ring-oven method.

Quantitative investigations

In the quantitative investigations, the fixation of Pb^{2+} ion on oxycellulose, from water, from different solvents and from solutions of organic compounds, was followed by the dithizone method.²

One hundred ml of the solvent, containing 1–5 μg of Pb^{2+} ion, were shaken with 5 mg of oxycellulose for 5 min and the oxycellulose fibrils were collected as usual.¹ The oxycellulose disc was put into a volumetric flask, and the lead ion was extracted by a dithizone-carbon tetrachloride solution in the presence of potassium cyanide. The colour of the solution was compared with that of a lead-dithizone standard solution.

Table II shows the result of the collection of Pb^{2+} ion from water on oxycellulose. By repeated collection, 1–5 μg of Pb^{2+} ion could be removed quantitatively.

TABLE II.—QUANTITATIVE COLLECTION OF Pb^{2+} FROM WATER WITH OXYCELLULOSE AFTER REPEATED COLLECTION

Added Pb^{2+} ion, $\mu\text{g}/100 \text{ ml}$	Pb^{2+} ion, μg ,									Arithmetical mean of Pb^{2+} ion found, μg
	First collection			Second collection			Third collection			
1.0	0.6	0.7	0.6	0.4	0.3	0.3				1.0
2.0	1.2	1.3	1.2	0.5	0.5	0.5	0.3	0.2	0.2	2.0
3.6	1.6	1.6	1.9	0.6	0.7	0.6	0.4	0.5	0.3	2.7
4.0	2.8	3.0	2.8	0.7	0.6	0.6	0.3	0.2	0.2	3.7
5.0	3.5	3.4	3.2	0.8	0.8	1.0	0.3	0.4	0.3	4.6

Table III indicates that there may be some relation between the amount of Pb^{2+} ion removed by oxycellulose and the dielectric constant of the solvent.

As mentioned earlier, the water content of the solvent has a marked effect on the collection. Only a few per cent of the added metal ions can be removed by oxycellulose from anhydrous solvents (water content less than 10^{-2} – $10^{-3}\%$). If the oxycellulose was swollen with water before adding it to the anhydrous solvents, the quantity of the bound ion increased. This suggests that swelling of the oxycellulose is of considerable importance in binding the metal ions. (According to results in the literature,³ water has the greatest swelling effect on oxycellulose.)

TABLE III.—EFFECT OF DIELECTRIC CONSTANT ON THE COLLECTION OF Pb^{2+} ION
(Pb^{2+} ion: 5 $\mu\text{g}/50 \text{ ml}$; oxycellulose: 5 mg)

Solvent	Dielectric constant, ϵ	Arithmetical mean of Pb^{2+} ion found, μg
Water	78	3.8
Dimethylformamide	37	2.7
n-Butyl alcohol	18	2.0
Methyl alcohol	32	1.5
Ethyl alcohol	24	0.9
n-Propyl alcohol	20	0.8
Ethyl acetate	6.0	0.5
Ether	4.0	0.4
Dioxan	2.2	0.3
Acetone	21	0.2

The results in Table IV show the extent of removal of Pb^{2+} ion from different solvent-water mixtures.

In Table V the results of the quantitative collection of $1 \mu g$ of Pb^{2+} ion from organic compounds are summarised. The compounds were dissolved in 30 ml of water.

TABLE IV.—COLLECTION OF Pb^{2+} BY OXYCELLULOSE FROM SOLVENT WITH DIFFERENT WATER CONTENTS
(Pb^{2+} ion: $5 \mu g/50$ ml)

Solvent	Arithmetical mean of Pb^{2+} ion found, μg			
	Water content, <i>v/v</i> %			
	1.5%	10%	20%	50%
Acetone	0.2	0.4	1.1	2.2
Dimethylformamide	2.7	2.7	2.8	3.0
Dioxan	0.3	1.2	1.3	2.8
Ethyl alcohol	0.9	1.0	1.2	2.0
Methyl alcohol	1.5	1.7	1.6	3.0

TABLE V.—COLLECTION OF Pb^{2+} BY OXYCELLULOSE FROM ORGANIC COMPOUNDS
(Pb^{2+} ion: $1.0 \mu g/30$ ml of water)

Compound	Compound in 30 ml of water, <i>g</i>	Arithmetic mean of Pb^{2+} ion found, μg
Acetamide	1	1.0
Antipyrine	1	1.0
Glucose	1	0.6
Hydroquinone	1	1.1
Carbamide	1	0.9
Thiocarbamide	1	0.7
Urethane	1	1.0
Atropine sulphate	0.1	0.6
Ephedrine hydrochloride	0.1	0.5
Hyoscine hydrobromide	0.1	0.7
Quinidine sulphate	0.1	0.5

CONCLUSIONS

From the results of experiments dealing with the collection of frequent metal contaminants of various organic solvents and organic compounds, it is apparent that oxycellulose is a suitable collector for metal ions, not only from aqueous but also from non-aqueous solutions.

Zusammenfassung—Oxycellulose wurde zur Anreicherung folgender Metallverunreinigungen in organischen Lösungsmitteln und verschiedenen organischen Verbindungen verwendet: Cu^{2+} , Fe^{3+} , Ni^{2+} , Pb^{2+} und Zn^{2+} . 1–20 μg dieser Ionen wurden aus 100 ml Lösungsmittel mit 5 mg Oxycellulose angereichert. Die Lösungen der organischen Verbindungen waren 1–3%. Der Wassergehalt der Lösungsmittel war von großem Einfluß auf die Anreicherung. Durch wiederholte Anreicherung konnte das Ion quantitativ entfernt werden.

Résumé—On a utilisé l'oxycellulose comme collecteur pour recueillir les ions métalliques suivants, contaminants de solvants organiques et de divers composés organiques: Cu^{2+} , Fe^{3+} , Ni^{2+} , Pb^{2+} , Zn^{2+} . Avec

5 mg d'oxycellulose, on recueille 1–20 μg d'ions de 100 ml de solvants. La concentration des solutions de composés organiques est de 1–3%. La teneur en eau des solvants a une grande influence sur la séparation. Par traitements répétés, l'ion peut être séparé quantitativement.

REFERENCES

- ¹ E. Schulek, Zs. Rempert-Horváth and A. Lásztity, *Talanta*, 1963, **10**, 821.
- ² L. Barcza, *Acta Pharm. Hung.*, 1961, **31**, 250.
- ³ E. Ott and H. M. Spurlin, *Cellulose and Cellulose Derivatives, Part I: High Polymers: Vol. V*. Interscience Publishers, New York, 1954.

THE CHROMATOGRAPHY OF *p*'-SUBSTITUTED-*p*-HYDROXYAZOBENZENES ON ALUMINA-IMPREGNATED PAPER*

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(Received 9 November 1963. Accepted 28 January 1964)

Summary—*R_f* values of *p*'-substituted-*p*-hydroxyazobenzenes on paper, glass-fibre "paper", and these papers impregnated with different amounts of alumina are given. Results indicate that the alumina is primarily responsible for sorption. The effect of the electrical nature of the *p*'-substituent on sorption is small. Sorption is considered to be a result of hydrogen bonding between oxygen centres in the sorbed molecule and active hydrogen centres on the hydroxylated alumina.

INTRODUCTION

THE suggested relation between *R* values from column adsorption chromatography and linear adsorption isotherms has been substantiated by Claesson.¹ This worker successfully constructed linear adsorption isotherms for a number of homologous series of organic compounds from results obtained by using the interferometric method of Tiselius and Claessen² with the techniques of frontal analysis, displacement analysis and carrier-displacement analysis.

LeRosen and his coworkers³ related the structure of a molecule to its sorption on silicic acid. Martin⁴ established a theoretical relation between the chemical potential of a molecule and its partition coefficient for a two-phase system of ideal solutions when the two phases are in equilibrium, and derived the expression

$$\Delta\mu_{(F)}A = RT \ln \left(\frac{N_A^M}{N_A^S} \right)$$

where $\Delta\mu_{(F)}A$ = the free energy required to transport 1 mole of A from phase S to phase M,

N_A^M = the mole fraction of A in phase M,

and N_A^S = the mole fraction of A in phase S.

He also showed that where the molecule A is composed of the several groups X, Y and Z, then the free energy required to transport A from phase S to phase M is the sum of the free energies required to transport the individual groups X, Y and Z from phase S to phase M.

* Presented at a joint meeting of the Institute of Chemistry of Ireland and the Scottish Section of the Society for Analytical Chemistry in Dublin, 5 September, 1963.

Later, Sporer and Trueblood⁵ carried out a quantitative study of the relation between the molecular structure of a number of aromatic compounds and their adsorption affinities on silicic acid-celite columns using benzene as the eluent. These workers observed that Langmuir isotherms calculated from observed chromatographic development rates agreed with those evaluated from static adsorption studies determined for the same systems. They also suggested that the standard free energy change for a molecule on adsorption, as given by the equation

$$\Delta F^{\circ} = -RT \ln K$$

is, to a first approximation, the sum of the free energy changes for the component atoms which comprise the molecule. This established for adsorption chromatography a similar thermodynamic concept to that proposed by Martin⁴ for partition chromatography.

Erió, Goode and Ibbitson⁶ have carried out static adsorption studies of phenols from cyclohexane onto alumina, while Ibbitson, Jackson, McCarthy and Stone⁷ have similarly investigated azobenzenes sorbed from benzene. In each case the free energy changes of sorption have been determined in terms of the equation

$$\Delta G^{\circ} = -RT \ln K.$$

Because of the foregoing we have sought to correlate data obtained from static sorption studies of hydroxyazobenzenes from benzene onto alumina by Stone,⁸ with R_f values determined for the same compounds by adsorption chromatography on alumina-impregnated papers with benzene as the eluent, and with other known physical parameters. In each case the compounds were chromatographed on untreated paper of a comparable grade as control experiments. The compounds investigated were *p*-hydroxyazobenzenes with substituents of different electrical character in the *p'*-position.

EXPERIMENTAL

Five grades of paper were used in the investigation:

- (a) untreated Whatman No. 1 paper,
- (b) Whatman No. 1 paper impregnated with 2% of alumina,
- (c) Whatman No. 1 paper impregnated with 7.5% of alumina,
- (d) untreated glass-fibre paper,
- (e) glass-fibre paper impregnated with 7.5% of alumina.

The papers were activated at 120° for 15 min (heating for longer periods caused yellowing of the paper), then cooled in a vacuum desiccator.

Samples (2.5 μ l) of the hydroxyazobenzenes (1% w/v solutions) were applied at a point 6 cm from the base of a paper and at intervals of 2 cm from each other. The dispersing solvent was removed by a current of warm air directed at the point of application of the samples.

The eluent, M.F.C. grade benzene, was dried over sodium wire, redistilled, and the fraction boiling at 80.1° (760 mm pressure) collected. This gave a single peak when examined by gas-liquid chromatography on a dinonylphthalate column at 75°, using a Pye Argon Chromatograph.

The papers were conditioned in a tank saturated with benzene vapour for 15 min, then eluted by an ascending technique at a temperature of 25° \pm 0.5°. The length of run was governed by the distance reached by the solvent front (*ca.* 22 cm from the point of application), rather than by time, because of the different rates of flow of the eluent through the different grades of paper. For both grades of glass-fibre paper the eluent rose to the desired height in 1 hr. The three grades of filter paper were slower, the solvent taking 3–5 hr to rise through the paper; the untreated paper was the fastest and the paper impregnated with 7.5% of alumina the slowest. After elution, the chromatograms were dried and viewed under an ultraviolet lamp to mark the positions of compounds.

RESULTS

The results collected in Table I represent the mean of 5 runs. The R_f values are reproducible to ± 0.01 of an R_f unit.

DISCUSSION

From Table I it can be seen that on untreated glass-fibre paper the compounds travelled with the solvent front. Some sorption took place on untreated Whatman No. 1 papers but all of the compounds had high R_f values, there being little differentiation between the values for the different compounds. Impregnation of the papers with alumina resulted in a substantial increase in the degree of sorption, with R_f values ranging from 0.33 to 0.54 on the 2% alumina-impregnated paper, 0.08 to 0.15 on the 7.5% alumina-impregnated paper, and 0.03 to 0.05 on the 7.5% alumina-impregnated glass-fibre paper. Hence, it is concluded that the alumina surface is responsible for the sorption of the compounds, with the "paper" substrate playing little or no part in sorption.

TABLE I.— R_f VALUES OF *p'*-SUBSTITUTED-*p*-HYDROXYAZOBENZENES

<i>p'</i> -Substituent	R_f^*				
	(a)	(b)	(c)	(d)	(e)
Nitro	0.95	0.37	0.09	1.0	0.02
Chloro	0.97	0.54	0.15	1.0	0.03
Bromo	0.96	0.52	0.14	1.0	0.03
Iodo	0.96	0.52	0.12	1.0	0.03
Hydrogen	0.96	0.52	0.13	1.0	0.04
tert-Butyl	0.95	0.48	0.13	1.0	0.04
Methyl	0.95	0.46	0.12	1.0	0.05
Methoxyl	0.94	0.33	0.08	1.0	0.04

* (a) Untreated Whatman No. 1, (b) Whatman No. 1 paper impregnated with 2% of alumina, (c) Whatman No. 1 paper impregnated with 7.5% of alumina, (d) untreated glass-fibre paper, (e) glass-fibre paper impregnated with 7.5% of alumina.

Three other factors may now be considered: (a) the effect of the electrical nature of the *p'*-substituent, (b) the mechanism of sorption, and (c) the alignment of the sorbed molecule onto the surface of the adsorbent.

(a) Effect of electrical nature of p'-substituent

Stone,⁸ from static sorption studies, has suggested that compounds of this type are adsorbed from benzene onto alumina as a result of hydrogen bonding between the hydrogen atom of the hydroxyl group of the molecule and the active oxygen centres on the alumina surface. He found that though the free energy decrease of sorption could be correlated with the electrical character of the *p'*-substituent, those compounds with electron-attracting groups being more strongly adsorbed than those with electron-releasing groups, the magnitude of the free energy change is small.

This effect has been confirmed and explained by Catchpole, Foster and Holden⁹ who determined the hydroxyl stretching frequencies for hydroxyazobenzenes, including a number of the compounds investigated here. A plot of the hydroxyl stretching frequencies for these compounds against Hammett σ functions,¹⁰ was compared with a similar plot for comparable phenols using the data of Flynn, Werner and Graham.¹¹ Both plots were linear, with the former having a smaller slope than the latter. Catchpole, Foster and Holden⁹ suggested, therefore, that the electronic effect of the *p'*-substituent in the one benzene ring suffers a decrease in intensity when transmitted across the azo group to the *p*-hydroxyl group in the other benzene ring

of the conjugated system. Catchpole and coworkers^{9,12} showed that the electrical effect of the p' -substituent on the acid dissociation constants of these hydroxyazo-benzenes is also small.

From Table I it can be seen that for the 2% alumina-impregnated papers and the 7.5% alumina-impregnated papers the R_f values, in general, change with the electrical nature of the group but once again the magnitude of the change is small.

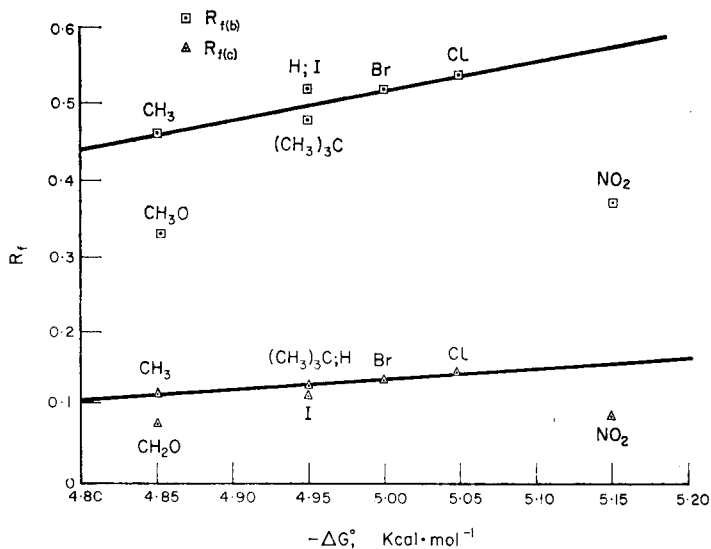


FIG. 1

(b) Mechanism of sorption

For the mechanism of sorption of the compounds onto alumina-impregnated paper to be the same as that proposed by Stone⁸ for static sorption, one would expect that the order of R_f values would parallel the order of free energy changes of sorption and that a plot of R_f values against $-\Delta G^\circ$ values would be linear. Furthermore, one would expect plots of R_f values against hydroxyl stretching frequencies, Hammett σ functions and dissociation constants to be linear.

However, from Table I and from Fig. 1 it can be seen that the R_f values do not parallel the free energy changes. For substituents which do not contain an oxygen atom, the R_f values are lower, indicating stronger adsorption for electron-releasing groups than for electron-attracting groups, *i.e.*, the reverse of that expected from Stone's work. Those compounds in which the p' -substituent contains an oxygen atom are strongly adsorbed irrespective of whether the oxygen atom is part of the electron-attracting nitro group or of the electron-releasing methoxyl group.

Further, for compounds containing non-oxygenated substituents in the p' -position, the higher R_f values, relative to the values for the unsubstituted parent compound, in the presence of electron-attracting substituents are associated with (a) hypsochromic shifts of the hydroxyl stretching frequencies (Fig. 2), (b) positive Hammett σ functions (Fig. 3), and (c) stronger acid dissociation constants (Fig. 4), while the lower R_f values for the electron-releasing substituents are associated with (a) bathochromic shifts, (b) negative Hammett σ functions, and (c) weaker acid dissociation constants. As

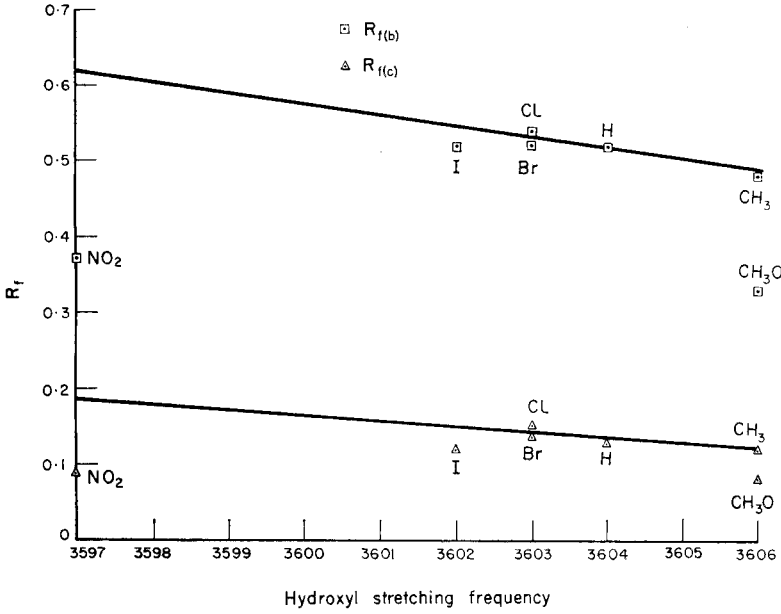


FIG. 2

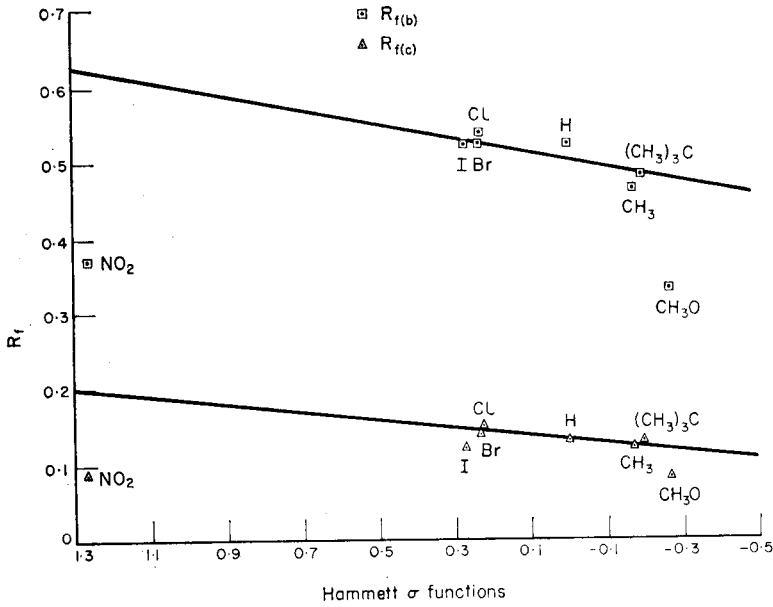


FIG. 3

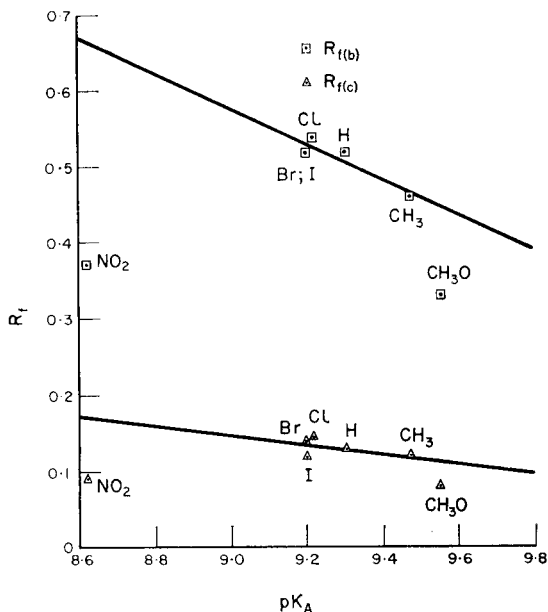


FIG. 4

in the case of the plot of the R_f values against $-\Delta G^\circ$ values, however, the positions of the compounds with oxygen atoms in the substituent groups are anomalous.

Because of these facts we consider that a different mechanism of bonding must operate on the alumina-impregnated papers from that on static beds of alumina.

We propose that, in accordance with the suggestion of Bernal,¹³ the alumina is hydroxylated, presenting at its active sites not oxygen atoms but hydrogen atoms, and that the mechanism of sorption is hydrogen bonding *via* the phenolic oxygen and these active hydrogen sites. The electron-attracting halogen atoms decrease the electron density around the phenolic oxygen, thus resulting in a weakening of the hydrogen bond and an increase in the R_f values. The electron-releasing groups increase the electron density at the phenolic oxygen atom and hence increase the tendency to hydrogen bond with the proton-donating hydroxylated alumina. Compounds containing a nitro or methoxyl group hydrogen bond by the oxygen atoms at either end of the molecule. They are thus more strongly adsorbed, and hence have lower R_f values.

This view is substantiated by the results of other workers. Thus, Ibbitson, Jackson, McCarthy and Stone,⁷ who observed an unexpectedly low free energy change for *p*-acetoxyazobenzene, proposed that the compound was sorbed by one of two mechanisms: either the carbonyl group activates a hydrogen atom of the methyl residue and this activated hydrogen atom bonds with the active oxygen of the alumina, or the acetyl group acts as an acceptor group for hydrogen bonding while the alumina acts as a proton donor. The latter of these two explanations is in accordance with our view.

Bark and Graham¹⁴ observed that for substituted phenoxyacetic acids chromatographed on paper, those with oxygen atoms in the substituent groups had lower R_f values than the unsubstituted acid, whilst those with halogen or alkyl groups had

higher R_f values. Sporer and Trueblood⁵ concluded from their studies that the active sites on silicic acid were hydroxyl groups. Smith¹⁵ observed that halogenated phenols had higher R_f values than alkyl phenols when sorbed from benzene onto silica gel. Bark and Graham¹⁶ have similarly explained the behaviour of nitrophenols on alumina-impregnated papers.

(c) *Alignment of sorbed molecule onto surface of absorbent*

From column adsorption chromatography, Zechmeister,¹⁷ Brockmann¹⁸ and Sporer and Trueblood⁵ have proposed the group anchoring site concept for attachment of the sorbed molecule to the surface. From studies of hydrocarbons and azobenzenes sorbed onto alumina-impregnated glass fibre paper, Klemm and coworkers¹⁹ proposed a "flat-wise" π complex for the former and a partial "flat-wise" sorption through the π electrons of the benzene ring and the lone pair of electrons of the azo-nitrogen atoms.

The presence of a single spot and the absence of tailing for each compound on our chromatograms suggests the absence of the unstable cis isomers, and that the compounds migrate as the stable trans forms. Hence, for the proposed mechanism of bonding to occur, *i.e.*, the attachment of the phenolic oxygen to the substrate, the azo-skeleton is tilted slightly away from the substrate, into the organic mobile phase. Even so, the angle of the tilt is sufficiently small for the oxygen atoms of the nitro and methoxyl groups to be sufficiently close to the substrate surface for hydrogen bonding to occur.

Acknowledgement—We thank Messrs. Reeve Angel and Co. Ltd. for the gift of impregnated papers.

Zusammenfassung— R_f -Werte *p*'-substituierter *p*-Hydroxyazobenzole an Papier, Glasfasser-"papier" und mit verschiedenen Mengen Aluminiumoxyd imprägnierten Papieren werden angegeben. Die Ergebnisse zeigen, daß in erster Linie das Aluminiumoxyd für die Sorption verantwortlich ist. Der Einfluß des elektrometen Effekts des *p*'-Substituenten ist gering. Die Sorption wird als Ergebnis von Wasserstoffbrücken zwischen Sauerstoffatomen im sorbierten Molekül und aktiven Wasserstoffatomen am hydroxylhaltigen Aluminiumoxyd angesehen.

Résumé—On donne les valeurs R_f de *p*-hydroxyazobenzènes *p*'-substitués, sur papier, papier en fibre de verre, et sur les mêmes papiers imprégnés de différentes quantités d'alumine. Les résultats indiquent que l'alumine est essentiellement responsable de la sorption. L'effect, sur la sorption, de la nature électrique du substituant en *p*' est faible. On considère que la sorption est un résultat de la liaison hydrogène entre les centres oxygène dans la molécule sorbée et les centres hydrogène actif de l'alumine hydroxylée.

REFERENCES

- ¹ S. Claesson, *Arkiv. Kemi, Min., Geol.*, 1946, **23A**, No. 1, 133 pp.
- ² A. Tiselius and S. Claesson, *ibid.*, 1942, **15B**, No. 18, 1.
- ³ A. LeRosen *et al.*, *Analyt. Chem.*, 1951, **23**, 730; 1953, **25**, 666; 1954, **26**, 928.
- ⁴ A. J. P. Martin, *Biochem. Soc. Symp.*, 1950, **3**, 4.
- ⁵ A. H. Sporer and K. N. Trueblood, *J. Chromatog.*, 1959, **2**, 499.
- ⁶ B. Eric, E. V. Goode and D. A. Ibbitson, *J. Chem. Soc.*, 1960, 55.
- ⁷ D. A. Ibbitson, T. Jackson, A. McCarthy and C. W. Stone, *ibid.*, 1960, 5127.
- ⁸ C. W. Stone, Ph.D. Thesis, University of London, 1963.
- ⁹ A. G. Catchpole, W. B. Foster and R. S. Holden, *Spectrochim. Acta*, 1962, **18**, 1353.
- ¹⁰ L. Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 96.
- ¹¹ T. D. Flynn, R. L. Werner and B. H. Graham, *Austral. J. Chem.*, 1959, **12**, 575.
- ¹² A. G. Catchpole and H. M. Catchpole, unpublished work, see reference 9.

- ¹³ J. D. Bernal, in *Hydrogen Bonding*, Ed. D. Hadži. Pergamon Press, London, 1959, p. 450.
- ¹⁴ L. S. Bark and R. J. T. Graham, *Analyst*, 1960, **85**, 907.
- ¹⁵ B. Smith, *Acta Chem. Scand.*, 1962, **16**, 843.
- ¹⁶ L. S. Bark and R. J. T. Graham, Paper presented at a Symposium on Modern Aspects of Chromatography, Dublin (1963): *Talanta*, 1964, **11**, 839.
- ¹⁷ L. Zechmeister, *Discuss. Faraday Soc.*, 1949, **7**, 54.
- ¹⁸ H. Brockmann, *ibid.*, 58.
- ¹⁹ L. H. Klemm, E. P. Antoniadis, G. Capp, E. Chiang and E. Y. K. Mak, *J. Chromatog.*, 1961, **6**, 420.

AMMONIUM HEXANITRATOCERATE(IV) AS AN OXIDISING AGENT—III*

PHOTOMETRIC DETERMINATION OF MANGANESE^{II} THROUGH OXIDATION TO MANGANESE^{VII}

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(Received 6 January 1964. Accepted 6 March 1964)

Summary—Manganese^{II} is oxidised to permanganic acid by treatment with a slight excess of ammonium hexanitratocerate(IV) in a 0.5–2M nitric acid medium at room temperature. The reaction is markedly catalysed by silver nitrate, so that quantitative oxidation is possible within 1 min. Conditions have been developed for utilising the catalysed reaction for the colorimetric determination of manganese over the range 0.33–19.93 mg/litre. The new method has the advantage over those currently available in that the oxidation to manganese^{VII} is stoichiometric at room temperature. Under the conditions prescribed the permanganic acid formed is stable for at least 24 hr. Interference from sulphate and from chloride, bromide and iodide can be eliminated by treating the test solution with barium nitrate or silver nitrate, respectively, before the oxidation with cerium^{IV}. Application of the method to the determination of manganese in steel is considered.

THE colorimetric determination of manganese has engaged the attention of chemists for over a century. Crum¹ appears to have been the first to observe the oxidation of manganese^{II} to permanganate by lead dioxide in nitric acid solution. Pichard² and a host of workers employed this reaction for the colorimetric determination of manganese. Reddrop and Ramage³ as early as 1895 proposed the oxidation of manganese^{II} to permanganate with sodium bismuthate. The method seems to have been forgotten until Dufty⁴ again drew attention to it in 1901. In the procedures employing both lead dioxide and sodium bismuthate, excess oxidising agent should be separated from the solution by filtration before the colour comparisons are made. Moreover, both methods suffer from the defect that a high temperature is necessary to complete the oxidation of manganese^{II} to permanganate. It is also possible that some of the permanganate may decompose at the high temperature and high acidities recommended. Marshall,⁵ Von Knorre⁶ and Walters⁷ used potassium persulphate with a silver salt as catalyst in the oxidation of manganese^{II} to manganese^{VII} in the colorimetric determination of manganese. The general procedure that has been evolved as a result of the investigations of several workers is to heat the manganese^{II} in a sulphuric acid medium (containing some phosphoric acid) with excess persulphate and a trace of silver salt as catalyst. Phosphoric acid serves to prevent the precipitation of manganese dioxide. Gortner and Rost⁸ and Applebaum⁹ criticised the persulphate method, stating that the oxidation of manganese^{II} is often incomplete and that the permanganate colour frequently fades in a short time.

* Part II: *Talanta*, 1963, 10, 657.

In view of the erratic nature of the persulphate-manganese^{II} reaction,⁶ Willard and Greathouse¹⁰ proposed the use of potassium periodate for the oxidation of manganese^{II} to manganese^{VII} in sulphuric, phosphoric or nitric acid or in a mixture of two or more acids. Chromium^{III}, cerium^{III}, *etc.*, are also oxidised by periodate in acid solution. A disadvantage is that a large excess (about fifty to one hundred times) of periodate has to be used. Koroleff¹¹ proposed the use of a silver salt to speed up the reaction and this also assists in economising on the amount of periodate. Although Willard and Greathouse proposed a minimum concentration of 1.75*M* sulphuric acid, Richards¹² found that when the concentration of manganese is low (a few μg in 10 ml), a high concentration of phosphoric acid prevents the full development of the colour. Richards recommends an acidity of 2.0*N* in sulphuric acid. While determining manganese^{II} in caustic soda, Williams and Andes¹³ add sufficient phosphoric acid to produce a pH of 2 at which the oxidation by periodate is conducted. Nydahl¹⁴ recently stated that the colorimetric determination of manganese according to the periodate method requires rather a long period of heating for the full development of colour, especially in very dilute solution, even when it is carried out as proposed by Richards or by Koroleff. When the amount of manganese is 1 $\mu\text{mole}/100$ ml, Nydahl observed the oxidation to take place only to 49% extent in 1 hr, on a steam bath, and to 57% in 2 hr when carried out under the optimum conditions prescribed by Richards. In the presence of 0.1 mmole of silver nitrate the corresponding figures were 86 and 91%, respectively.

Strickland and Spicer¹⁵ carried out a fairly systematic study of the important factors governing a satisfactory analytical application of the periodate oxidation. They observed that

1. The extinction obtained from a given quantity of manganese can vary in magnitude and reproducibility according to the conditions.
2. The rate of oxidation is mainly dependent upon the acidity of the solution and has a minimum value when the reaction takes place (at 100°) in a nitric or sulphuric acid medium of 1.5*M* concentration. At lower acidities the reaction becomes very rapid, but the extinctions are rather erratic and the use of a low acidity to increase the rate is not recommended. With more strongly acid solutions there is again an increase in the rate of the reaction, but the final extinction under these conditions decreases less rapidly and the extinctions are reproducible. Nevertheless, for several reasons, the acidity must not exceed certain approximate values. It is suggested that the most satisfactory acid range to use with sulphuric acid at 100° is 3–6*M* and the corresponding range for nitric acid at 100° is 4–7*M*.
3. With sulphuric acid concentrations greater than 6*M* the decrease of extinction becomes very rapid, largely because of the formation of permanganic anhydride. The effect with nitric acid is not so pronounced and is mainly the result of the formation of quadrivalent manganese. If the acidity becomes too great in nitric acid media, manganese dioxide may precipitate. In view of the above effects, the acidity of sample and standard solutions should be reproduced to within at least 0.5*M* and care should be taken to ensure that concentration changes from evaporation, *etc.*, do not exceed 5–10%.
4. If solutions are boiled, the additional complication of permanganic acid volatility is encountered in the case of sulphuric acid solutions. This can lead to appreciable errors in acid solutions more concentrated than 6*M*.

5. Because the rate of oxidation increases two or three times for an increase in temperature of 20°, it is obvious that as high a temperature as practicable should be used. The maximum extinction from a given quantity of manganese can vary by a few per cent, however, according to the exact temperature and the latter should be controlled to within 10°. Superheating (which is marked with sulphuric acid) may be avoided by the addition of glass beads, *etc.*

6. The reaction does not depend to any appreciable extent on the concentration of periodate, provided that this exceeds the concentration of manganese some fifty or one hundred times. It is suggested that 0.5 g of potassium periodate is used for every 100 ml of solution in which the concentration of manganese^{II} should not exceed about $5 \cdot 10 \times 10^{-4} M$.

7. The nature of the reaction is such that complete oxidation is never theoretically achieved and the extinction-time curve approaches a maximum asymptotically. Although in practice the extinction rapidly attains a maximum value within the sensitivity of measurement of the absorptiometer, the relatively slow approach to this value makes a visual estimation deceptive and it is essential to allow further time to elapse after the colour appears to be fully developed.

Tomula and Aho¹⁶ proposed a colorimetric method for the determination of manganese^{II} through its oxidation to manganese^{III} in a sulphuric acid medium by potassium bromate, the resulting manganese^{III} being stabilised by complexation with phosphoric acid. Purdy and Hume¹⁷ in a recent communication criticised the method and stated "in attempting to study the reproducibility and sensitivity of their method, the authors were unable to obtain consistent results". The latter authors improved the method and determined manganese as the tervalent complex in strong sulphuric acid. As much as 70 mg of manganese/100 ml could be determined. The recommended procedure was to treat the sample solution with enough concentrated sulphuric acid to give an over-all 8M acidity on dilution to 100 ml, followed by the addition of 2 ml of 0.5M potassium cyanide and 5 ml of 0.17M potassium bromate. After diluting to 100 ml, the absorbance of the solution was measured at 500 m μ in a spectrophotometer. Working at such high acid concentrations is not, however, always convenient, and the use of potassium cyanide is associated with the obvious dangers.

In view of what has been said above it was considered advantageous to possess a reagent which can oxidise manganese^{II} to permanganate quantitatively at room temperature. We have observed that ammonium hexanitratocerate(IV) does this in a dilute nitric acid medium. Silver nitrate accelerates the reaction to such an extent that the oxidation is complete within 1 min at room temperature. We have developed conditions under which the reaction can be used for the colorimetric determination of manganese over the range 0.33 to 19.93 mg/litre. Nitrate, perchlorate and borate do not interfere. Interference from chloride, bromide and iodide can be eliminated by adding sufficient silver nitrate to precipitate the silver halide, which is filtered off. Sulphate is similarly removed by the addition of barium nitrate to the hot test solution. Nickel^{II}, iron^{III}, copper^{II}, calcium^{II}, barium^{II} and molybdenum^{VI} do not interfere even when present in large quantities; when cobalt^{II} is present a correction for its own colour becomes necessary. Chromium^{III} interferes because it is oxidised along with the manganese^{II}, but curiously enough the oxidation of manganese^{II} does not go to quantitative completion at room temperature in the presence of chromium^{III}.

EXPERIMENTAL

Reagents

Ammonium hexanitratocerate(IV). An approximately 0.05M stock solution of this reagent was prepared as described in Part I of this series.¹⁸ From this a 0.01M solution is prepared by suitable dilution with 1.0M nitric acid which has been previously boiled out to free it from any traces of nitrous acid. No standardisation of this reagent is required because it is added in excess to the manganese^{II} solution.

Manganese^{II} solution. An approximately 0.025M solution of manganese^{II} was prepared by dissolving analytical reagent grade manganese^{II} sulphate (B.D.H. Ltd., England) in doubly distilled water and diluting to 1 litre. The solution was standardised potentiometrically by the methods of Lingane and Karplus¹⁹ and Gopala Rao and Kanta Rao.²⁰ This standard solution is suitably diluted as required.

Nitric acid solution. An approximately 8M solution of nitric acid was prepared by twice diluting analytical reagent-grade nitric acid with doubly distilled water, was boiled out to drive off any oxides of nitrogen, and was stored in an amber coloured bottle protected from light.

Silver nitrate solution. A 5% solution of analytical reagent grade silver nitrate was used as catalyst. All other reagents employed in this investigation were of analytical reagent quality.

Apparatus

A Klett-Summerson photoelectric colorimeter with optically matched tubes was generally used for colour comparison, with a green filter transmitting at a wavelength of 525–540 m μ . A Hilger Uvispek spectrophotometer with 1-cm cells was also used whenever necessary.

Influence of time

Five ml of 0.001510M manganese^{II} solution were taken in a 50-ml calibrated flask, acidified with sufficient 1:1 nitric acid to give an over-all acid concentration of 1.0M when diluted to 50 ml, then treated with 10 ml of 0.01M ammonium hexanitratocerate(IV) and the mixture diluted to the mark. It was immediately transferred to the colorimeter and the absorption of the solution measured against a blank of ammonium hexanitratocerate(IV) solution of equivalent concentration. The dial readings of the instrument noted at different times are recorded in Table I. In these experiments the molar ratio of manganese^{II}:cerium^{IV} was 1:10.

TABLE I

Time, min	1	5	15	30	45	60	120	180	240	300
Dial reading of colorimeter	26	61	101	142	161	169	179	187	194	194

The results in Table I show that about 4 hr are required for complete oxidation of manganese^{II} at room temperature.

Influence of temperature

Somewhat similar experiments to those above, but carried out at the temperature of a boiling water bath yielded the observations recorded in Table II.

TABLE II

Time of heating, min	1	2	5	10	15	30	60
Dial reading of colorimeter	45	61	108	122	149	193	194

It is evident that the oxidation of manganese^{II} is complete in about 30 min.

Influence of cerium^{IV} concentration

Experiments made at room temperature by varying the ratio of manganese^{II}:cerium^{IV} yielded the observations presented in Table III. In these experiments the concentration of manganese^{II} was maintained constant and that of the cerium^{IV} varied. It may be noted that 1 mole of manganese^{II} requires 5 moles of cerium^{IV} for complete oxidation to manganese^{VII}.

TABLE III

Time, min	Molar ratio of manganese ^{II} :cerium ^{IV}				
	1:5	1:10	1:15	1:20	1:40
	Dial reading of colorimeter				
1	14	26	38	65	76
2	29	41	49	89	92
5	43	61	71	114	118
15	76	101	108	168	170
30	94	142	159	192	193
60	103	169	184	194	194
120	147	179	194	194	194
240	178	194	194	194	194
300	182	194	194	194	194

Manganese taken: 0.0075 mmole

From Table III the rate of oxidation of manganese^{II} at room temperature can be increased by increasing the concentration of cerium^{IV} relative to that of manganese^{II}. With a fairly large excess of cerium^{IV} (1:20) the time of reaction can be reduced to 1 hr.

Influence of catalysts

With a view to further reducing the time of reaction at room temperature the use of catalysts, such as cobalt^{II}, nickel^{II}, osmium^{VIII} and silver^I salts, was investigated. Of the substances tried, only silver^I nitrate markedly accelerated the reaction.

Experiments were made to ascertain the optimum concentration of catalyst required for rapid oxidation of manganese^{II} by cerium^{IV} in a nitric acid medium at room temperature.

Five ml of 0.001510M manganese^{II} solution were acidified with sufficient 1:1 nitric acid to give an over-all acid concentration of 1.0M on dilution to 50 ml in a calibrated flask. The mixture was treated with varying volumes of 5% silver nitrate solution followed by 10 ml of 0.01M ammonium hexanitratocerate(IV) solution, then diluted to 50 ml with doubly distilled water. It was immediately transferred to the colorimeter and the dial readings noted at varying intervals of time. In these experiments the molar ratio of manganese^{II} to cerium^{IV} was 1:10.

TABLE IV

5% AgNO ₃ , ml	Time, min								Remarks
	0.5	1	2	5	10	15	30	60	
	Dial reading of colorimeter								
—	16	26	41	61	84	101	142	169	
0.10	48	69	94	126	157	186	194	194	
0.20	63	94	126	157	186	194	194	194	
0.50	108	137	157	192	194	194	194	194	
1.0	158	187	194	194	194	194	194	194	
2.0	192	194	194	194	194	194	194	194	
5.0	192	194	194	194	194	194	194	194	
7.50	190	190	192	192	192	192	192	192	Brown precipitate* on standing 6 hr.
10	149	149	149	151	151	151	160	168	Brown precipitate* on standing 3 hr.
15	—	—	—	—	—	—	—	—	Brown precipitate* immediately on mixing the solutions

* MnO₂

TABLE V

Over-all HNO ₃ M	Time, min							Remarks
	0.5	1	2	3	4	5	10	
	Dial reading of colorimeter							
0.25	146	164	176	182	189	192	194	
0.50	174	188	192	194	194	194	194	
1.0	188	194	194	194	194	194	194	
2.0	192	194	194	194	194	194	194	
3.0	159	163	174	184	188	188	188	Development of colour very slow.
4.0	108	126	128	134	138	142	154	No pink colour; on standing a colloidal brown precipitate formed.
5.0	—	—	—	—	—	—	—	On mixing the solutions a brown precipitate formed immediately.

It is evident from Table IV that the reaction is complete in about 1 min when the silver catalyst concentration corresponds to 2.0 ml of 5% silver nitrate solution/50 ml of reaction mixture. When the concentration increases beyond that corresponding to 10 ml, the reaction is definitely retarded. When the catalyst concentration corresponds to 15 ml a brown precipitate is formed immediately the solutions are mixed, leaving a clear yellow supernate.

Influence of nitric acid concentration on silver catalysed reaction

To ascertain the optimum concentration of nitric acid required for this reaction the following experiments were carried out. Five ml of 0.001510M manganese^{II} solution were treated with sufficient 1:3 nitric acid to reach different over-all acidities, followed by 2 ml of 5% silver nitrate solution and 10.0 ml of 0.01M ammonium hexanitratocerate(IV) solution, then the mixtures diluted to 50 ml in calibrated flasks. The various solutions were measured in the colorimeter at different intervals of time. Allowance was made for the nitric acid introduced through the hexanitratocerate(IV) solution.

In view of the observations in Table V it was decided to maintain the concentration of nitric acid between 0.5 and 2.0M in subsequent experiments. If the concentration exceeds 2.0M, the reaction may be retarded and manganese dioxide may be precipitated.

Influence of cerium^{IV} concentration on silver catalysed reaction

Five ml of 0.001510M manganese^{II} solution were acidified with sufficient 1:1 nitric acid to give an over-all acidity of 1.0M when diluted to 50 ml in a calibrated flask, then 2 ml of 5% silver nitrate

TABLE VI

Manganese ^{II} :cerium ^{IV}	Time, min	
	1	2
	Dial reading of colorimeter	
1:5	140	— ^a
1:10	194	194
1:15	193	194
1:20	194	193

^a Because added hexanitratocerate(IV) solution is in insufficient excess, a colloidal brown precipitate of manganese dioxide was obtained.

solution and sufficient 0.02M ammonium hexanitratocerate(IV) solution to give the desired molar ratio of reactants added. The final volume was made to 50 ml with doubly distilled water, and the developed color measured in the colorimeter.

From the observations in Table VI it is evident that, under the conditions employed, the reaction is complete in 1 min when the ratio of manganese^{II}:cerium^{IV} is 1:10.

Stoichiometry of reaction

In all procedures previously prescribed for the colorimetric determination of manganese^{II} based on oxidation with lead dioxide, sodium bismuthate, potassium persulphate or potassium periodate, it appears to be tacitly assumed that the product is permanganic acid, without any precise data regarding the stoichiometry of the reaction being provided. In the present case proof is provided as follows. Five ml of 0.001510M manganese^{II} solution were oxidised with excess ammonium hexanitratocerate(IV) under the conditions prescribed in the recommended procedure, then diluted to 50 ml. The solution contains nitric acid at 1.0M concentration. The developed colour of the solution was measured in the colorimeter against a blank of cerium^{IV} solution of equivalent concentration, the dial reading of the instrument being 194. A carefully standardised solution of analytical reagent grade potassium permanganate (B.D.H. Ltd., England) was suitably diluted to give a 0.001510M solution of the salt in 1.0M nitric acid. This solution gave a dial reading of 193 in the colorimeter. Furthermore, the absorption spectrum of a similarly prepared experimental solution (containing 0.0002M manganese^{II}) and that of 0.0002M permanganate were determined in 1.0M nitric acid using a Hilger Uvispek spectrophotometer and 1-cm cells in the region 480–760 m μ . The absorption of the experimental solution was measured against a blank of cerium^{IV} solution of equivalent concentration. The two absorption curves very nearly overlap (Fig. 1). The molecular extinction coefficient of the experimental solution is 2.30×10^5 and that of the potassium permanganate 2.275×10^5 , an agreement within 1.1%, which must be considered sufficiently good considering the extreme dilution at which the absorption measurements are made.

The data presented is sufficient to show that:

- (1) The product of the oxidation of manganese^{II} by ammonium hexanitratocerate(IV) in a nitric acid medium is permanganic acid.
- (2) The manganese^{II} is stoichiometrically converted into permanganic acid.

Stability of permanganic acid formed

The constancy of the optical absorption of the experimental solution over a period of at least 24 hr shows that the permanganic acid is very stable. Hence the new method can be considered well suited to routine work under ordinary laboratory conditions.

Limits of applicability

Working with solutions of different concentrations of manganese^{II} it has been observed (Fig. 2) that Beer's Law is applicable for experimental solutions containing 0.0332–1.9932 mg/100 ml.

Recommended procedure

A volume of 5–10 ml of test solution, containing about 0.033 to 2 mg of manganese^{II}/100 ml, is treated with sufficient 1:1 analytical reagent grade nitric acid to give an over-all acid concentration of 0.5–2.0M on dilution to 50 ml, followed by the addition of 2 ml of 5% silver nitrate solution and an approximately ten-fold molar excess of hexanitratocerate(IV) solution. The total volume is then made to 50 ml in a calibrated flask. After allowing to stand for 2 min, the developed colour is measured in a Klett-Summerson photoelectric colorimeter, using a green filter transmitting in the wavelength region 525–540 m μ , against a blank solution containing an equivalent amount of cerium^{IV} solution to that used in the test sample.

Typical results of such determinations are presented in Table VII. The amount of manganese^{II} present in each sample is deduced from a calibration curve (Fig. 2), or alternatively the manganese content can be deduced by comparing the colour of the test solution against that of a standard permanganate solution of about the same strength in 1.0M nitric acid.

INTERFERENCES

Nitrate (as sodium or ammonium salt) does not interfere even when present up to 720 mg/50 ml. Similarly, perchlorate and borate (as their sodium salts) do not interfere even at a concentration of 150 mg/50 ml. Traces of chloride, bromide and iodide inhibit the reaction. However, the interference of these ions can be eliminated by precipitating them with silver nitrate and filtration before the oxidation with cerium^{IV} solution. Our results show that the interference of up to at least 21.6 mg

TABLE VII

Manganese ^{II} taken, <i>mg</i>	Manganese ^{II} found, <i>mg</i>
0.04957	0.04977
0.07128	0.07099
0.09914	0.09896
0.1496	0.1510
0.2478	0.2501
0.3892	0.3932
0.4698	0.4704
0.9912	0.9936

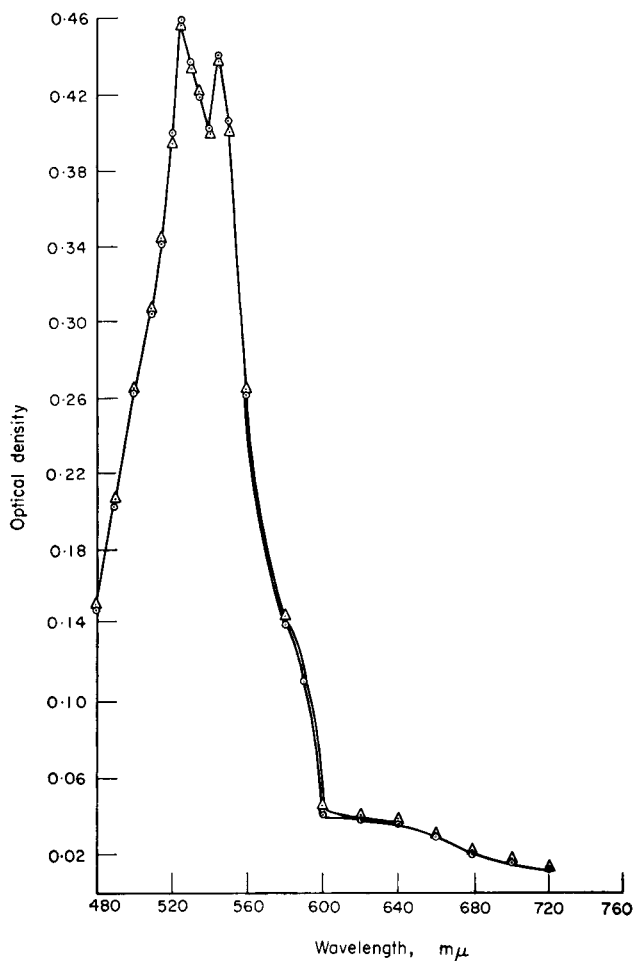


FIG. 1.—Absorption spectra of manganese^{VII} in 1.0M nitric acid:

- △—△ 0.0002M manganese^{VII} from potassium permanganate,
 ○—○ 0.0002M manganese^{VII} after oxidation of manganese^{II} with
 hexanitratocerate(IV).

of chloride ion/50 ml can be eliminated in this way. Similar experiments have shown that the interference of up to at least 16 mg of bromide and 25.4 mg of iodide can be eliminated satisfactorily. Sulphate ion does not interfere when present below 2 mg/50 ml. The interference of larger amounts can be eliminated by initially treating the hot test solution with barium nitrate and filtering off the precipitated barium sulphate. In this way the interference of sulphate even up to a concentration of 38.4 mg/50 ml can be overcome.

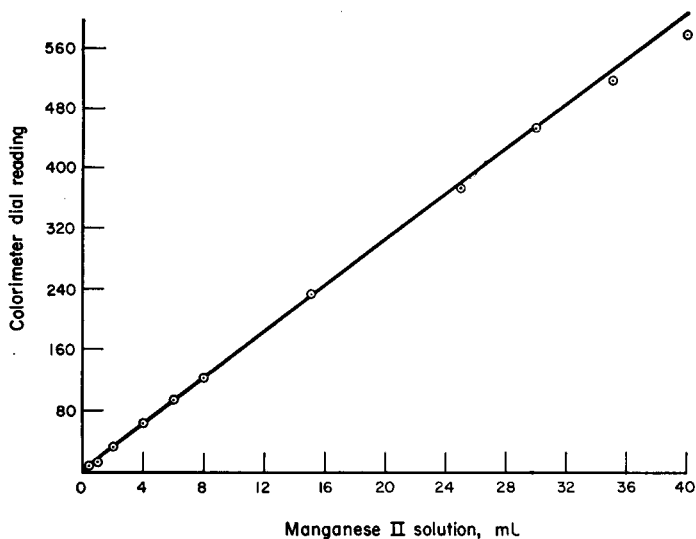


FIG. 2.—Beer's law curve for determination of manganese^{II} with hexanitratocerate(IV) ($6.04 \times 10^{-4}M$ manganese^{II} sulphate solution).

Previously published colorimetric procedures for manganese also suffer interference from chloride. In the bismuthate method the sample is usually evaporated with nitric and sulphuric acids to remove chlorides. In the persulphate method chloride is removed by adding an excess of silver nitrate. Concerning the interference of chloride in the periodate method, the statement of Willard, as quoted by Yoe,²¹ is interesting: "It has been stated in various references to this method that the presence of chloride would not interfere. This is true only to a limited extent and only when the operator has taken care to add sufficient periodate to oxidise all the chloride. It is preferable to remove chloride by evaporation with nitric or sulphuric acid." Thomson and Wilson,²² who applied the periodate method to the determination of manganese in sea water, removed the chloride by treating the evaporation residue with concentrated sulphuric acid, heating to expel the acid and fuming the salts.

The interference of sulphate constitutes a drawback for the new method as compared with the persulphate and periodate procedures. According to Yoe²³ the bismuthate method is satisfactory only when most of the sulphuric acid has been driven off. He states that this is necessary for the reason that the shade of the permanganate is not the same in sulphuric and nitric solutions.

Nickel^{II}, iron^{III}, copper^{II}, calcium^{II}, barium^{II} and molybdenum^{VI} do not interfere even when present up to 40 mg/50 ml. Cobalt^{II}, when compensated for its own colour, does not interfere even up to 100 mg/50 ml. Tungsten^{VI} interferes because of precipitation of tungstic acid in the mineral acid medium. The interference from chromium^{III} has been mentioned above (chromium^{III} also interferes in the periodate and persulphate methods).

Application of New Method to Determination of Manganese in Steel

About 1 g of silico-manganese spring steel (supplied by Messrs Globe Steels, Bombay, India) was treated with 60 ml of 1:1 nitric acid in a 600-ml Pyrex beaker, then heated on a hot-plate for 40–50 min, by which time all volatile and carbonaceous matter was completely decomposed. The resulting yellow solution contained a spongy brown mass (colloidal silicic acid with adsorbed iron^{III}) in suspension which was filtered off, after dilution to about 200 ml, through a Whatman No. 42 filter paper, the filtrate being collected in a 500-ml calibrated flask. The residue on the filter paper, after being washed twice with distilled water, was transferred along with the filter paper to a silica crucible and incinerated to a brown mass. After cooling to room temperature, it was leached with a few drops of 1:1 nitric acid and a few drops of hydrofluoric acid, and the extract transferred to a platinum dish and evaporated to dryness. The resulting mass, after twice evaporating with a mixture of 2 ml of 1:1 nitric acid and 2 ml of hydrofluoric acid, readily dissolved in dilute nitric acid. The solution obtained was transferred to the calibrated flask containing the main bulk of the solution and diluted to the mark. Three different aliquots of this solution (5, 10 and 15 ml) treated according to the new procedure gave the manganese present in the sample as 1.128, 1.127 and 1.130%, respectively, as against a value of 1.150% by the potentiometric procedure of Lingane and Karplus.¹⁹ The agreement between the two methods is considered satisfactory.

Acknowledgement—One of us (P. V. K. R.) desires to thank the Council of Scientific and Industrial Research (India) for the award of a Junior Research Fellowship.

Zusammenfassung—Es wurde beobachtet, daß Mangan(II) durch einen schwachen Überschuß von Ammoniumhexanitratocera(IV) in 0.5–2M HNO₃ bei Zimmertemperatur zu Permangansäure oxydiert wird. Die Reaktion wird durch Silbernitrat merklich katalysiert, sodaß die quantitative Oxydation von Mangan(II) in einer Minute beendet ist. Es wurde eine Arbeitsvorschrift entwickelt, die die katalysierte Reaktion zur kolorimetrischen Bestimmung von Mangan zwischen 0.33 und 19.93 mg/l zu verwenden gestattet. Die neue Methode hat vor den derzeit verfügbaren den Vorteil, daß die Oxydation von Mangan(II) bei Zimmertemperatur stöchiometrisch zu Ende geht. Unter den vorgeschriebenen Bedingungen ist die gebildete Permangansäure mindestens 24 Stunden beständig. Die Störung durch Sulfat und Halogenide (Chlorid, Bromid und Jodid) kann durch Behandlung der Probelösung mit Bariumnitrat beziehungsweise Silbernitrat vor der Oxydation mit Cer(IV)-Lösung eliminiert werden. Die Anwendung der Methode auf die Manganbestimmung in Stahl wird erörtert.

Résumé—On a observé que le manganèse(II) est oxydé en acide permanganique par traitement avec un léger excès d'hexanitratocérate(IV) d'ammonium en milieu acide nitrique 0,5 à 2M à température ambiante. La réaction est nettement catalysée par le nitrate d'argent, de sorte que l'oxydation quantitative du manganèse(II) est complète en une minute. On a établi les conditions d'emploi de la réaction catalysée pour le dosage colorimétrique du manganèse entre 0.33 et 19.93 mg par litre. Par rapport aux méthodes couramment disponibles, cette méthode est avantageuse par le fait que l'oxydation du manganèse(II) est effectuée à température ambiante, de façon stoechiométrique. Dans les conditions prescrites, l'acide permanganique formé est stable 24 heures. L'interférence des sulfates et des halogénures (chlorure, bromure et iodure) peut être éliminée en traitant la solution essai au nitrate de baryum ou au nitrate d'argent, respectivement, avant oxydation par la solution de cérium(IV). On considère aussi l'application de la méthode au dosage du manganèse dans l'acier.

REFERENCES

- ¹ W. Crum, *Ann.*, 1845, **55**, 219.
- ² P. Pichard, *Compt. rend.*, 1872, **75**, 1821; see also *Dingler's Polytech. J.*, 1873, **207**, 136.
- ³ J. Reddrop and H. Ramage, *J. Chem. Soc.*, 1895, **67**, 268.
- ⁴ L. Dufty, *Chem. News*, 1901, **84**, 248.
- ⁵ Hugh Marshall, *ibid.*, 1901, **83**, 76.
- ⁶ G. Von Knorre, *Z. angew. Chem.*, 1901, **14**, 1149.

- ⁷ H. E. Walters, *Chem. News*, 1901, **84**, 239.
- ⁸ R. O. Gortner and C. O. Rost, *J. Ind. Eng. Chem.*, 1912, **4**, 522.
- ⁹ Applebaum, *Chem. Analyst*, 1913, **17**, 222.
- ¹⁰ H. H. Willard and L. Greathouse, *J. Amer. Chem. Soc.*, 1917, **39**, 2366.
- ¹¹ F. Koroleff, *Acta Chem. Scand.*, 1947, **1**, 503.
- ¹² M. B. Richards, *Analyst*, 1930, **55**, 554.
- ¹³ D. Williams and R. V. Andes, *Ind. Eng. Chem., Analyt.*, 1945, **17**, 28.
- ¹⁴ F. Nydahl, *Analyt. Chim. Acta*, 1949, **3**, 144.
- ¹⁵ J. D. H. Strickland and G. Spicer, *ibid.*, 1949, **3**, 517.
- ¹⁶ E. S. Tomula and V. Aho, *Ann. Acad. Sci. Fennicae*, 1939, **A52**, No. 4; *idem.*, *ibid.*, 1940, **A55**, No. 1.
- ¹⁷ W. C. Purdy and D. N. Hume, *Analyt. Chem.*, 1955, **27**, 256.
- ¹⁸ P. V. Krishna Rao, K. S. Murty and G. Gopala Rao, *Talanta*, 1962, **9**, 835.
- ¹⁹ J. J. Lingane and R. Karplus, *Ind. Eng. Chem., Analyt.*, 1946, **18**, 191.
- ²⁰ G. Gopala Rao and P. Kanta Rao, *Talanta*, 1963, **10**, 1251.
- ²¹ John H. Yoe, *Photometric Chemical Analysis, Vol. I, Colorimetry*. John Wiley and Sons, Inc., New York, 1928, p. 279.
- ²² T. G. Thompson and T. L. Wilson, *J. Amer. Chem. Soc.*, 1935, **57**, 233.
- ²³ Reference 21, p. 280.

POLAROGRAPHIC DETERMINATION OF DISSOLVED OXYGEN IN PETROL

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(Received 24 February 1964. Accepted 5 April 1964)

Summary—A method is described for the determination of dissolved oxygen in petrol using a cathode ray polarograph. Oxygen produces two waves, with reduction potentials at -0.67 V and -1.25 V against a mercury pool anode, when an ethanolic solution of lithium chloride is used as supporting electrolyte. Calibrations are carried out using water of known oxygen content for the preparation of standards and the wave at -0.67 V is preferred for quantitative measurement.

INTRODUCTION

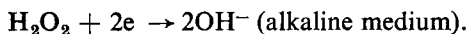
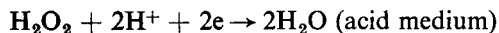
THE determination of oxygen in hydrocarbons has been carried out in these laboratories by a chemical procedure based upon that of McArthur,¹ who developed an analytical method for determination of the oxygen content of various plant gases. As applied to hydrocarbons, this method depends upon the removal of oxygen in a stream of oxygen-free nitrogen and its absorption into a $0.01N$ solution of chromium^{II} chloride. The excess chromium^{II} chloride is subsequently determined by titration with cerium^{IV} sulphate using ferroin as indicator.

Polarography has been used for the determination of oxygen in a number of materials and it appeared an attractive alternative, having the virtues of speed and specificity.

It is well established that dissolved oxygen is reduced at the dropping mercury electrode to produce two waves.² The first wave results from reduction to hydrogen peroxide:



The second wave corresponds to the reduction of the hydrogen peroxide either to water or hydroxyl ion, depending on the pH:



The diffusion currents are normally well-defined and show a linear dependence on oxygen concentration. However, three main difficulties are encountered in the application of polarography to the determination in petrol: the limited solubility of petrol in aqueous or semi-aqueous electrolyte systems, the exclusion of atmospheric oxygen in handling samples and the accurate calibration of the instrument. The first

difficulty was resolved by adopting a supporting electrolyte of lithium chloride in absolute alcohol and the second by the design of a special cell. Two ways of calibrating the polarograph were investigated: by using water of known dissolved oxygen content directly as a calibration standard, and by using air-saturated alcoholic electrolyte as a secondary standard, the dissolved oxygen content being determined polarographically using water as a primary standard.

EXPERIMENTAL

A 0.1M ethanolic solution of lithium chloride proved a suitable supporting electrolyte and gave reduction waves from dissolved oxygen at -0.67 V and -1.25 V.

In early experiments calibrations were achieved by determining the dissolved oxygen content of the supporting electrolyte and using this as a secondary standard. However, the calibration procedure given below was preferred because, under the conditions given, petrol, electrolyte and water formed a completely homogeneous system.

Apparatus

Polarograph. A Southern Analytical Differential Cathode Ray Polarograph was used, but any conventional polarograph of adequate sensitivity would be suitable.

Sampling tube. A sampling tube connected to the polarographic cell is shown in Fig. 1. It comprises a tube of about 5-ml capacity with two 3-way taps C and D, but so arranged that the sample is delivered *via* tap C to the polarographic cell. The volume of the sample tube is determined by filling it with water and weighing.

Polarographic cell. This is also illustrated in Fig. 1. A specially designed cell is so arranged that the dropping electrode, sample inlet tube and stirrer emerge through a tight-fitting bung into the cell. It contains two taps A and B, A being a 3-way tap, the inlet of which is connected to an argon supply and arranged so that the electrolyte can be degassed. Tap A can also be fitted to tap D of the sample tube and argon used to gently transfer the petrol through taps C and B into the cell, the latter being connected by means of polyvinylchloride tubing. A side arm is also provided for the anode connection, thus preventing any fouling by the stirrer.

Reagents

0.1M Lithium chloride. Prepare a 0.1M ethanolic solution of lithium chloride by dissolving 4.24 g of lithium chloride in absolute alcohol and diluting to 1 litre with this solvent.

Air-saturated water of known oxygen content. For most purposes a published value can be assumed for the oxygen content,³ but for more accurate work the dissolved oxygen should be determined by the Winkler method.⁴ Air-saturated water may be prepared by shaking a partially filled flask of water for several minutes, recording the temperature at which this is done.

Argon (oxygen-free). High quality nitrogen may be used as an alternative.

Procedure

Calibration of polarograph. Add 35 ml of 0.1M lithium chloride and 5 ml of petrol to the polarographic cell, which contains a mercury pool as anode. Fit the bung to the cell, close tap B and degas the solution by turning tap A and bubbling argon through the electrolyte for 5–10 min. Close tap A. Set the start potential at -0.2 V and measure the wave height of any remaining oxygen at -0.67 V (this should be very small; if not, continue degassing). Record this reading. Introduce 5 ml of air-saturated distilled water at a known temperature by means of a microburette through tap B and stir rapidly by switching on the electric motor after closing tap B. When a homogeneous solution is obtained, with start potential at -0.2 V, measure the height of the oxygen wave at -0.67 V. Record this reading and empty the cell.

Now take 35 ml of 0.1M lithium chloride, 5 ml of petrol and 1 ml of water into the polarographic cell and degas with argon *via* tap A for 5–10 min. Close tap A and measure the wave height of any residual oxygen. Introduce 4 ml of air-saturated water by means of a microburette through tap B, stir and record the wave height of the resulting polarogram.

Repeat this procedure with 35 ml of 0.1M lithium chloride/5 ml of petrol/2 ml of water, 35 ml of 0.1M lithium chloride/5 ml of petrol/3 ml of water and 35 ml of 0.1M lithium chloride/5 ml of petrol/4 ml of water, degas, then add 3, 2 and 1 ml of water, respectively. Convert ml of water to mg of oxygen from the tables relating temperature of water to dissolved oxygen content⁵ and construct a graph relating peak height to concentration of oxygen.

Determination of dissolved oxygen in petrol. Connect the sample tube to sample point with polyvinylchloride tubing (Notes 1 and 2) and purge well with petrol. Close taps C and D so that the tube is completely filled with petrol.

Add 35 ml of 0.1M lithium chloride solution to the polarographic cell and 5 ml of water. Connect the rubber bung to the cell and close tap B. Degas the system by bubbling argon *via* tap A into the

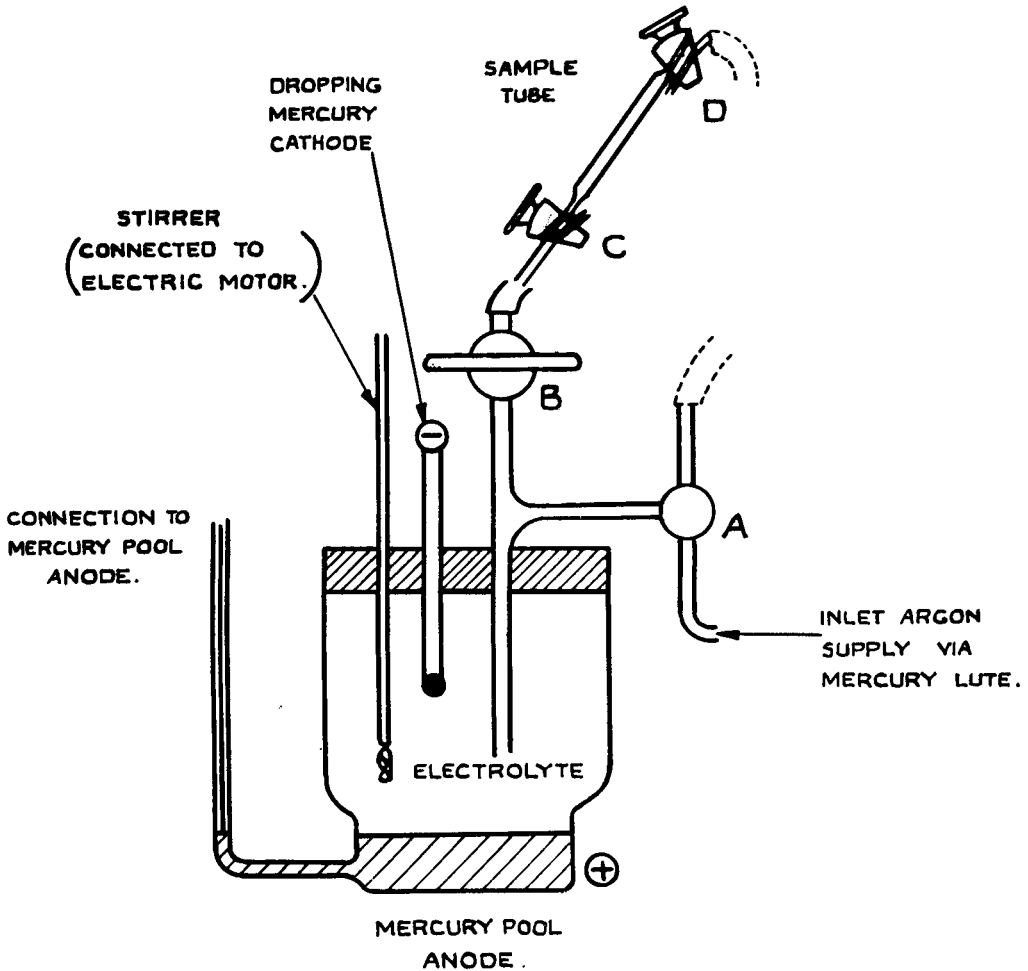


Fig. 1

solution for 5–10 min. Close tap A and with start potential at -0.2 V record the polarogram of the solution. If a wave appears, continue degassing, then repeat the voltage sweep until no oxygen wave or only a small 'blank' is recorded.

Connect the sample tube to the cell with polyvinylchloride tubing between taps B and C and between taps A and D as shown in Fig. 1. Turn tap A so that argon purges through tap D for about 1 min, then close tap D and open taps B and C and purge with argon for the same period. Close taps B and C. Close tap A to the cell and turn it to the polyvinylchloride connection between A and D, opening taps D and C in that order and then tap B in such a manner that the sample is very slowly added to the cell. Close tap B after the addition of sample.

Record the polarogram from a start potential of -0.2 V at a sensitivity to give a maximum wave height. Measure the wave height of the oxygen wave and read the mg of oxygen to which this is equivalent from the calibration graph.

Notes

1. Avoid the use of rubber tubing and silicone tap grease because this interferes with the polarographic determination.
2. The amount of polyvinylchloride tubing should be kept to a minimum because it is porous to oxygen.

Calculation

Let a be the mg of oxygen from the graph and v be the volume of sample. Hence

$$(\text{ppm w/v}) = \frac{a \times 10^3}{v}$$

RESULTS AND DISCUSSION

In all experiments the total volume and electrolyte/petrol/water ratios were maintained the same, thus providing identical backgrounds for the evaluation of the oxygen wave heights. The quantitative nature of the two oxygen waves at -0.67 V and -1.25 V was demonstrated by polarographing varying amounts of a sample of air-saturated petrol in a water and alcoholic solution of $0.1M$ lithium chloride, but maintaining the total volume and ratio of water/petrol and electrolyte the same. The linear variation of peak height with concentration is shown in Table I.

TABLE I.—MEASUREMENT OF OXYGEN WAVE AT -0.67 V AND -1.25 V

Air-saturated petrol, ml	Peak height at -0.67 V converted to the same scale factor	Peak height at -1.25 V converted to the same scale factor
5	186	156
3	112	96
1	35	33

It was found preferable, however, to use the oxygen wave at -0.67 V because polarographic determination in this electrolyte/petrol media caused serious streaming of the dropping mercury electrode at the higher potential.

An important feature of the polarographic method is the fact that by degassing the sample cell with argon or nitrogen, all of the dissolved oxygen is completely removed. Thus, any doubts that it is the oxygen wave being measured can be confirmed by the simple technique of degassing, when this wave will disappear. Using this technique, the calibration was easily checked by preparing standard solutions of oxygen from air-saturated water and degassed petrol and the recoveries obtained are shown in Table II.

TABLE II.—RECOVERIES OF OXYGEN ON STANDARD SOLUTIONS

Oxygen added, ppm	Oxygen found, ppm
44	43
26	25
26	26
9	10
9	7

The determination on samples taken in duplicate shows the polarographic method to be highly reproducible, a number of petrol samples being analysed which were

shown to have dissolved oxygen contents between <1 ppm and 30 ppm. The fact that figures of <1 ppm could be recorded also confirmed that the special sampling and cell arrangement precluded absorption from atmospheric oxygen. The results on duplicate samples are given in Table III.

TABLE III.—DUPLICATE DETERMINATIONS OF DISSOLVED OXYGEN (ppm) IN SAMPLES OF PETROL

Detm.	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8
1	0.8	1.3	1.6	10	14	21	23	30
2	0.8	1.4	1.8	11	16	21	25	33

Finally, by the analysis of identical samples of petrol, a comparison of the polarographic and chemical^I methods was made. In the latter the petrol was degassed in a stream of oxygen-free nitrogen and the oxygen absorbed in an acid solution of 0.01*N* chromium^{II} chloride. The change in chromium^{II} ion concentration was then related to the amount of oxygen which the sample contained. The excess chromium^{II} ion was determined by adding the solution under test to iron^{III} alum solution and the equivalent iron^{II} ion produced titrated with a standard solution of cerium^{IV} sulphate using ferroin as indicator. Comparison of the two techniques is shown by the results in Table IV.

TABLE IV.—COMPARISON OF RESULTS FOR DISSOLVED OXYGEN BY POLAROGRAPHIC AND CHEMICAL TECHNIQUES

By polarography, ppm	By chemical method, ppm
0.8	<1
4.5	4.0
3	2.5
6	9
15	13
10	7
15	10
36	32

These results show reasonable agreement, but the speed with which determinations can be completed by polarography compared with the chemical method and the high reproducibility on duplicate samples makes this the more attractive method for the determination of dissolved oxygen in petrol.

Acknowledgements—The author wishes to thank Mr. G. E. Penketh for his helpful advice and Mr. B. Chapman for his suggestions and valuable assistance with the experimental work.

Zusammenfassung—Eine Methode zur Bestimmung von gelöstem Sauerstoff in Petroleum mit Hilfe eines Kathodenstrahlpolarographen wird beschrieben. Sauerstoff gibt zwei Stufen mit Reduktionspotentialen bei $-0,67$ V und $-1,25$ V gegen das Bodenquecksilber als Anode, wenn als Trägerelektrolyte eine äthanolische Lithiumchloridlösung benutzt wird. Geeicht wird mit Wasser bekannten Sauerstoffgehalts zur Herstellung von Standardlösungen; die Stufe bei $-0,67$ V wird zur quantitativen Messung vorgezogen.

Resume—On décrit une méthode de dosage de l'oxygène dissous dans l'essence, au moyen d'un polarographe oscillographique. L'oxygène produit deux vagues, avec des potentiels de réduction à $-0,67$ V et $-1,25$ V, par rapport à une anode à masse de mercure, lorsque l'électrolyte support est une solution éthanolique de chlorure de lithium. Les étalonnages sont effectués en utilisant de l'eau à teneur en oxygène connue pour la préparation des étalons et, pour les mesures quantitatives, on préfère la vague à $-0,67$ V.

REFERENCES

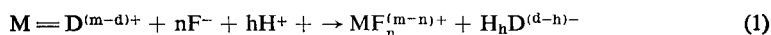
- ¹ I. A. McArthur, *J. Appl. Chem.*, Vol. II, Pt. II, Feb. 1952, 91-96.
- ² I. M. Kolthoff and J. L. Lingane, *Polarography*, Vol. II. Interscience Publishers, New York, 1952, p. 552.
- ³ G. A. Truesdale, A. L. Downing and G. F. Lowden, *J. App. Chem.*, 1955, 53.
- ⁴ L. W. Winkler, *Ber.*, 1888, **21**, 2843.

SHORT COMMUNICATIONS

New ideas on the reaction mechanism of determinations based on decolorisation

(Received 1 November 1962. Revised 2 April 1964. Accepted 4 April 1964)

PHOTOMETRIC determinations of fluoride are mostly based on decolorisation, *i.e.*, decrease in colour intensity of a metal-dye (MD) chelate and increase in that of the free dye. All decolorisation determinations of fluoride have, therefore, been interpreted as being indirect methods, based on a substitution mechanism, which can be formulated as

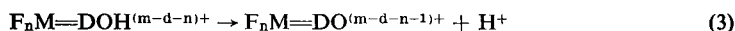


where M^{m+} is a metal ion, D^{d-} and $H_hD^{(d-h)-}$ are different protonation forms of a dye, $=$ represents the chelate ring responsible for the colour of the metal-dye chelate, and $h \leq 0$.

Probably the first direct colour (colorisation) reaction of fluoride was described by Feigl and Rajmann,^{1,2} but today this reaction is forgotten because of its small practical use. A direct determination of fluoride which has received wide attention, is that of Belcher and coworkers:^{3,4} a yellow solution of alizarin complexan gives rise to a red chelate with cerium^{III}, and this in turns yields a blue ternary complex with fluoride. When the fluoride concentration increases, the solution becomes yellow because of the rupture of all of the MD bonds according to equation (1). Belcher and coworkers' interpretation of the blue colour may be generalised as follows. The strongly electronegative fluoride ion, after reacting with a metal-dye chelate derived from the dye DOH^{d-} (which even after reacting with the metal still has a free hydroxyl group)



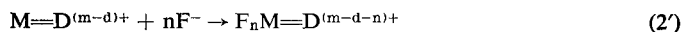
labilises the hydrogen in the free hydroxyl group of the dye:



This reaction is accompanied by a change of colour, which clearly indicates the formation of a ternary complex.

For reaction (3) to occur, at least two conditions must be fulfilled: (i) The dye, after having reacted with the metal, must have at least one hydroxyl (phenolic) group conjugate with the resonance system of the dye. (ii) The pH at which reaction (2) takes place must be such that (a) the dissociation of the free hydroxyl group does not take place spontaneously, and (b) the dissociation of the free hydroxyl group which is labilised by the reaction between the metal-dye chelate and fluoride must not be suppressed. Alizarin complexan forms coloured binary chelates with a number of metals. Binary complexes fulfilling these conditions, which are easily identified by colour changes, are formed with cerium^{III}, lanthanum and praseodymium. Ternary complexes with other metals probably formed at a pH other than that required by condition (ii), are not easily identified.

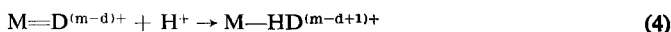
Dyes which have one or two dicarboxymethylaminomethyl groups but no free hydroxyl group, as does alizarin complexan, can react analogously to reaction (2) in the following manner



Such dyes as Semixylenol Orange and Xylenol Orange (SXO, XO) have no superfluous hydroxyl group and therefore reaction (3), with the accompanying colour change indicating the formation of a ternary complex, cannot take place.

By generalisation of the interpretation of Belcher and coworkers, the existence of FDM complexes with the same colour as the binary metal chelate may be assumed. From the work of Pribil and Kopanica⁵ ternary complexes having the same colour as the free dye is possible. They found

that slight acidification caused the violet complex of copper^{II} with Xylenol Orange to turn yellow. Because copper^{II} ions could not be detected (polarographically) in this solution, the colour change could not be explained in terms of the replacement of copper^{II} in the copper-Xylenol Orange chelate by hydrogen ion. Even in this more acidic solution copper^{II} must still be bound by the dicarboxymethylaminomethyl group of Xylenol Orange. The existence of a "decolorised" binary complex that originated in accordance with the reaction



has to be anticipated, by analogy with copper-Xylenol Orange. Of course, one cannot easily prove (polarographically) that zirconium has not been replaced by hydrogen ion.

The present author has shown that six coloured MD chelates which he studied, are decolorised by fluoride (and sulphate) only by a higher acidity than that pH at which these chelates mostly originate. This means that fluoride "decolorises" the system MD until the conditions are reached when the chelate is decolorised under the influence of hydrogen ions.

Fluoride that has reacted with a binary chelate in accordance with reaction (2) or (2'), labilises, of course, not only the hydrogen bound in the "remote" phenolic group but also, and preferentially, that in the "nearer" bonds between M and D. In the case when fluoride reacts with zirconium-Xylenol Orange under such acidity conditions that reaction (4) has already partially taken place, labilisation of the bond between the metal and the functional group of the resonance system of the dye (which is much weaker than the bond between the metal and the strongly complexing dicarboxymethylaminomethyl group) makes possible the reaction



by which (already when $n = 1$) the "decolorised" ternary complex originates more easily than the analogous "decolorised" binary system in accordance with reaction (4). If the concentration of fluoride increases considerably, so many fluoride ions react with the metal that all of the metal-dye bonds are broken, *i.e.*, reaction (4') passes over to reaction (1). Reaction (1), which corresponds to the existing ideas about the mechanism of decolorisation determinations of fluoride, appears as one limiting case of reactions that are probably best considered from the new point of view.

All that has been said about decolorisation methods for fluoride also applies analogously to decolorisation determinations of (or interferences from) sulphate and other anions. As long as individual decolorisation determinations are not conclusively proved experimentally to be methods with an indirect mechanism of the type of reaction (1), the possibility that the cause of decolorisation is really colorisation of a ternary complex of the same basic colour as the free dye cannot be excluded.

The only experimental data quoted here in support of the new conception of decolorisation reaction mechanisms is as follows. After having added a sufficient quantity of fluoride to the red solution of zirconium-Xylenol Orange, one obtains a yellow solution whose spectrum agrees qualitatively with that of a solution of the same amount of dye, though quantitatively it is less intense. Only after the addition of even higher amounts of fluoride do the spectra of the two solutions become identical from the quantitative point of view. It is, therefore, necessary to assume that before the limiting reaction (1)—connected with the identification of both spectra—occurs, a ternary complex is present in accordance with reaction (4'), and its colour intensity is (always slightly) lower than that of the free dye. If fluoride is added to a solution of zirconium-Xylenol Orange (or better if Semixylenol Orange is used), a polarographic curve is obtained which is intermediate between the curve of the free dye and the curve of the binary chelate (*i.e.*, after the addition of fluoride the curve with $\pi_{1/2}$ of the free dye does not appear).

The interference from sulphate, *etc.*, in the determination of fluoride with zirconium-Xylenol Orange in hydrochloric acid solution is less than in perchloric acid solution. The "protective" influence of chloride and other facts may best be explained by means of "undecolorised" ternary complexes of the type $ClZrXO$. By "decolorising" these complexes a quaternary complex of the type $F(Cl)ZrXO$ presumably originates.

Other aspects of the author's ideas have already been reported,⁶ and experimental data will be published elsewhere.⁷

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Summary—The existence of fluoride-metal-dye (FDM) ternary complexes which have a different colour from that of the MD chelate and of the free dye, as well as the existence of MD binary chelates with the same colour as the free dye, is known. By analogy, the existence of FDM ternary complexes with the same colour as MD or as D

may be assumed. Such ternary complexes may be formed in some determinations based on "decolorisation", so that these determinations should not generally be considered as indirect methods.

Zusammenfassung—Ternäre Fluorid-Metall-Farbstoff-(FMD)-Komplex mit von der des Metall-Farbstoff-(MD)-Chelats und des freien Farbstoffs verschiedener Farbe sind bekannt, desgleichen binäre Chelate MD mit derselben Farbe wie der freie Farbstoff. Analog kann die Existenz von ternären FDM-Komplexen mit derselben Farbe wie MD oder D angenommen werden. Solche ternären Komplexe können bei einigen auf "Entfärbung" beruhenden Bestimmungen gebildet werden; daher sind diese Bestimmungen nicht allgemein als indirekte Methoden zu betrachten.

Résumé—On connaît l'existence de complexes ternaires fluorure-métal-colorant (FDM) dont la couleur diffère de celle du chélate métal-colorant (MD) et de celle du colorant libre (D), ainsi que l'existence de chélates binaires métal-colorant (MD) de même couleur que le colorant libre. Par analogie, on peut supposer l'existence de complexes ternaires FDM de même couleur que MD ou D. De tels complexes ternaires peuvent se former lors de quelques dosages basés sur la "décoloration", de sorte que ses dosages ne devraient pas en général être considérés comme des méthodes indirectes.

REFERENCES

- ¹ F. Feigl and E. Rajmann, *Mikrochemie*, 1932, **12**, 133.
- ² H. F. Liddel, *Analyst*, 1953, **78**, 494.
- ³ R. Belcher, M. A. Leonard and T. S. West, *Talanta*, 1959, **2**, 92.
- ⁴ R. Belcher and T. S. West, *ibid.*, 1961, **8**, 853.
- ⁵ R. Přibil and M. Kapanica, private communication.
- ⁶ R. Valach, 19th Wholstate Chemical Congress, Brno, 1962.
- ⁷ *Idem*, *Z. analyt. Chem.*, submitted.

The determination of chlorosuccinic acid in aqueous solutions

(Received 27 July 1963. Accepted 10 March 1964)

INTRODUCTION

THE electrochemical reduction of dichloromaleic acid in buffered media has been shown to yield both chlorosuccinic and succinic acids.¹ Furthermore, the relative amounts of these products depend on the pH at which the reduction is accomplished. It was therefore necessary to develop a method for the determination of small amounts of chlorosuccinic acid (10^{-3} – $10^{-2}M$) in the presence of succinic citric and phosphoric acids (the two last occurring as components of the buffer used in the reduction). A simple procedure has been developed which involves the dehydrohalogenation of chlorosuccinic acid followed by a polarographic determination of the fumaric acid formed.

EXPERIMENTAL

Reagents

Fumaric acid: Matheson, Coleman and Bell, technical grade (99+%) fumaric acid was recrystallised several times from water.

Sodium hydroxide: Fisher Scientific Co., aqueous 50%, by weight.

Hydrochloric acid: Fisher Scientific Co., concentrated, reagent-grade.

Chlorosuccinic acid: Delta Chemical Works, Inc., purified by recrystallisation from ethyl acetate and light petroleum ether and vacuum sublimation: m.p. found 146–148°, reported 146–148°.²

Apparatus

Polarograph, constant temperature bath, H-cell with saturated calomel electrode as reference, purified nitrogen.

Procedure

Dehydrohalogenation: The following procedure was used to analyse solutions containing 10^{-3} – $10^{-2}M$ chlorosuccinic acid. An aliquot (5–25 ml) of the solution was pipetted into a 100-ml volumetric flask, 5 ml of 50% w/w sodium hydroxide were then added, and the solution was allowed to stand for 60 min. After the addition of 10–15 ml of distilled water and 10 ml of hydrochloric acid, the solution was cooled and was diluted to the mark with distilled water.

Polarographic analysis: After removal of oxygen by passing nitrogen through the solution for 10 min, a portion of the above solution was transferred to the H-cell and polarographed. The limiting current at $-0.85v$ vs. SCE was recorded and corrected for the residual current of the supporting electrolyte. A stock solution of $5-8 \times 10^{-4}M$ fumaric acid in the same supporting electrolyte was used to obtain the current-concentration ratio, i_d/c . The concentration of chlorosuccinic acid was then calculated in the following manner.

$$\frac{i_d}{K} \times \frac{100}{A} = \text{molarity of chlorosuccinic acid in the original solution}$$

i_d = corrected limiting current at $-0.85v$ vs. SCE,

K = current-concentration ratio for fumaric acid,

A = aliquot of sample which was dehydrohalogenated.

RESULTS AND DISCUSSION

Effect of pH and ionic strength

The variation in current-concentration ratio with pH and ionic strength was checked to determine how closely the procedure should be standardised. It was found that the constant did not change significantly in the pH range 0.45–1.5. However, a two-fold variation in ionic strength caused deviations of 6–7% (relative), the ratio increasing with decreasing ionic strength. Thus, if a standard-addition method was used to determine the fumaric acid, a negative bias was introduced, the magnitude of which depended on the change in ionic strength which occurred upon addition of the aliquot of fumaric acid. For example, if 25 ml of the final solution were analysed and a 2-ml aliquot of fumaric acid stock solution (in water) was added to the cell, the results were consistently low by approximately 1% (relative). For highly accurate work this error was eliminated by standardising the procedure so that the ionic strength of the final solution was always the same, and the ratio was determined in this electrolyte. The accuracy and precision of the method were evaluated by analysing solutions of pure chlorosuccinic acid. The 95% confidence limits of any single determination were found to be $\pm 3.4\%$ (relative). The average of 10 determinations was within 0.2% of the true value.

Interferences

Although no interferences were noted in this research, a number of possible complications can be expected. Polarographically reducible material (inorganic and organic) in the original solution, which is not affected by base, need not cause any significant error even if reducible at the same potential as fumaric acid. The difference in the limiting current before and after dehydrohalogenation can be used to determine the chlorosuccinic acid. The magnitude of this difference will determine the reliability of the determination.

Material sensitive to base may be divided into compounds which are originally reducible and are transformed into other compounds on treatment with base, and compounds which are originally inactive but are transformed to active material under basic conditions. Both chloromaleic and chlorofumaric acids fall in the first category.¹ Chlorofumaric acid may be determined by polarographing at pH 9.5, where chloromaleic acid interference is minimised. Chloromaleic acid is determined at pH 7.2, where the reduction of chlorofumaric is more negative than the supporting electrolyte discharge. Both of these acids are dehydrohalogenated to acetylene dicarboxylic acid, which does not interfere if the pH is much above 3. The final solution is adjusted to pH 5.1 for the analysis of the fumaric acid, and the limiting current is recorded at $-1.30v$ vs. SCE. Dichlorosuccinic acid is not reducible; it is, however, dehydrohalogenated to chlorofumaric acid, and thence

to acetylene dicarboxylic acid. Again the pH of the final solution is adjusted to 5.1 for polarography of the fumaric acid. (Small amounts of chlorofumaric acid which may still be present will not interfere at this pH.)

Acknowledgement—The financial aid of the National Science Foundation in the form of a Undergraduate Research Grant to one of the authors (T. J. B.) is gratefully acknowledged.

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Summary—Chlorosuccinic acid is determined by dehydrohalogenation and polarographic determination of the fumaric acid formed.

Zusammenfassung—Chlorbernsteinsäure wird bestimmt durch Abspaltung von Chlorwasserstoff und polarographische Bestimmung der gebildeten Fumarsäure.

Résumé—On dose l'acide chlorosuccinique par déhydrohalogénéation et dosage polarographique de l'acide fumarique formé.

REFERENCES

- ¹ R. Annino, J. Mahler and L. Alexander, *Polarographic Behavior of Dichloromaleic, Chloromaleic, Mucochloric and Mucobromic Acids*, presented to the Division of Analytical Chemistry, American Chemical Society, Washington, D.C., March 21–24, 1962.
- ² L. R. Duncanson, *J. Chem. Soc.*, 1952, 1753.

Microtitration of plutonium^{III} and hydrogen peroxide present with plutonium^{IV} in hydrochloric acid solutions

(Received 12 November 1963. Accepted 3 April 1964)

A METHOD of estimation of a few tens of micrograms of plutonium^{III} and hydrogen peroxide in hydrochloric acid solutions, also containing similar amounts of plutonium^{IV}, was required for some investigations concerning redox reactions between hydrogen peroxide and plutonium ions. Such solutions are unstable because of (a) the redox reaction of hydrogen peroxide with plutonium^{IV}, and (b) the slow catalytic decomposition of hydrogen peroxide. They are, therefore, not of unique composition but time dependent. Nevertheless, it is possible to evaluate such mixtures because hydrogen peroxide is quantitatively destroyed as soon as an excess of potassium dichromate or of iron^{II} sulphate is added. For this purpose Newton and Baker's method,¹ applicable to milligram quantities in a sulphuric acid medium, has been suitably modified.

In the modified method, two aliquots of the mixture are taken separately in 1.5–2.0 ml of approximately 2.5*M* sulphuric acid. To one portion a sufficient excess of standard 0.005*N* potassium dichromate solution is added by a micropipette to oxidise both the hydrogen peroxide and plutonium^{III}, followed by addition of a known quantity of standard 0.005*N* iron^{II} sulphate solution, also in excess. The solution is titrated against standard 0.005*N* cerium^{IV} sulphate solution delivered from an Agla micrometer syringe burette, using ferroin as internal indicator (20 μ l of approximately 1.2 mM ferroin). This titration gives a measure of the sum of plutonium^{III} and hydrogen peroxide. To the second aliquot the same quantities of dichromate and iron^{II} solutions are added, but in the reverse order, and the titration is completed as before. This gives a measure of the difference between the plutonium^{III} and hydrogen peroxide. From these measurements the concentrations of plutonium^{III} and hydrogen peroxide can easily be calculated. During a titration the solution is stirred either by a stream of nitrogen bubbles or by a suitable magnetic stirrer. The nitrogen stream did not produce any significant difference, indicating that the method is independent of the presence of dissolved air.

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Microestimations carried out by the above method in the presence of a hydrochloric acid content between 0.1 and 0.3 mmole and with known amounts of plutonium^{III} ($1.5\text{--}5.2 \times 10^{-4}$ mmole) have yielded results the error range of which lies between +3.0% and -2.0%, the mean error being +1.4%. The errors obtained in experiments with known amounts of hydrogen peroxide ($0.80\text{--}7.96 \times 10^{-4}$ mmole) lie between +3.8% and -5.5%, the mean error being -0.6%.

Typical results of estimations with mixtures of hydrogen peroxide, plutonium^{III} and plutonium^{IV}, produced by the addition of known amounts of hydrogen peroxide to known amounts of plutonium^{IV} in 2M and 6M hydrochloric acid solutions, are shown in Table 1. The values in columns 3 and 4

TABLE I

HCl, M	Time, min	Pu ^{III} (by present method), mequiv $\times 10^6$	Pu ^{IV} remaining (by difference from total Pu taken), mequiv $\times 10^6$	H ₂ O ₂ remaining (by present method), mequiv $\times 10^6$	Pu ^{III} produced (calculated by difference from data of column 3), mequiv $\times 10^6$	H ₂ O ₂ consumed (calculated by difference from data of column 5), mequiv $\times 10^6$
2	0	Nil	(500.0 ^a)	(375.0 ^b)	—	—
	10	169.8	330.2	203.8	169.8	171.2
	62	351.7	148.3	19.0	181.9	184.8
	166	366.9	133.1	1.0	15.2	18.0
6	0	Nil	(500.0 ^a)	(450.0 ^b)	—	—
	10	251.4	248.6	195.4	251.4	254.6
	0	38.5	(461.5 ^a)	(50.0 ^b)	—	—
	35	67.5	432.5	20.0	29.0	30.0

^a Known amount of Pu^{IV} taken initially.

^b Known amount of H₂O₂ taken initially.

were checked independently by spectrophotometric measurements, showing that the determination of plutonium^{III} by the present method is possible in the presence of both plutonium^{IV} and hydrogen peroxide. The data in columns 6 and 7 seem to show clearly that the equivalent of hydrogen peroxide consumed in each experiment was very close to that of plutonium^{III} formed, as expected, and thereby afford an indirect check on the estimation of hydrogen peroxide. The data in the table show a very slow rate of catalytic decomposition as compared to the reaction rate between hydrogen peroxide and plutonium^{IV}. Concentrations of plutonium^{IV} in up to about a twenty-fold excess over plutonium^{III} can be tolerated. Blank experiments confirming the stability of plutonium^{IV} through the method have been carried out.

In the method described above, dichromate and cerium^{IV} sulphate are used as oxidising agents, while potassium permanganate and dichromate, respectively, were recommended by Newton and Baker. It has been observed in the present work that the use of excess potassium permanganate or cerium^{IV} sulphate as the initial oxidising agent is unsuitable because of the presence of chloride ions, the error being as high as +80% with permanganate and +20% with cerium^{IV} sulphate. While finishing the titration potentiometrically with dichromate, as in the method of Newton and Baker, it has been found that the change in potential towards the end-point is not sharp under our experimental conditions. Further, the use of an internal indicator, *e.g.*, ferroin is more convenient, provided a stronger oxidising agent, *viz.*, potassium permanganate or cerium^{IV} sulphate is used, which when employed for completing the titration does not seem to introduce significant error, even up to a hydrochloric acid content of 0.5 mmole. The effect of larger amounts of hydrochloric acid has not, however, been investigated. The method, as described, is applicable to as low as about $2 \times 10^{-5}M$ plutonium^{III} and $8 \times 10^{-6}M$ hydrogen peroxide in 0.3M hydrochloric acid. At higher hydrochloric acid concentrations the sensitivity may decrease.

Acknowledgement—The authors wish to express their sincere thanks to the Head of the Radiochemistry and Isotope Division for his interest in this work and for helpful suggestions.

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Summary—A method has been developed for the estimation of a few tens of micrograms of plutonium^{III} and hydrogen peroxide in hydrochloric acid solutions containing plutonium^{IV}. The sum of plutonium^{III} and hydrogen peroxide is obtained by successive addition, in excess, of known quantities of potassium dichromate and iron^{II} sulphate to one aliquot of the mixture, then titrating with cerium^{IV} sulphate using ferroin as indicator. Their difference is obtained by adding the same quantities of the first two reagents in reverse order to another aliquot, then completing the titration as before.

Mikrotitration von Plutonium(III) und Wasserstoffperoxyd neben Plutonium(IV) in salzsauren Lösungen.

Zusammenfassung—Eine Methode zur Bestimmung einiger Zehntel Mikrogramm Plutonium(III) und Wasserstoffperoxyd in Plutonium(IV) enthaltenden salzsauren Lösungen wurde entwickelt. Die Summe von Plutonium(III) und Wasserstoffperoxyd erhält man durch aufeinanderfolgende Zugabe bekannter überschüssiger Mengen Kaliumdichromat und Eisen(II)-sulfat zu einem aliquoten Teil der Lösung und nachfolgende Titration mit Cer(IV)-sulfat und Ferroin als Indikator. Die Differenz erhält man durch Zugabe derselben Mengen der beiden ersten Reagentien in umgekehrter Reihenfolge zu einem andern aliquoten Teil der Lösung und Abachluß der Titration wie vorher.

Résumé—On a élaboré une méthode de dosage de quelques dizaines de microgrammes de plutonium (III) et d'eau oxygénée dans des solutions chlorhydriques contenant du plutonium (IV). La somme du plutonium (III) et de l'eau oxygénée est obtenue par addition successive, en excès, de quantités connues de bichromate de potassium et de sulfate de fer (II) à une partie aliquote du mélange, puis titrage au moyen de sulfate de cérium (IV) en présence de ferroïne comme indicateur. Leur différence est obtenue en ajoutant, à une autre partie aliquote, les mêmes quantités des deux premiers réactifs, dans l'ordre inverse, puis en terminant le dosage comme précédemment.

REFERENCE

- ¹ T. W. Newton and F. B. Baker, *J. Phys. Chem.*, 1956, **60**, 1417.

The response of cation-sensitive glass electrodes to alkali metal ions in partially aquated media

(Received 18 January 1964. Accepted 29 February 1964)

IN 1957, Eisenman¹ reported on the properties of cation-sensitive glass electrodes which developed potentials proportional to the logarithm of the univalent cation activity. Improved electrodes of this type are now commercially available.

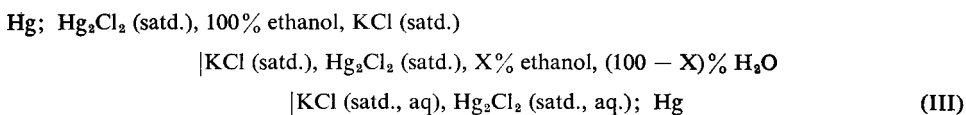
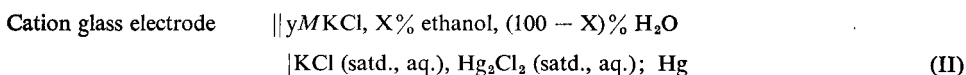
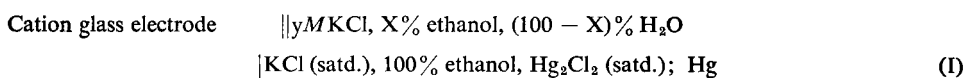
A Beckman Model 76 Expanded Scale pH Meter equipped with a 39137 cation-sensitive glass electrode and a fibre-junction saturated calomel electrode (constrained diffusion junction type) was used to measure the response of the glass electrode to 10^{-1} – $10^{-8}M$ alkali metal chlorides in mixtures of water and ethanol, ethylene glycol, acetone, and *N,N*-dimethylformamide (DMF),² respectively. These represent the amphiprotic (alcohols), aprotic (ketones) and protophilic (DMF) solvent types.³ Protogenic (acids) solvents were not used owing to the response of the cation electrode to the hydrogen ion below pH = 5. Electrodes are preconditioned in the appropriate solvent, containing 0.1M KCl, for approximately 18–24 hr before use, washed with solvent after each measurement, and stored in the conditioning solution between measurements. Stable, reproducible responses to alkali metal ions in 0–90 volume-% of organic solvent were obtained. The slopes of plots of mv vs. $-\log [M^+]$ at 25.0 ± 0.5° are summarised in Table I. Deviations from the predicted⁴ Nernst slope of 55.0 mv at high concentrations of ethanol and acetone can be attributed to ion association and ion pairing.^{5,6} The selectivity order of the cation electrode response in all solvents is found to be $K^+ > Rb^+ > Na^+ > Cs^+ > Li^+$, as would be predicted from theoretical considerations.⁷

TABLE I.—RESPONSE OF CATION-SENSITIVE GLASS ELECTRODES TO ALKALI METAL IONS IN MIXED SOLVENTS. SLOPES OF PLOTS OF mv *vs.* $-\log [M^+]$.

	10	30	50	70	90 volume-%
Ethanol					
KCl	56.0	55.0	55.0	56.0	53.0
KCl*	56.0	55.0	55.0	56.0	53.0
RbCl	56.0	55.0	55.5	56.0	53.0
NaCl	55.5	53.0	55.0	54.0	52.0
Acetone					
KCl	57.0	54.5	55.0	53.0	44.0
KCl†	57.0	54.5	55.0	53.0	44.0
RbCl	55.0	55.0	55.5	50.0	44.0
NaCl	55.0	54.0	54.5	49.0	43.7
Ethylene glycol					
KCl	56.0	57.0	57.0	56.0	56.0
RbCl	57.5	56.0	56.0	55.8	55.7
NaCl	56.0	56.0	55.0	55.0	55.0
					<i>volume %</i>
	8.3	25.0	41.7	58.3	75
DMF					
KCl	52.5	53.3	54.0	51.0	50.0
RbCl	53.5	50.0	55.7	50.0	48.0
NaCl	51.0	51.0	55.0	51.0	52.5

* *vs.* ESCE † *vs.* ASCE

Increasing fractions of organic constituent in the solvent mixture yielded increasing cell e.m.f.'s for any given concentration of solute. This effect may be attributed to changes in the liquid-junction potential at the reference electrode rather than to a change in the response of the cation-sensitive electrode. This view is supported by the work of Zielen,⁸ Uiter⁹ and Bates⁵ on e.m.f. measurements in solutions of strong acids, salts, and buffers in aqueous and partially aqueous media. For experimental confirmation of this hypothesis, the following cells were constructed:



The reference electrode for cell (I), an ethanolic saturated calomel electrode (ESCE) was constructed in a typical "H" cell with a sintered-glass frit providing a constricted diffusion junction. The electrolyte solution was saturated with KCl and Hg₂Cl₂ in absolute ethanol. Preparation of the ESCE is as follows: a dry mixture of Hg₂Cl₂, KCl and Hg is intimately ground together and then placed into the prepared cell. A layer of KCl crystals is deposited on the mixture, and the cell is filled with the electrolyte solution. Contact with the mercury pool is made by means of a platinum wire sealed in soft glass. The cell is then sealed to prevent evaporation of the ethanol. The ESCE was found to be stable and gave reproducible responses in cell (III), where X = 100%, of +36.0 ± 0.5 mv after 8-67 days. An acetone-saturated calomel electrode (ASCE) was constructed in a similar manner, and gave reproducible e.m.f. readings of +30.9 ± 0.5 mv after 3.5 days of aging.

If Ecell (II) - Ecell (I) = Ecell (III), the change in e.m.f. noted upon replacement of water by organic constituents in the solvent mixture cannot have arisen at the glass electrode, but must result

TABLE II.—POTENTIAL MEASUREMENTS WITH NON-AQUEOUS REFERENCE ELECTRODES

	Glass <i>vs.</i> SCE, <i>mV</i>	Glass <i>vs.</i> ESCE, <i>mV</i>	Column 1 - 2, <i>mV</i>	Δ , <i>mV</i>
Ethanol				
10 volume-%			+40.0*	
0.1M KCl	+145	+105	+40.0	0
0.05	128	90	38.0	+2.0
0.025	110	72	38.0	+2.0
0.01	88	52	36.0	+4.0
30 volume-%			+39.5*	
0.1	163	124	39.0	+0.5
0.05	148	107	41.0	-1.5
0.025	130	91	39.0	+0.5
0.01	109	70	39.0	+0.5
50 volume-%			+38.0*	
0.1	185	148	37.0	+1.0
0.05	169	132	37.0	+1.0
0.025	150	117	33.0	+5.0
0.01	130	93	37.0	+1.0
70 volume-%			+37.0*	
0.1	209	173	36.0	+1.0
0.05	190	152	38.0	-1.0
0.025	175	141	34.0	+3.0
0.01	153	117	36.0	+1.0
90 volume-%			+36.5*	
0.1	273	239	34.0	+2.5
0.05	256	223	33.0	+3.5
0.025	240	205	35.0	+1.5
0.01	220	186	34.0	+2.5
Acetone				
		Glass <i>vs.</i> ASCE		
10 volume-%			+24.0†	
0.1	160	138	22.0	+2.0
0.05	142	120	22.0	+2.0
0.025	125	101	24.0	0
0.01	103	81	22.0	+2.0
30 volume-%			+27.0†	
0.1	173	148	25.0	+2.0
0.05	157	130	27.0	0
0.025	140	112	28.0	-1.0
0.01	119	94	25.0	+2.0
50 volume-%			+27.3†	
0.1	194	166	28.0	-0.7
0.05	178	153	25.0	+2.3
0.025	160	133	27.0	+0.3
0.01	139	111	28.0	-0.7
70 volume-%			+28.0†	
0.1	223	196	27.0	+1.0
0.05	209	181	28.0	0
0.025	190	163	27.0	+1.0
0.01	170	140	30.0	-2.0
90 volume-%			+31.0†	
0.1	281	250	31.0	0
0.05	269	239	30.0	+1.0
0.025	254	224	30.0	+1.0
0.01	237	207	30.0	+1.0

* SCE *vs.* ESCE, cell(III) † SCE *vs.* ASCE, cell (III)

from effects involving the reference electrode. The confirmatory experimental results using the appropriate non-aqueous reference electrodes are summarised in Table II for both the ethanol-water and acetone-water mixtures. Table II is constructed in the following manner. Subtraction of column 2 from column 1 gives the values in column 1-2. This is equivalent to $E_{\text{cell}}(\text{II}) - E_{\text{cell}}(\text{I}) = E_{\text{cell}}(\text{III})$ (calculated). The numbers marked with asterisks and quotation marks in column 1-2 are the values of $E_{\text{cell}}(\text{III})$ obtained by direct experimental measurements. Column Δ is obtained by subtracting $E_{\text{cell}}(\text{III})$ calculated values from $E_{\text{cell}}(\text{III})$ experimental values to find apparent differences; according to our theory, $E_{\text{cell}}(\text{III})$ calculated should equal $E_{\text{cell}}(\text{III})$ experimental. The values of column Δ fall well within the range of experimental error using the high-resistance glass electrodes, and confirm our prediction. The average deviations of ΔmV are +1.05 and +0.66 mV for the ethanol-water and acetone-water systems, respectively. The average deviation of the mean of ΔmV is +0.24 mV for the ethanol-water mixtures and +0.15 mV for the acetone-water mixtures. Furthermore, using a knowledge of degenerate activity coefficients for single ions, Gutbezahl and Grunwald¹⁰ have calculated liquid-junction potentials (E_L) for the hydrogen electrode *vs.* SCE (aqueous) of various acids in ethanol-water solvents, and have obtained E_L 's that are dependent only on solvent compositions. These results agree well with ours for systems containing up to 87 weight-% of ethanol. Thus, the effects caused by changes in activity coefficients of salt solutions with changes in solvent composition (replacement of water with organic solvent) are small compared to the change in liquid-junction potential and may be neglected.

We conclude, therefore, that the response of the cation-sensitive glass electrode is essentially solvent-independent, but depends on the nature and concentration of the solute. The results also suggest that such electrodes might be useful as reference electrodes in solvent mixtures containing substantial concentrations of alkali metal cations.

Acknowledgement—The financial aid of NIH grant GM-10086 is gratefully acknowledged.

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Summary—The response of cation-sensitive glass electrodes to alkali metal ions in ethanol-water and acetone-water mixtures has been evaluated. The increase in measured potential when water is replaced with organic solvent is proved result from the changing liquid-junction potential of the reference electrode. The response of the glass electrode is essentially solvent-independent for a given concentration and type of solute.

Zusammenfassung—Das Ansprechen der Kationenempfindliche Glaselektroden auf Alkalimetallionen in Äthanol-Wasser- und Aceton-Wasser-Gemischen wurde gemessen. Es wird gezeigt, daß das Ansteigen des gemessenen Potentials bei Ersatz von Wasser durch organisches Lösungsmittel auf der Änderung des Diffusionspotentials in der Brücke zur Referenzelektrode beruht. Die Empfindlichkeit Glaselektrode ist bei gegebener Konzentration und Art des gelösten Stoffes im wesentlichen vom Lösungsmittel unabhängig.

Résumé—On a évalué la réponse de ces électrodes aux ions métalliques alcalins dans des mélanges éthanol-eau et acétone-eau. On a démontré que l'accroissement du potentiel mesuré que l'on observe lorsqu'on remplace l'eau par un solvant organique, est dû à la variation de potentiel du liquide de jonction de l'électrode de référence. La réponse de l'électrode de verre est essentiellement indépendante du solvant, pour une concentration et un type de soluté donnés.

REFERENCES

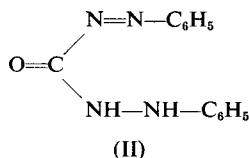
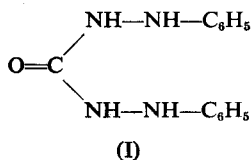
- ¹ G. A. Rechnitz, S. A. Katz and S. B. Zamochnick, *Analyt. Chem.*, 1963, **35**, 1322.
- ² J. Allen and E. T. Geddes, *J. Pharm. Pharmacol.*, 1957, **9**, 990.
- ³ G. Mattock and G. R. Taylor, *pH Measurement and Titration*. Heywood, London, 1961, pp. 336-58.

- ⁴ Beckman Instruments, Inc., Fullerton, California, Instructions 1154-A (1962).
⁵ R. G. Bates *et al.*, *J. Phys. Chem.*, 1963, **67**, 1833.
⁶ H. S. Harned and B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, 3rd. ed. Reinhold, New York, 1958, pp. 283–327.
⁷ G. Eisenman, *Biophysical J.*, 1962, **2**, Part 2 (supplement), 259.
⁸ A. J. Zielen, *J. Phys. Chem.*, 1963, **67**, 1474.
⁹ L. G. Van Uitert and C. G. Hass, *J. Amer. Chem. Soc.*, 1953, **75**, 451.
¹⁰ B. G. Gutbezahl and E. Grunwald, *ibid.*, 1953, **75**, 565.

Separation of commercial diphenylcarbazone into its components

(Received 11 February 1964. Accepted 25 March 1964)

KRUMHOLZ and Krumholz verified in 1937 that "diphenylcarbazone" (1,5-diphenylcarbohydrazone), m.p. 157°, was probably an intermolecular compound of diphenylcarbazide (I) and pure diphenylcarbazone, m.p. 127° (II), which they succeeded in separating by batch extraction of alkaline solutions of the product with ethyl ether.¹ Diphenylcarbazone, being acidic, remains in solution in its anionic form, whereas diphenylcarbazide, which is not acidic, is carried into the organic solvent.



However, the commercial AnalaR grade product available nowadays is still the substance melting at 157° and catalogues do not list the existence of a different form.

In an attempt to confirm Krumholz's results we have found that commercial diphenylcarbazone could be separated into its components by thin-layer chromatography. The support used was a layer of Merck Silica-gel GF₂₅₄, and the eluent was a mixture of chloroform (75%) and acetone (25%). In recently-coated plates, pure diphenylcarbazone showed up as a red spot ($R_f \approx 0.75$) and diphenylcarbazide as a purple one ($R_f \approx 0.20$) after spraying with a dilute acid solution of potassium chromate. The time of elution was 15–20 min. This confirms the findings of the previous workers, but this method is not very suitable for preparing substantial amounts of the reagent. We have therefore adapted Krumholz's procedure to a continuous liquid-liquid extraction technique which gave excellent results.

An extractor similar to that used by Ashley and Murray for the extraction of FeCl₃ with ether² appeared to be best suited for the purpose and the procedure was as follows. One g of commercial diphenylcarbazone (m.p. 157°) was dissolved in 100 ml of 5% NaOH containing a few mg of KCN. The solution was transferred to the extractor, and the necessary volume of ethyl ether was added to fill the extractor up to the level of its horizontal arm. The Erlenmeyer flask containing about 100 ml of ethyl ether was connected, and the solvent was refluxed for about 36 hr.

Diphenylcarbazide was carried into the Erlenmeyer flask, where it crystallised in long colourless needles, m.p. 172–3°. The basic aqueous solution was then taken out of the extractor, filtered through a sintered-glass filter-funnel, and acidified with dilute H₂SO₄. A precipitate formed, and the suspension was allowed to settle for 1 hr when the solid was collected and dissolved in the minimum amount of hot ethanol. Twice its volume of de-ionised water was added with stirring, and the solution was allowed to crystallise. Deep orange crystals of pure diphenylcarbazone were obtained in small needles, m.p. 126–7° (rapid heating). The yield for the first crystallisation was 120 mg (~24%).

Pure diphenylcarbazone is easily soluble in ethanol, chloroform and methylene dichloride up to concentrations of the order of 10⁻³M; it is also soluble, but not so easily, in ether, benzene and carbon tetrachloride, among the more usual solvents.

For solutions in carbon tetrachloride, the following absorption maxima and respective molar extinction coefficients were observed:

λ_{max}	ϵ_{max}
290 m μ	12,750
466 m μ	3,300
563 m μ	800

The samples we obtained using Krumholz's technique were more reddish in colour and had lower values of ϵ_{max} than those prepared by the method now described. Balt and van Dalen,³ who recently started a systematic study of the metal complexes of diphenylcarbazone, and purified their reagent according to the previous authors, reported values for ϵ_{max} close to ours but not quite so high.

Spectra, and more detailed observations, will be published elsewhere.⁴

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Summary—Confirming results of previous workers, it is shown that commercial AnalaR diphenylcarbazone can be separated into its components (diphenylcarbazide and pure diphenylcarbazone) by thin-layer chromatography or continuous liquid-liquid extraction, the latter method being preferred for preparative purposes. Some physical properties of pure diphenylcarbazone are reported.

Zusammenfassung—In Übereinstimmung mit Ergebnissen früherer Forscher wird gezeigt, daß handelsübliches analysenreines Diphenylcarbazon durch Dünnschichtchromatographie oder kontinuierliche flüssig-flüssig-Extraktion in seine Komponenten Diphenylcarbazid und reines Diphenylcarbazon aufgetrennt werden kann. Die zweite Methode ist für präparative Zwecke vorzuziehen. Einige physikalische Eigenschaften des reinen Diphenylcarbazons werden angegeben.

Résumé—On confirme des résultats d'autres chercheurs en montrant que la diphénylcarbazone p.a. commerciale peut être séparée dans ses composants (diphénylcarbazide et diphénylcarbazone pure) par chromatographie sur couche mince et par extraction liquide-liquide continue, cette dernière méthode étant préférée pour sa préparation. On indique quelques propriétés physiques de la diphénylcarbazone purifiée.

REFERENCES

- ¹ P. Krumholz and E. Krumholz, *Monatsh.*, 1937, **70**, 431.
- ² S. E. Ashley and W. M. Murray, *Ind. Eng. Chem. Analyt.*, 1938, **10**, 367.
- ³ S. Balt and E. Van Dalen, *Analyt. Chim. Acta*, 1962, **27**, 188.
- ⁴ J. J. R. F. da Silva, J. C. G. Calado and M. L. Moura, *Revista Portuguesa de Química*, to be published.

LETTER TO THE EDITOR

The determination of phosphate in the presence of calcium by the molybdovanadate method

SIR,

THE method of Bridger *et al.*,¹ incorporating the methods of Maksimova *et al.*² and Misson,³ *i.e.*, the molybdovanadate colorimetric method for the determination of phosphorus, has been applied to the determination of orthophosphate in the presence of calcium.

It has been found that grossly unreliable results are obtained when the phosphate (P_2O_5):calcium (Ca) ratio exceeds 1:10,000. Temperature effects are quite noticeable, in that if the determination is carried out at temperatures in excess of 22° the results are erratic, being approximately double the expected level. The most reliable temperature for carrying out the determination is below 14°, but even at this temperature poor results are obtained if the phosphate:calcium ratio is greater than 1:20,000. The position is not improved if the extraction finish, as described by Elwell *et al.*,⁴ and by Booth *et al.*,⁵ is used.

The quinoline molybdophosphate method of Wilson⁶ gives satisfactory results down to a phosphate:calcium ratio of 1:50,000. The "molybdenum blue" method of Berenblum *et al.*,⁷ gives satisfactory results down to a phosphate:calcium ratio of 1:200,000, provided that the determination is carried out in the temperature range 18°–24°.

Acknowledgements—The writer thanks the Directors of John & E. Sturge Limited, for permission to publish this letter.

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9 April 1964

REFERENCES

- ¹ G. L. Bridger, D. R. Boylan and J. W. Markey, *Analyt. Chem.*, 1953, **25**, 336.
- ² N. V. Maksimova and M. T. Kolovsky, *J. Analyt. Chem., U.S.S.R.*, 1947, **2**, 353.
- ³ G. Misson, *Chem.-Zig.*, 1908, **32**, 633.
- ⁴ W. T. Elwell and H. N. Wilson, *Analyst*, 1956, **81**, 136.
- ⁵ E. Booth and A. Parker, A.E.R.E., Report AM4, 1959.
- ⁶ H. N. Wilson, *Analyst*, 1954, **79**, 735.
- ⁷ I. Berenblum and E. Chain, *Biochem. J.*, 1938, **32**, 286.

NOTICES

(Material for this section should be sent directly to the Associate Editor)

Guides to Guides to Scientific Literature

About 40% of the references to Scientific literature are obtained from abstracting and indexing periodicals. There are now about 2,000 of these. Two useful guides to abstracting and indexing publications exist. They are

A Guide to the World's Abstracting and Indexing Services in Science and Technology: National Federation of Science Abstracting and Indexing Services, Washington, D.C., 1963 (\$5.00)
obtainable from:

National Federation of Science Abstracting and Indexing Services, 324 East Capitol Street, Washington, 3 D.C., U.S.A.

and

Index Bibliographies, 4th Edition, Vol. 1: *Science and Technology*: Federation Internationale de Documentation, The Hague, 1959

obtainable from:

Federation Internationale de Documentation,
6 Willem Witsenplein, The Hague, Netherlands.

BUNDESREPUBLIK DEUTSCHLAND

6. Juni bis 2 Juli 1964: **Deutschsprachige Spektrometer-Tagung**: Frankfurt/Main.

Die Fachgruppe "Analytische" der Gesellschaft Deutscher Chemiker, der Deutsche Arbeitskreis für Spektroskopie, die Arbeitsgruppe Massenspektrometrie der Deutschen Physikalischen Gesellschaft und die Chemikerausschüsse der Gesellschaft Deutscher Metallhütten- und Bergleute, des Steinkohlenbergbauvereins und des Vereins Deutscher Eisenhüttenleute veranstalten gemeinsam eine Tagung über "Moderne Methoden der anorganischen Analyse". Diese Tagung soll vom 5. - 7. Oktober 1964 in Düsseldorf stattfinden.

Es sind folgende Hauptthemen für die Tagung vorgesehen:

1. Nichtmetalle in Metallen.
2. Analyse von Verbindungsformen und ihre Verteilung im festen Zustand
3. Probenahme
4. Erfassen und Verwerten analytischen Zahlenmaterials.

Zu diesen Themen werden Hauptvorträge von folgenden Kollegen gehalten:

Prof. Dr. J. FISCHER, Frankfurt (Gruppe 1)

Prof. Dr. W. KOCH, Duisburg (Gruppe 2)

Dr. ZETTLER, Hamburg, und

Dipl.-Ing. SPORBECK, Essen (Gruppe 3)

N.N. Gruppe 4)

FRANCE

La Commission Internationale d'Essais "C.I.E." du COMITE INTERNATIONAL DE LA DETERGENCE (C.I.D.) a tenu, sous la présidence du Dr. GÖTTE (Allemagne), sa session annuelle les 23 et 24 Mars 1964 à Düsseldorf, sur aimable invitation du Deutscher Ausschuss für Grenzflächenaktive Stoffe.

C'est la 7ème fois que les pays membres de cette Commission sont appelés ainsi à se réunir depuis sa fondation, et 10 pays ont répondu à cette invitation: Allemagne, Autriche, Belgique, Espagne, France, Italie, Pays-Bas, Portugal, Royaume Uni et Suisse. L'INTERNATIONAL ORGANIZATION FOR STANDARDIZATION "I.S.O.", qui suit tous les travaux du C.I.D., avait délégué un de ses collaborateurs.

Les travaux de la C.I.E. étant considérés comme suffisamment avancés sur un certain nombre de sujets, il a été décidé que 5 projets de normes pouvaient être adoptés définitivement et seraient

présentés dans le courant de l'année au Comité Technique ISO/TC-91 "Agents de Surface" pour homologation sur le plan international. Il s'agit des normes suivantes:

Stabilité des agents de surface à l'eau dure,

Eau distillée (conditions requises pour essais physicochimiques relatifs aux agents de surface),

Eau dure (définition et propriétés),

Masse volumique apparente des pâtes,

Point de trouble des agents de surface non-ioniques selon la méthode au butyldiglycol.

Le nombre des travaux soumis à l'ISO/TC-91 par la C.I.E. se trouvera ainsi porté à 9.

Par ailleurs, les membres de la C.I.E. effectueront des essais inter-laboratoires dans leurs pays, pour améliorer ou vérifier certaines études actuellement au stade expérimental:

Solubilité des agents de surface,

Pouvoir protecteur vis-à-vis des savons calcaires, en utilisant un savon préparé à l'avance,

Tension superficielle selon une méthode dite "de la bulle par pression", pour laquelle un appareil nouveau a été mis au point en Allemagne. Les mesures seront comparées à celles du pouvoir mouillant sur coton.

Viscosité des agents de surface sur appareils Roto-Visco et Rhéomat,

Stabilité des solutions d'agents de surface, en utilisant la chromatographie par couche mince,

Mesure de la couleur par comparaison de différentes échelles colorimétriques,

Contrôle du lessivage à l'aide de bandes-témoins non souillées; un groupe de travail a été spécialement créé à cet effet et fait appel au concours de techniciens du lavage.

Enfin, un travail bibliographique et documentaire sera entrepris pour différentes questions nécessitant encore de longues études, telles que les pouvoirs détergent, dispersant, émulsionnant et la stabilité des émulsions, la concentration critique de micelles, l'action des oxydants et leur influence sur les taches, la préparation des détergents en pastille, le dish washing test et la tension d'adhésion.

Ce programme de travail est important et nécessite, de la part des laboratoires, de longues et patientes recherches mais leurs efforts s'avèrent, de par les résultats déjà obtenus, particulièrement fructueux et appréciés sur le plan international.

Rappelons que le but de la Commission Internationale d'Essais est de mettre au point des méthodes d'essais facilement reproductibles et utilisables de par le monde. C'est pourquoi elles sont établies selon un schéma uniformisé et recommandent des appareillages connus de tous les techniciens.

La prochaine session de la C.I.E. aura lieu en Mars 1965, sur invitation du British National Committee on Surface Active Agents, et elle se déroulera à Londres.

UNITED KINGDOM

Thursday-Saturday 2-4 July 1964: Symposium on Pollution: Society for Analytical Chemistry, Western Section: University College, Singleton Park, Swansea.

The programme is as follows:

Thursday, 2 July: Morning

Opening Address—Environmental pollution.

D. T. LEWIS

The effects on industry of recent legislation on the discharge of trade effluent.

A. I. BIGGS

Thursday, 2 July: Afternoon

Water pollution with respect to sewage.

S. H. JENKINS

Water pollution of all kinds.

L. KLEIN

Friday, 3 July: Morning

Atmospheric pollution.

S. G. BURGESS

Effects of pollution on vegetation.

J. WEBBER

Friday, 3 July: Afternoon

Lecture and visit to the Lower Swansea Valley Project.

Saturday, 4 July: Morning

Biological effects of pollution.

R. D. BRINKHURST

Tidal pollution.

P. N. J. CHIPPERFIELD

Further information may be obtained from Dr. T. G. MORRIS, Brockleigh, Clevedon Avenue, Sully, Glamorgan.

Thursday-Friday 2-3 July 1964: Summer Meeting on Limitations of Detection in Spectrochemical Analysis: Institute of Physics and Physical Society, Spectroscopic Group: University of Exeter (see Talanta, 1964, 11, April, vi).

Sunday-Saturday 19-25 July 1964: Third International Congress for Polarography: Polarographic Society: University of Southampton.

Tuesday 28 July 1964: Lecture by W. KEMULA: Society for Analytical Chemistry and Polarographic Society: Burlington House, London W.1.

British Standards Institution has announced the following *New British Standard*:

B.S. 1728: Methods for the analysis of aluminium and aluminium alloys: Part 13: 1964: Method for the determination of titanium in aluminium and aluminium alloys (absorptiometric chromotropic acid method). This specifies reagents required, recommended methods of sampling and analytical procedure for the determination of titanium in alloys having a titanium content between 0.005 and 0.3%. (Price 4s.)

The following *Amendment Slip* has also been announced:

B.S. 1016: Methods for the analysis and testing of coal and coke: Part 1: 1957: Total moisture of coal. Amendment No. 1: PD 5146.

UNITED STATES OF AMERICA

Tuesday–Thursday 6–8 October 1964: Eighth Conference on Analytical Chemistry in Nuclear Technology: Analytical Chemistry Division of Oak Ridge National Laboratory: Mountain View Hotel, Gatlinburg, Tennessee.

The subject will be **Determination of Interstitials and Trace Constituents in Reactor Materials and Products**. The Conference will be composed of six sessions embracing the following subtitles:

1. *Spectrochemical and X-ray Methods of Analysis.*
2. *Mass Spectrometric Methods of Analysis.*
3. *Nuclear Methods of Analysis.*
4. *Gas Chromatographic Methods of Analysis.*
5. *Determination of Carbon, Hydrogen, Oxygen and Nitrogen in Metals.*
6. *Determination of Trace Constituents by Diverse Methods.*

Participation in the Conference will be on the basis of invited contributions. However, a limited number of papers, up to 25 min in length, are solicited and will be accepted provided the subject matter of such contributions fits in with the over-all objectives of the Conference and meets with the approval of the Programme Committee.

Those who wish to make contributions are requested to submit an abstract of 200–500 words not later than 10 July, giving the name of the intended speaker and the amount of time that will be required for the presentation. Abstracts of papers and any enquiries concerning the Conference should be directed to C. D. SUSANO, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tennessee.

Monday–Thursday 19–22 October 1964: 78th Annual Meeting of Association of Official Agricultural Chemists: Marriott Motor Hotel, Twin Bridges, Washington D.C. 20044.

The programme will have almost 300 scientific papers on analysis of foods, drugs, cosmetics, food and colour additives, beverages, pesticides, extraneous materials in foods and drugs, fertilisers, feeds, and many other commodities important to agriculture and public health. In addition, six outstanding European scientists will present key addresses to general sessions on such topics as drugs, pesticides, food laws, chromatography detectors, food additives and fish composition. The six invited speakers are: J. A. LOVERN (Scotland); J. F. REITH (Netherlands); D. C. GARRATT, A. T. JAMES (England); H. CHEFTEL (France) and FINN BRO-RASMUSSEN (Denmark). Dr. D. T. LEWIS, Head, Laboratory of the Government Chemist, England, will keynote the Monday evening banquet with his address, *The Changing Environment of Mankind*. Another feature of the banquet will be honoring the winner of the Harvey W. Wiley Award for notable contributions to analytical methodology.

The meeting will include about 30 exhibits of the latest equipment and supplies for analytical chemists. Other information is available from LUTHER G. ENSMINGER, Association of Official Agricultural Chemists, Box 540, Benjamin Franklin Station, Washington, D.C. 20044, U.S.A.

The **ORNL Master Analysis Manual** is a collection of the analytical methods developed and used in the Analytical Chemistry Division of Oak Ridge National Laboratory. The manual was begun in 1963, but includes methods used earlier. In 1957, the Office of Technical Services of the U.S. Department of Commerce reprinted the unclassified sections of the manual for public sale and since then has issued annual supplements that contain reprints of new or revised methods. These reprinted parts are designated TID-7015.

The Oak Ridge National Laboratory has now published a paperbound volume which consists of a key word index composed from method titles, a bibliographic index that is equivalent to a table of contents for the manual, an author index, and method-number cross indexes. The bibliographic index gives the complete history and current status of every method. The titles entered in this publication are those of all unclassified methods included in the manual from 1953 through 1962.

The indexes will be brought up-to-date annually. This publication, TID-7015 (Indexes), is available from the U.S. Department of Commerce, Office of Technical Services, Washington, D.C. 20230 (\$2.50).

The publication of **Nuclear Magnetic Resonance Abstracts** has been announced. This is intended to include the total world literature on all aspects of nuclear magnetic resonance; theoretical and applied papers in both high resolution and broad line areas, techniques, apparatus, *etc.*, will be covered. The abstracts will be in English. Further information is available from Preston Technical Abstracts Co., 1718 Sherman Avenue, Evanston, Ill. 60201.

The American Society for Testing and Materials has announced the publication of *Report on Available Standard Samples, Reference Samples, and High-Purity Materials for Spectrochemical Analysis* (1963); STP 58-E. This provides an up-to-date reference to the availability and sources of 5050 samples and materials. The introduction presents the scope and form of the report and a discussion of definitions and nomenclature.

The following parts of the 1964 *Book of ASTM Standards* are now available: *Part 30: General Testing Methods; Quality Control; Appearance Tests; Temperature Measurements; Effects of Temperature* (Price \$11.00; \$7.70 to ASTM members).

Part 31: Metallurgy; Nondestructive Testing; Radioisotopes and Radiation Effects; Industrial Chemicals; Emission, Absorption and Mass Spectrometry (Price \$12.00; \$8.40 to ASTM members).

Part 32: Chemical Analysis of Metals (Price \$14.00; \$9.80 to ASTM members).

PAPERS RECEIVED

- Direct titrimetric determination of iron with disodium cyclohexanediamine tetra-acetate:** L. W. MARPLE. (2 April 1964).
- Extraction and spectrophotometric determination of microamounts of aluminium, chromium, copper, iron, manganese, molybdenum and nickel in pure water: Use of 8-hydroxyquinoline and dimethylglyoxime as reagents:** KENJI MOTOJIMA and NASUMI ISHIWATARI. (3 April 1964).
- Determination of scandium, yttrium, samarium and lanthanum in standard silicate rocks G-1 and W-1 by neutron-activation analysis:** H. B. DESAI, R. KRISHNAMOORTHY IYER and M. SANKAR DAS. (9 April 1964).
- The determination of phosphate in the presence of calcium by the vanadomolybdate method:** M. L. RICHARDSON. (9 April 1964).
- Successive determination of thorium and rare earths by complexometric titrations:** ASIM K. GUPTA and JACK E. POWELL. (10 April 1964).
- Ammonium hexanitratocerate(IV) as an oxidising agent-IV: Titration of hydrazine and isonicotinic acid hydrazide at room temperature:** G. GOPALA RAO and P. V. KRISHNA RAO. (13 April 1964).
- A study of the oxidation of manganese(II) and chromium(III) ions by silver(II) oxide:** C. P. LLOYD and W. F. PICKERING. (14 April 1964).
- Some problems in the analysis of gaseous decomposition products:** PAUZ D. GARN. (15 April 1964).
- Miniature magnetic stirring motor for student or analytical-control laboratories:** G. FREDERICK SMITH and A. H. SMITH. (17 April 1964).
- Ultraviolet spectra of piaseleol derivatives:** MASAKO TOTO and KYOJI TOEI. (17 April 1964).
- Mesityl oxide as an extracting agent:** S. M. KHOPKAR. (21 April 1964).
- Spectrophotometric determination of small amounts of tellurium with diphenylthiourea:** H. YOSHIDA and S. HIKIME. (22 April 1964).
- An examination of the atomic absorption spectroscopy of silver:** R. BELCHER, R. M. DAGNALL and T. S. WEST. (22 April 1964).
- Systematic titration errors I: General considerations and neutralisation titrations:** U. A. TH. BRINKMAN. (24 April 1964).
- Rapid iodometric determination of copper in alloys with tin, antimony and other metals:** J. AGTERDENBOS. (28 April 1964).
- The preparation of ceric hydroxide from ammonium hexa-nitratocerate (IV) by employing kinetically controlled precipitation through urea dissociation:** G. FREDERICK SMITH. (28 April 1964).
- Separation of bismuth from lead, copper and other elements by means of anion exchange:** F. FEIK and J. KORKISCH. (30 April 1964).
- A Spectrophotometric study of the complexes formed between uranyl and oxalate ions in water and water-dioxan solvents:** CARZ L. GRIFFIS, NIRMAL K. SHASTRI and EDWARD S. AMIS. (1 May 1964).
- A thermogravimetric pyrolysis study of the interaction of di(1,2,3-benzotriazolium) hexacyanoosamat (IV) with certain organic amines:** RAY F. WILSON and PHILLIP MERCHANT, JR. (5 May 1964).
- Extraction and spectrophotometric determination of rhenium(VIII) with 2-thenoyltrifluoroacetone:** ANIL K. DE and M. SYEDUR RAHAMAN. (6 May 1964).
- Use of masking agents in chelatometric titrations-IV: Dimercaptosuccinic acid:** TÔRU MEKADA, KÔICHI YAMAGUCHI and KEIHEI UENO. (6 May 1964).



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