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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 27, No.3, September 1962

THEORETICAL INVESTIGATION OF LOW LIQUID LOAD AND LOW TEMPERATURE OPERATION IN GAS CHROMATOGRAPHY

The change in resolution resulting from the simultaneous reduction of liquid load and temperature is theoretically treated. The effects of decreases in load and temperature are formulated in terms of a standard reduction (in which the zone to gas velocity ratio is constant) plus any small changes in temperature required to match the observed changes in zone velocity. Taking the standard reduction as the norm, it is found that both the thermodynamic (relative peak elution times) and rate (peak spreading) effects favor the liquid load and temperature decreases. This is discussed specifically in relationship to diatomaceous earth and glass beads as the solid support and also to capillary columns.

J. C. Giddings, *Anal. Chim. Acta*, 27 (1962) 207–212

THE SEPARATION OF HEXACHLOROCYCLOHEXANE ISOMERS BY VAPOUR PHASE CHROMATOGRAPHY

(in French)

Hexachlorocyclohexane isomers can be separated by a glass bead technique with polypropylene glycol Niax 1025 as the stationary phase. The principal isomers separated are the γ-hexachlorocyclohexane (Lindane isomer), the α, β, ε, and δ isomers and γ-heptachlorocyclohexane. The life of the glass bead column is short — about 20 days in constant use. A longer column life can be obtained by pretreatment of the glass beads.

C. L. Guillemin, *Anal. Chim. Acta*, 27 (1962) 213–218

IDENTIFICATION OF NITRILES IN PETROLEUM PRODUCTS. COMPLEX FORMATION AS A METHOD OF ISOLATION

Nitrogen compounds were completely removed from a hydrogenated furnace oil by shaking with a mixture of ferric chloride and zinc chloride. The resulting complexes were separated from the oil and thermally decomposed to liberate the nitrogen compounds. After removal of nitrogen bases with hydrochloric acid and indoles, carbazoles, and phenazines with perchloric acid, the nitrogen compounds remaining in the concentrate were separated by fractional elution from an aluminum oxide column and gas chromatography. The following compounds were identified or their presence was indicated in the resulting fractions by their ultraviolet and/or mass spectra: dicyanobenzene, dicyanobenzene, dicyanocyclohexane, cyanoindene, cyano-2,3-dihydroindene, cyanonaphthalene, dicyanoindene, dicyano-2,3-dihydroindene, dicyanonaphthalene, cyanobiphenyl, dicyano-octahydronaphthalene, and/or several of their alkyl derivatives.

G. K. Hartung and D. M. Jewell, *Anal. Chim. Acta*, 27 (1962) 219–232

PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF MAGNESIUM IN ROCKS

The method of Mann and Yoe has been adapted to the determination of small amounts of magnesium in a "rapid method" scheme of rock analysis. The effect of calcium is found to be different from that described by the original authors. Triethanolamine is introduced as a masking agent for aluminum. Anomalous instability of the color system requires a revised photometric technique.

S. Abbey and J. A. Maxwell, *Anal. Chim. Acta*, 27 (1962) 233–240

SPECTROPHOTOMETRIC DETERMINATION OF SCANDIUM WITH 4-(2-PYRIDYLAZO)RESORCINOL

(in German)

4-(2-Pyridylazo)resorcinol (PAR) forms 2 red chelates with scandium in aqueous solution at pH $\geqslant$ 2 or 5: $ScRH^{2+}$ and ScR_2^-. The former can be used to determine 0.05–2.4 μg Sc/ml at pH 3.5–4.5 with $\mu = 0.4$; measurement is done at 530 mμ. Many ions interfere and separation is necessary.

L. Sommer and M. Hniličková *Anal. Chim. Acta*, 27 (1962) 241–247

COUNTERCURRENT EXTRACTION SEPARATION OF SOME PLATINUM GROUP METALS. PART II

Binary mixtures of Pt and Rh, Pt and Ir, Pd and Rh, and Pd and Ir were resolved by a countercurrent extraction technique. The metals were partitioned between an acidic aqueous phase containing potassium thiocyanate and an organic phase, *n*-tributylphosphate. Distribution coefficients were determined for each metal for a thiocyanate: metal mole ratio of 10 : 1 and 200 : 1 at pH values of 1, 2, 3, and 3.8. Optimum conditions for separations were determined to be a thiocyanate: metal mole ratio of 10 : 1 and a pH of 1. Under these conditions the K_d values for Pd, Pt, Rh and Ir were 139, 62.3, 0.19 and 0.09 resp. Effective separations were achieved with each binary mixture on a Craig extraction apparatus utilizing less than 10 equilibrium stages. There was a 95% average recovery of each of the metals.

E. W. Berg and E. Y. Lau, *Anal. Chim. Acta*, 27 (1962) 248–252

SOME THEORETICAL CONSIDERATIONS IN ANALYTICAL CHEMISTRY

VII. THE INFLUENCE OF ABSOLUTE CONCENTRATION ON THE PARAMETERS OF REDOX TITRIMETRY

Redox reactions are classified into symmetrical, homogeneous and inhomogeneous reactions. Reaction deficiencies when expressed as concentrations are dependent on absolute reactant concentrations, but have been proved to be independent of dilution when expressed as ratios in symmetrical and homogeneous reactions. An expression relating change of reaction deficiency with dilution for inhomogeneous reactions has been derived; dilution of the reactants very rapidly decreases the reaction deficiency.

Expressions for potentials in terms of concentration ratios have been derived for homogeneous and symmetrical reactions and prove to be independent of dilution. For inhomogeneous reactions the absolute potential falls on dilution, although the relative potential change, *e.g.*, from the midpoint of a titration, increases asymptotically to a maximum.

New derivations of the equivalence point potential and of an expression for the quantitativeness, for symmetrical and homogeneous reactions, confirm the classical expressions and demonstrate their independence of dilution. For inhomogeneous reactions, methods of calculation of quantitativeness and equivalence point potentials through reaction deficiencies are proposed. For such reactions, the equivalence point potential rises sharply with dilution, giving titration curves of increasing steepness. The dependence of midpoint potentials and relative change of potential during titration upon dilution are also examined.

E. Bishop, *Anal. Chim. Acta*, 27 (1962) 253–261

A STUDY OF SOME FACTORS WHICH AFFECT THE ADSORPTION OF TITAN YELLOW ON MAGNESIUM HYDROXIDE

A study is made of factors which influence the adsorption of Titan yellow on magnesium hydroxide. Variation in composition of different dye samples is investigated and the photochemical decomposition of the dyestuff studied. Polyvinyl alcohol is the best of the colloid protectors examined. The effects of phosphate, calcium, aluminium, iron and manganese on the reaction depend on the protective colloid system employed and the relative concentrations of interfering element and magnesium present.

E. G. BRADFIELD, *Anal. Chim. Acta*, 27 (1962) 262–271

DETERMINATION OF TRACES OF HYDROGEN IN FLUORO-ORGANIC COMPOUNDS

The determination of traces of hydrogen in highly fluorinated compounds has been studied. Nitrogen and sulphur in the sample interfere slightly in the pyrolytic method of MILLER *et al.* A straightforward combustion method is proposed in which the sample is burned in oxygen over magnesium oxide at 900° and the water formed is determined either gravimetrically or titrimetrically.

R. BELCHER, M. K. BHATTY, A. M. G. MACDONALD, S. A. SALAM AND J. C. TATLOW, *Anal. Chim. Acta*, 27 (1962) 271–277

THE DETERMINATION OF MICROGRAM QUANTITIES OF SULPHIDE IN BIOLOGICAL MATERIALS

Several methods for the estimation of microgram quantities of sulphide in biological material and enzymatic reaction mixtures were investigated. The optimum conditions for separation of sulphide by isothermal distillation are given. The formation of methylene blue is recommended for the spectrophotometric determination of sulphide; modifications are described to improve the reliability and sensitivity of the method.

S. S. PATEL AND C. P. SPENCER, *Anal. Chim. Acta*, 27 (1962) 278–282

MICROANALYSIS WITH THE AID OF ION EXCHANGE RESINS

PART XX. DETECTION OF NANOGRAM AMOUNTS OF TITANIUM(IV) WITH TIRON

A sensitive test for nanogram quantities of titanium(IV) is proposed. A resin spot test technique is applied to the colour reaction of titanium(IV) with tiron. The limit of identification is 26 ng of titanium(IV) ($1:1.5 \cdot 10^6$) after 50 min standing. Vanadium(V), chromium(VI), molybdenum(VI) and uranium(VI) interfered seriously. Iron(III) could be masked with EDTA, and iron(III) and titanium(IV) were detected simultaneously.

MASATOSHI FUJIMOTO AND YUKIO NAKATSUKASA, *Anal. Chim. Acta*, 27 (1962) 283–287

o-DIAMINES AS REAGENTS FOR SELENIUM

PART I. 4-DIMETHYLAMINO-1,2-PHENYLENEDIAMINE

4-Dimethylamino-1,2-phenylenediamine is investigated as a photometric and qualitative reagent for selenium. With this reagent selenium(IV) forms 5-dimethylamino-2,1,3-benzoselenadiazole, a red colored compound, with an absorption maximum in the visible region at 500 mμ. Variables such as reagent stability, extinction stability, reaction rate, influence of acidity, foreign ions, validity of Beer's law are discussed. The reagent is highly selective for selenium, has good sensitivity and reproducibility, and is also useful for qualitative purposes.

D. DEMEYERE AND J. HOSTE, *Anal. Chim. Acta*, 27 (1962) 288–294

THE SCREENING OF METALLOFLUORESCENT INDICATORS

(Short Communication)

G. F. KIRKBRIGHT AND W. I. STEPHEN, *Anal. Chim. Acta*, 27 (1962) 294–295

A SOLVENT EXTRACTION METHOD FOR THE DETERMINATION OF MICROGRAM AMOUNTS OF CHROMIUM

(Short Communication)

D. G. TUCK, *Anal. Chim. Acta*, 27 (1962) 296–297

SEPARATION OF TITANIUM FROM OTHER ELEMENTS WITH N-BENZOYL-N-PHENYLHYDROXYLAMINE

(Short Communication)

V. R. M. KAIMAL AND S. C. SHOME, *Anal. Chim. Acta*, 27 (1962) 298–300

DETERMINATION OF CARBON AND HYDROGEN IN SILICON CONTAINING COMPOUNDS

(Short Communication)

Y. A. GAWARGIOUS AND A. M. G. MACDONALD, *Anal. Chim. Acta*, 27 (1962) 300–302

A SIMPLE SAFETY PRECAUTION IN OXYGEN FLASK COMBUSTIONS

(Short Communication)

P. GOUVERNEUR AND C. D. F. EERBEEK, *Anal. Chim. Acta*, 27 (1962) 303–304

NITRITE AS AN OXIDANT FOR ANTIMONY IN ITS SPECTROPHOTOMETRIC DETERMINATION WITH RHODAMINE B

(Short Communication)

R. GREENHALGH AND J. P. RILEY, *Anal. Chim. Acta*, 27 (1962) 305–306

PAUL-E. WENGER
1888—1962

Alors que rien ne le laissait prévoir, le professeur P. E. Wenger est mort brusquement le 10 mai 1962. Le matin même, il avait donné son cours de microchimie.

Professeur de chimie minérale, de chimie analytique et de microchimie à l'Université de Genève, il y enseigna pendant 44 ans. Il publia, avec divers collaborateurs, plusieurs ouvrages didactiques qui eurent un succès mérité: un manuel de volumétrie, un manuel de chimie analytique qualitative en 1933, deux traités de chimie analytique qualitative en 1946 et 1958. A côté de son activité de professeur, il entreprit de nombreuses recherches et en 1930, il créa, avec ses collaborateurs, un laboratoire de microchimie, parfaitement équipé, qui lui permit d'effectuer de nombreux travaux dont nous ne citerons que quelques-uns d'entre eux: Un microdosage de l'urée dans le sang; un microdosage gravimétrique de potassium en présence de sodium; un microdosage volumétrique de potassium dans le sérum sanguin; un microdosage électrolytique du zinc, du cobalt et du cadmium; une contribution à l'étude du microdosage du cadmium dans le sérum sanguin.

Pendant plusieurs années, son intérêt s'est porté sur l'emploi des réactifs organiques pour l'identification des éléments. De nombreuses publications en exposent les résultats, qui sont résumées dans les 2ème et 4ème rapports de la commission des réactions et réactifs analytiques nouveaux de l'Union internationale de chimie.

Outre l'identification, il a aussi utilisé les réactifs organiques, particulièrement l'acide anthranilique et l'*o*-oxyquinoléine pour les dosages, c'est ainsi qu'il a mis au point plusieurs méthodes, dont celle du dosage du zinc, du cobalt et du cadmium par l'acide anthranilique et celle du zinc par l'*o*-oxyquinoléine.

Tout le long de sa carrière, le professeur Wenger a tenu à équiper ses laboratoires des appareillages les plus modernes, grâce auxquels il mit au point, avec l'aide de ses collaborateurs, des nouvelles méthodes physico-chimiques, par exemple: un dosage colorimétrique des fluorures, un dosage spectrophotométrique du magnésium, une étude potentiométrique de l'α-nitroso-β-naphtol, un dosage polarographique indirect de l'ion potassium et tout dernièrement plusieurs travaux ont paru, il en est encore un qui est sous presse, concernant la chromatographie par électrophorèse. En tout, plus de 170 publications.

Le professeur Wenger a rendu de très grands services à notre Université, d'abord comme doyen de 1946 à 1954, puis comme vice-recteur et recteur. Il eut aussi une brillante activité internationale, ce qui lui valu de nombreuses distinctions, dont nous relèverons celles qui nous semble les plus importantes: Docteur honoris causa de l'Université de Sao Paulo; Chevalier de la légion d'honneur pour les services rendus à la chimie pendant la dernière guerre; Médaille de Lavoisier; médailles des Universités de Gand, Liège et Bruxelles; Membre d'honneur de la Société de chimie industrielle de Paris et de la Société de pharmacie et de chimie de Sao Paulo où il fut appelé à donner cours et conférences pendant le semestre d'été 1951; Secrétaire européen de la section de chimie analytique de l'Union internationale de chimie pure et appliquée. Il représenta notre pays à de nombreuses conférences et congrès internationaux, notamment à Paris, Lisbonne, Vienne, Graz, . . .

C'est avec une grande tristesse que ses amis, ses collaborateurs et ses assistants ont appris la mort de leur "patron", homme sensible, extrêmement dévoué, ayant un sens profond de la justice.

Il a été pendant de longues années et dès sa création, rédacteur en chef avisé de cette revue, qui, sous son impulsion, s'est rapidement répandue dans le monde scientifique.

Genève, le 16 juin 1962
D. MONNIER

THEORETICAL INVESTIGATION OF LOW LIQUID LOAD AND LOW TEMPERATURE OPERATION IN GAS CHROMATOGRAPHY

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(Received February 12th, 1962)

The use of small liquid phase percentages on the solid supports of gas chromatography (GC) has been recommended for the improvement of resolution by several authors. HISHTA, MESSERLY AND RESCHKE[1] used glass beads with percentages of liquid as low as 0.125 for the analysis of high boiling compounds. FREDERICK AND COOKE[2] have compared the performance of Chromosorb P support containing as little as 0.5% liquid with lightly loaded glass bead columns, and have demonstrated the usefulness of such lightly loaded columns. SAWYER[3] has reported data on low load columns composed of a wide range of solid supports including the conventional porous supports as well as Fluoropak and beads composed of glass, stainless steel and other materials. These authors have all obtained results showing the general utility of low load combined with low temperature operation. The present work has been undertaken to provide a theoretical background to the existing experimental work on low load columns. The theoretical approach should be useful in correlating the performance of various supports and in indicating the supports which will show the best improvement with a reduction in the liquid percentage.

In general, both experimental and theoretical results show the desirability of reducing the liquid load and column temperature. There are, of course, certain practical limits which prevent the reduction of load and temperature *ad infinitum*. These have been enumerated by the previously quoted authors. Among these limits are the requirement for decreasing sample size and hence detectors of increasing sensitivity and the harmful effects of solute adsorption which occur more prominently at low loads. Partially offsetting the limitations are certain practical advantages of the technique in addition to the improvement of resolution. Thus the use of a reduced temperature greatly diminishes the decomposition of solutes and liquid phases and permits GC operation far below the boiling point of the sample.

The reduction of liquid loading could conceivably be made without a concomitant reduction in temperature. Generally, however, the peaks would be eluted far too rapidly, an effect which would seriously impair resolution. Usually the temperature is lowered to an extent such that the peaks are eluted in roughly the same time as required for the heavily loaded, high temperature columns. Thus the reduction of liquid loading and temperature are, to a first approximation, coupled such that the R value (zone velocity/gas velocity) remains constant. Such a reduction will henceforth be called a "standard reduction in liquid load and temperature", or simply a "standard reduction". The theory developed below will concern the effects of a standard reduction on resolution. If for some reason *R* does not remain constant, the effects of the reduction may be written in terms of 2 independent changes; first a standard reduction and second a change in temperature at constant liquid load. If, for example, *R* increases, the latter change (in temperature) will be positive. The effects of independent temperature changes have been investigated elsewhere[4]. The decomposition of the effects of liquid load and temperature changes into the 2 "vector" components mentioned above is far more useful than its formulation in terms of independent changes in load and in temperature. First of all a reduction at constant *R* is of greater theoretical convenience than independent changes in either load or temperature. In addition such a reduction corresponds more closely to practice and any departure from the assumed constancy of *R* can be considered as a rather small and well understood perturbation on the main effect.

THEORY

The degree of resolution of adjacent chromatographic peaks depends upon the disengagement of the peak centers and upon the narrowness of the individual peaks[5,6]. The disengagement requirement depends entirely upon thermodynamic quantities and their differences from one solute to another. In the usual case where peak disengagement (relative volatility) depends primarily upon enthalpy differences, a decrease in temperature will by itself lead to an increased relative disengagement of 2 peak centers[6]. Thus the thermodynamic factors are nearly always favorable for any procedure employing reduced temperatures, including the procedure using low liquid loading. This effect could possibly be offset by the factors involved in peak spreading, depending on their relationship to temperature and the amount of liquid. The role of peak spreading, as reflected in the plate height, will consequently be examined here in conjunction with low liquid phase loading.

The plate height expression for a GC column, either packed or capillary, may be written in the form

$$H = B/v + (C_l + C_g)v \tag{1}$$

where the various terms have their usual meaning. The eddy diffusion term for packed columns has been ignored because it apparently has no significant role in determining the plate height[7]. The following results are, however, independent of this omission. Pressure correction terms have also been ignored.

At very low flow velocities the plate height approaches B/v. Any reduction in temperature is beneficial in this flow range since B is proportional to the gaseous diffusion coefficient, D_g, which increases approximately with the 1.7 power of temperature. At high flow velocities the effect of a reduction in liquid content and temperature depends on the nature and relative importance of the C_l and C_g terms. The C_g term is inversely proportional to D_g for a standard reduction and thus the reduction is harmful insofar as this term is involved. The C_l term is proportional to d_f^2/D_l where d_f is the "effective" thickness of the liquid film and D_l is the liquid diffusion coefficient. Both d_f and D_l decrease in a standard reduction. The extent of decrease in the term d_f has only recently become calculable, and then only in approximate form[8,9]. The variation of C_l is critical in the examination of low liquid loading and thus changes in d_f must be treated as carefully as possible. For most columns the ensuing theory indicates that the ratio d_f^2/D_l decreases in a standard reduction and consequently that low loading conditions are favorable for reducing this term.

A more significant comparison of high and low liquid percentages probably involves the plate height at optimum flow rate. The differentiation of H with respect to flow velocity v in equation (1) yields

$$H_{opt.} = 2(BC_g + BC_l)^{\frac{1}{2}} \tag{2}$$

Since B and C_g have an exactly opposite dependence upon D_g, the product BC_g should be independent of the proposed change in liquid loading and temperature. The variation of $H_{opt.}$ depends, consequently, entirely on the term BC_l. As indicated previously the B term increases approximately with the 1.7 power of temperature and a standard reduction is thus favorable for the decrease of this term. The critical term, C_l, proportional to d_f^2/D_l, will now be investigated.

The concept of effective liquid film thickness, d_f, originated in the development of the VAN DEEMTER equation[10]. As originally treated, it was nearly impossible quantitatively to relate d_f to any of the physical characteristics of the solid support. Variations in film thickness from one point to another on the support, which in practice occur over wide extremes, were not amenable to treatment. In recent years the wide diversity in liquid configuration has been translated into plate height characteristics by means of simplified models for the structure of the support[8,9,11]. The effective film thickness, d_f, becomes in practice the mean square liquid thickness[11], $(\overline{d^2})^{\frac{1}{2}}$, the depth d of liquid in a pore[8], or some other characteristic thickness related to solid structure[9]. These specific terms will be used below in place of d_f in order to account for support characteristics and differences.

For glass bead and capillary columns, and perhaps to a lesser degree for columns packed with diatomaceous earth or firebrick, the liquid may be thought of as depositing in pores which have cross sectional area

$$a = \mathscr{H}x^n \tag{3}$$

where $\mathscr{H}$ is a constant and x is the distance from the bottom of the pore (in previous publications x was the distance from the gas-liquid interface). The depth to which the pore is filled with liquid is d. The exponent n, which can take on any value not less than zero, allows for pores of differing shape and taper. A uniform film is entirely equivalent to a pore of uniform cross section filled to an equal depth. This case is covered by $n = 0$. The point-of-contact pores in a glass bead column are covered by $n = 3$.

The rigorous nonequilibrium theory shows that an assemblage of pores, with cross sections as described in eqn. (3), makes the following contribution to the plate height[8]:

$$H = \frac{2}{(n+1)(n+3)} R(1-R)v\frac{d^2}{D_l} = C_l v \tag{4}$$

An expression has also been derived[9] for a mixture of pores, each with a different exponent, n.

In a standard reduction of liquid loading and of temperature the ratio

$$\frac{1-R}{R} = k = \frac{Kv_l}{v_g} \tag{5}$$

remains constant. The partition coefficient is K and the amount of liquid in each pore is v_l. The volume of gas per pore is v_g. From this expression the product Kv_l equals kv_g. Since k remains constant and v_g remains nearly constant, the Kv_l term may be considered a constant. The volume of liquid in a pore can be found as

$$v_l = \int_0^d a \, \mathrm{d}x = \frac{\mathscr{H} d^{n+1}}{n+1} \tag{6}$$

The partition coefficient can be expressed as follows

$$K = K^{+}.\mathrm{e}^{\Delta H/\mathscr{R}T} \tag{7}$$

where K^{+} is a contant, ΔH the enthalpy of vaporization, $\mathscr{R}$ the gas constant and T the absolute temperature. In view of eqns. (6) and (7) and the constancy of $K\,v_l$, the following term will be a constant:

$$d^{n+1}.\mathrm{e}^{\Delta H/\mathscr{R}T} = \text{constant} \tag{8}$$

From eqn. (4) it is readily noted that the plate height changes as d^2/D_l, the other terms remaining constant. If d^2 is obtained from eqn. (8) and D_l expressed in the usual exponential form

$$D_l = D_l^{+}.\mathrm{e}^{-b\Delta H/\mathscr{R}T} \tag{9}$$

where D_l^{+} and b are constants, then the d^2/D_l term is found to have the following dependence on temperature in a standard reduction:

$$\frac{d^2}{D_l} = \text{const.}\ x.\mathrm{e}^{\{b-2/(n+1)\}\Delta H/\mathscr{R}T} \tag{10}$$

This term, and the plate height, will become smaller as the liquid loading and temperature are reduced providing

$$2 > (n+1)b \tag{11}$$

The constant b is approximately 0.35 for small molecules and less for long chain solutes where diffusion is a result of the thermal motion of individual segments[6,12]. Assuming that $b = 0.35$, the above condition reduces to $n < 4.7$. This condition should be applicable to nearly all columns, and thus the reduction in liquid loading and temperature, where applicable, should prove beneficial. A specific discussion of different column types will now be made to illustrate this conclusion.

Capillary columns

It is usually assumed that a uniform liquid film adheres to the inner wall of capillary tubing. If, however, one calculates the adsorption forces which presumably hold the liquid to the wall, it is found that the attraction is practically negligible beyond 100 or so Å[9]. Any part of a liquid film within a smooth bore tube not affected by adsorption forces is unstable and will form droplets in regions of high curvature or across the entire tube. Thus the uniform film hypothesis is untenable. It is possible, however, to keep the liquid dispersed at the wall if the wall is rough and has pores of sufficient depth to hold the liquid by capillary forces. Fortunately, most tubing is already sufficiently rough[9].

The location of liquid in numerous, small surface pores is critical to the subject under discussion since the type of pore determines the value of n and the applicability of low loading conditions. As mentioned earlier, a uniform film is characterized by $n = 0$, and is thus safely less than 4.7. If a surface of sawtooth grooves is an adequate approximation, then $n = 1$. If the pores can be approximated by right circular cones, then $n = 2$. Values higher than 2 would be associated with pores which have convex walls in the x direction. Altogether, the collection of random pore structures existing in practice probably show concave as often as convex features, and a value somewhere between 1 and 2 is likely to apply. This is safely below the critical value, 4.7, and the reduction of liquid loading within the usual practical limitations should be profitable. The actual reduction of the C_l term can be estimated by means of eqn. (10). Assuming $b = 0.35$, $n = 1.5$, and $\Delta H/\mathscr{R}T = 10$, the C_l term is approximately halved for every change of 100° in the neighborhood of 500°K.

Glass bead columns

Under ordinary circumstances the bulk of liquid probably accumulates around the bead contact points as a result of capillary forces. This situation leads to $n = 3$. It is possible that some liquid exists either as a thin uniform coating on the outside of the beads ($n = 0$) or fills microscopic pores or fissures on the bead surface ($n \cong 1 - 2$). In any case n is less than 4.7 and the reduction of liquid loading should consequently improve resolution. The actual reduction of C_l with $n = 3$ is less than above, amounting to about 15% for each change of 50 degrees.

Diatomaceous earth and firebrick

Several approaches are open for the approximate treatment of the very complicated pore structure of these solids. The choice between them, insofar as they yield different results, will ultimately depend on their practical usefulness. The first quantitative theory for relating chromatographic performance to pore structure was based on the assumption that pore size distribution data (obtained from non-chromatographic experiments) would yield the number and the size of pores containing liquid[8]. Once this was done, the nonequilibrium theory was applied to determine the plate height. Another model, in many ways quite compatible with this, would be based on the existence of many single pores with varying cross section. The first liquid applied, other than that taken up by adsorption, would accumulate in the narrow restrictions of the pores. As more liquid is added, the units of liquid within each pore would enlarge in both width and depth. This situation can be approximated by the accumulation of liquid in tapered pores as described in this paper. If necessary, a more extended function than eqn. (3) could be used for the cross sectional area. The parameters ($\mathscr{H}$ and n) would be obtained from pore size distribution data.

Following the arguments used in regard to surface pores in capillary columns, the value of n is expected to be in the vicinity of 1 or 2. A preliminary analysis of BAKER's[13] data on pore size distribution in Chromosorb W indicates that the best value might be slightly less than unity. Suffice it to say for the purposes of this paper that n is undoubtedly less than 4.7 and that a standard reduction will improve resolution.

CONCLUSIONS

Within the practical limitations discussed earlier, the simultaneous reduction of liquid loading and temperature may be expected to improve resolution for most solute pairs. A few exceptions will be found in which the separation is actually caused by the difference in vaporization entropies of 2 solutes. Ignoring this infrequent occurrence, both the relative disengagement of peaks (a thermodynamic property) and the peak widths (a rate phenomenon) will favor the reduction for all types of columns, including capillaries.

There is little doubt that some experimental work will eventually appear which will contradict the above conclusions. Results of this kind might easily occur by exceeding the practical limitations of the system. Thus if the sample size is not reduced in proportion to the liquid percentage, serious overloading and subsequent loss of resolution can occur. A loss of resolution may also occur if excessive adsorption is not carefully avoided. One of the uses of the foregoing theory would be in indicating the sources of difficulty when the resolution on a low load column is less than expected.

ACKNOWLEDGEMENT

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SUMMARY

The change in resolution resulting from the simultaneous reduction of liquid load and temperature is theoretically treated. The effects of decreases in load and temperature are formulated in terms of a standard reduction (in which the zone to gas velocity ratio is constant) plus any small changes in temperature required to match the observed changes in zone velocity. Taking the standard reduction as the norm, it is found that both the thermodynamic (relative peak elution times) and rate (peak spreading) effects favor the liquid load and temperature decreases. This is discussed specifically in relationship to diatomaceous earth and glass beads as the solid support and also to capillary columns.

ZUSAMMENFASSUNG

Der Einfluss von reduzierter flüssiger Phase und tieferer Temperatur auf die Trennwirkung gaschromatographischer Kolonnen wird theoretisch behandelt.

RÉSUMÉ

L'auteur a effectué une étude théorique sur l'influence de la réduction de la phase liquide et l'abaissement de la température, lors de séparations sur colonnes, par chromatographie en phase gazeuse.

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SÉPARATION DES ISOMÈRES DE L'HEXACHLOROCYCLOHEXANE PAR CHROMATOGRAPHIE EN PHASE GAZ

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Parmi les chercheurs qui étudient l'analyse des insecticides chlorés par chromatographie en phase gaz on peut nommer: aux Etats Unis, D. M. COULSON et ses collaborateurs[1–3] et ZWEIG ET ARCHER[4,5]; et en Grande Bretagne, GOODWIN, GOULDEN, RICHARDSON ET REYNOLDS[6].

Aucune de ces études porte exclusivement sur le lindane et ses différents isomères. COULSON l'utilise comme étalon interne dans l'analyse quantitative de différents insecticides comme l'aldrin, le dieldrin, malathion, systox, chlordan, toxaphène, etc.

En général les conditions opératoires varient peu d'un auteur à l'autre: la température est toujours très élevée de 200 à 250°. COULSON a effectué une étude systématique entre 220 et 280°[1]. Par suite de la température élevée, le choix des phases stationnaires est limité aux liquides peu volatils, d'où l'emploi de graisse Silicone Dow Corning ou élastomère Siliconé E 301. Le garnissage de la colonne est constitué par un support classique, généralement le Chromosorb W avec des taux d'imprégnation de 15 à 30% en poids suivant les auteurs.

La séparation et l'identification des isomères est rendue délicate par suite de leurs propriétés chimiques et physiques identiques ou voisines. Après de multiples essais, nous avons choisi pour résoudre ce problème particulier la technique des billes de verre qui a déjà fait l'objet dans la littérature de publications diverses[7].

Cette technique répondait à deux de nos problèmes. (*a*) Opérer à température plus basse pour éviter la décomposition éventuelle des produits à analyser. (*b*) Permettre l'emploi d'une phase stationnaire polaire sans trop de risques d'élution ou de modification de la phase.

Différents essais nous ont alors conduits au garnissage suivant de la colonne: billes de verre de granulométrie 27/26 normes Afnor ou 40/60 mesh, imprégnées de 0,25% en poids de polypropylène glycol Niax 1025 (Union Carbide).

APPAREILLAGE ET CONDITIONS OPÉRATOIRES

Le chromatographe utilisé pour effectuer cette étude est un Fractovap B/f de la Société Carlo Erba (Milan). Cet appareil est équipé d'un détecteur à conductibilité thermique à 4 filaments de tungstène ayant une excellente sensibilité et stabilité à haute température.

Colonne: acier inox — diamètre intérieur 6 mm. Support: billes de verre de granulométrie 27/26 normes Afnor ou 40/60 mesh. Phase stationnaire: polypropylène glycol Niax 1025 à 0.25% en poids de support. Longueur de colonne: 3 m. Débit: 5 l/h helium. Température de la colonne et du détecteur: 170°. Température du vaporiseur: 240°. Sensibilité de l'enregistreur: 1 mV sur toute l'échelle. Quantité injectée: 5 μl d'une solution saturée du produit à analyser dans le xylène.

Les meilleures conditions d'élution ont été obtenues en faisant fonctionner le chromatographe jour et nuit en température et en débit de gaz vecteur. En effet les billes de verre constituent un milieu isolant où l'équilibre de température s'établit très lentement, il faut compter 4 à 5 h au minimum pour obtenir la stabilité de la ligne de base et un tracé correct des pics sur la sensibilité maximum.

RÉSULTATS

Pour traiter ce problème de séparation de l'hexachlorocyclohexane nous disposions des isomères suivants: hexachlorocyclohexane α, β, γ, ε, δ, et heptachlorocyclohexane γ. On trouvera au Tableau I et Fig. 1 les temps de rétention relatifs des différents isomères par rapport à l'hexachlorocyclohexane γ. Les temps de rétention relatifs ont été calculés en mesurant les temps de retention absolus depuis l'injection jusqu'à

TABLEAU I

TEMPS DE RÉTENTION RELATIFS DES DIFFÉRENTS ISOMÈRES DE L'HEXACHLOROCYCLOHEXANE PAR RAPPORT À L'HEXACHLOROCYCLOHEXANE γ

Composés	*Temps de rétention relatifs*	*Ecart maximum observé sur les temps de rétention relatifs (13 mesures) (%)*
hexachlorocyclohexane α	0.674	± 4
hepta γ	0.814	± 3
hexachlorocyclohexane γ	1	
hexachlorocyclohexane β	1.76	± 3·4
hexachlorocyclohexane ε	2.05	± 3·9
hexachlorocyclohexane δ	2.27	± 5·75

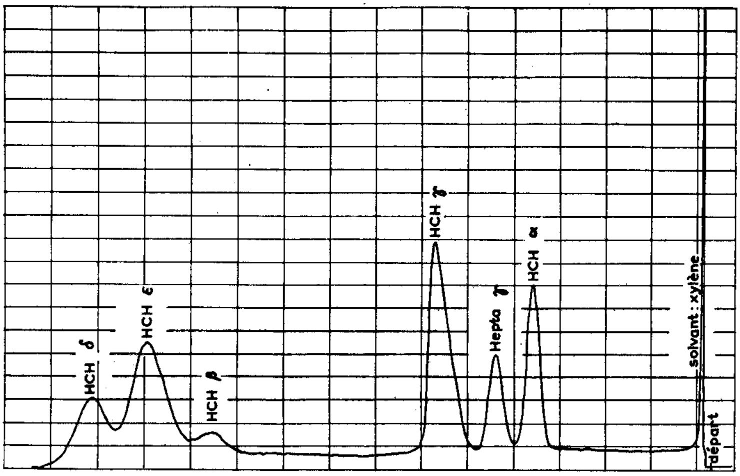

Fig. 1. Temps de rétention relatifs des différents isomères par rapport à l'hexachlorocyclohexane γ.

l'abscisse du sommet du pic sur la ligne de base. L'erreur maximum relative dans le calcul des temps de rétention relatifs, est proportionnelle au plus grand écart observé sur 13 mesures différentes.

DISCUSSION

L'expérience a montré que la durée d'utilisation d'une colonne à remplissage de billes de verre et de polypropylène glycol comme phase stationnaire, est plus courte que celle des colonnes à remplissage classique. La durée moyenne d'utilisation de nos colonnes n'a jamais excédé 3 semaines et pour mieux connaître le phénomène, nous avons entrepris l'étude systématique d'une telle colonne dans le temps.

L'efficacité de la colonne a été mesurée quotidiennement en calculant le nombre de plateaux théoriques pour l'isomère γ et pour une injection reproductible de 5 μl d'un mélange en proportions égales d'isomères γ et α en solution dans le xylène. De même il a été calculé l'indice de résolution γ/α[8]. La colonne a fonctionné dans les conditions opératoires décrites au paragraphe précédent, c'est-à-dire à la température de 170°, avec un débit de 5 l/h helium jour et nuit pendant 3 semaines avec seulement interruption en fin de semaine. Les chiffres indiqués au Tableau II représentent la moyenne effectuée sur 3 injections consécutives.

TABLEAU II

ÉVOLUTION D'UNE COLONNE À BILLES DE VERRE DANS LE TEMPS: MESURE DE L'EFFICACITÉ DE LA COLONNE ET DE L'INDICE DE RÉSOLUTION DES ISOMÈRES γ/α

Jours	*Nombre de plateaux théoriques calculé pour l'isomère γ*	*Indice de résolution des isomères γ/α*
1	980	3.80
2	870	3.57
3	836	3.51
4	934	3.64
5	925	3.64
6	908	3.55
7	883	3.54
8	795	3.36
9	817	3.52
10	772	3.37
11	787	3.39
12	725	3.31
13	730	3.23
14	750	3.25
15	710	3.24
16	706	3.22
17	680	3.09
18	678	3.14
19	656	3.10
20	666	3.07
21	678	3.12
22	583	2.80
23	503	2.68
24	398	2.35
25	350	2.29

Le nombre de plateaux théoriques a été calculé suivant la formule bien connue:

$$N = 16\left(\frac{x}{y}\right)^2$$

x = distance entre la perpendiculaire abaissée du sommet du pic sur la ligne de base et le point de départ. y = largeur du pic déterminée par l'intersection sur la ligne de base des tangentes au point d'inflexion.

Nous avons choisi l'indice de résolution plutôt que le temps de rétention relatif parce qu'il exprime d'une manière plus évidente la faculté pour une colonne de séparer deux constituants.

La résolution de deux pics chromatographiques peut être définie quantitativement comme le produit de deux rapports sans dimension: la séparation relative et l'étroitesse relative des pics.

Cet indice a pour expression:

$$R = QS_{2\cdot1}$$

$S_{2\cdot1}$ = séparation relative $(t_2-t_1)/t_1$; Q = étroitesse relative, t_2/y_2; t_2 et t_1 représentent respectivement les temps de rétention des constituants 2 et 1; y_2 représente la largeur du pic 2, mesurée en unités de temps. La valeur 2.5 pour R correspond à une complète résolution de 2 pics.

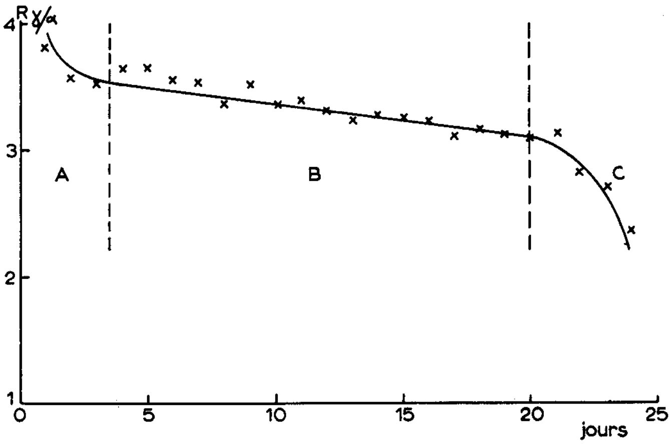

Fig. 2. Variation de l'indice de résolution des pics γ/α en fonction du temps.

Le Tableau II et la Fig. 2 montrent que l'indice de résolution des pics γ/α est sensiblement constant pendant les dix premiers jours de fonctionnement de la colonne et qu'ensuite il y a variation de la pente de la courbe, correspondant à un changement d'état lent de la colonne. La première explication de ce comportement peut être fournie par l'élution continue de la phase stationnaire entraînée par le gaz vecteur, puisque les billes de verre constituent un support lisse et sans surface. Mais le comportement des billes de verre utilisées comme support de phase stationnaire est plus complexe: la quantité de phase stationnaire déposée sur billes de verre étant très faible, on peut penser par analogie avec ce qui a été dit sur les colonnes capillaires[9] à la formation d'une couche monomoléculaire qui adhérerait à la surface des billes grâce à des forces d'attraction de nature variable, fonction du solvant et du support.

Dans le cas présent, ces forces seraient des liaisons hydrogène entre d'une part les OH provenant de l'hydratation de certains oxydes composants du verre, ou des molécules d'eau disposées en couches d'hydratation monomoléculaires et adhérant au verre, et d'autre part entre les OH des chaînes terminales du polypropylène glycol qui constitue la phase stationnaire. L'effet créé par les forces de Van der Waals se traduirait par un abaissement de la tension de vapeur de la phase, donc par une prolongation sensible de la durée d'utilisation des colonnes.

On notera l'importance du dégraissage préalable des billes de verre avant tout dépôt de phase afin de favoriser la création de ces forces d'attraction.

Si l'on observe la courbe Fig. 2 on constate qu'elle peut être découpée en trois parties distinctes: la partie A de la courbe correspondrait à l'élution de phase stationnaire ne contribuant pas à la formation de cette couche monomoléculaire; le palier B représenterait la durée de vie effective de la colonne dans ces conditions d'emploi, c'est-à-dire que pendant cette période d'utilisation on assisterait à la dégradation progressive mais constante des forces de Van der Waals, se traduisant par une élution continue de phase stationnaire; enfin la partie C amorçant une variation de pente représenterait un changement d'état de la colonne dû, d'une part à l'élution trop grande de phase stationnaire et d'autre part à la pollution du reste de phase stationnaire par des produits lourds existants dans le mélange de produits injectés.

Si l'hypothèse de la formation d'une couche monomoléculaire est valable, on peut aisément concevoir une amélioration de l'adhérence de la phase stationnaire par des voies différentes:

Soit en faisant subir aux billes de verre un prétraitement à l'acide fluorhydrique ou à la soude, qui en modifiant la surface du verre, favoriserait la tenue mécanique de la phase stationnaire, et qui permettrait en même temps la création d'OH supplémentaires en hydrolysant certains oxydes, composants du verre. Ces OH supplémentaires augmenteraient le nombre des forces d'attraction de Van der Waals.

Soit encore par utilisation de produits intermédiaires comme les agents d'ensimage. Un tel traitement s'apparentrait à l'ensimage des fibres de verre pour la fabrication des stratifiés[10]. Des composés tels que le chlorure méthacrylique chromique ou le vinyltrichlorosilane sont couramment utilisés dans ce cas.

Enfin une voie différente pour favoriser la tenue de la couche monomoléculaire de phase stationnaire consisterait en l'utilisation de billes métalliques: bronze, cuivre, aluminium, etc. Des forces d'attraction de nature différente, suivant le degré d'oxydation superficielle du métal, s'exerceraient directement entre la phase et le support sans risque, comme dans le cas des billes de verre, d'une altération des performances de la colonne toujours possible avec un agent intermédiaire, comme les produits d'ensimage.

Ces diverses modifications de la surface du support sont peut-être plus prometteuses que les billes de verre utilisées tel quel, d'autant plus que les billes métalliques constituant un milieu conducteur faciliteraient la mise en température d'une telle colonne chromatographique.

CONCLUSION

La séparation des isomères de l'hexachlorocyclohexane a été réalisée dans des conditions beaucoup moins sévères que celles adoptées par les différents auteurs qui ont analysé des produits insecticides voisins. Cette technique peut, d'une manière générale, être utilisée dans tous les cas où les produits risquent une décomposition à trop haute température. Cependant, malgré les avantages certains, les billes de verre restent une technique délicate et exigeante à cause de la préparation du garnissage lui-même et des propriétés propres de la colonne ainsi garnie, toutes choses qui conditionnent impérativement les performances d'une colonne à billes de verre et notamment sa durée d'utilisation.

L'élution continue de la phase stationnaire dans le temps a pour cause une insuffisance dans l'adhérence sur le support. La nature physicochimique des forces de liaisons qui régissent ces phénomènes pourraît être modifiée par des traitements divers, comme les agents d'ensimage des fibres de verre. Ces traitements intermédiaires favoriseraient une meilleure tenue de la phase stationnaire sur les billes de verre avec, pour conséquence, une augmentation de la durée d'utilisation de la colonne.

RÉSUMÉ

La séparation de quelques isomères de l'hexachlorocyclohexane a été réalisée grâce à la technique des billes de verre avec le polypropylène glycol Niax 1025 (Union Carbide) comme phase stationnaire. Les principaux isomères séparés sont l'hexachlorocyclohexane γ ou Lindane, les isomères α, β, ε, δ, ainsi que l'heptachlorocyclohexane γ. L'étude systématique d'une telle colonne montre qu'on ne peut dépasser une vingtaine de jours en opérant jour et nuit en température et débit de gaz vecteur. Le prolongement de la durée d'utilisation d'une telle colonne pourrait être obtenu par des traitements intermédiaires des billes de verre, comme par exemple les agents d'ensimage qui favoriseraient la tenue de la couche monomoléculaire de phase stationnaire sur le support en créant des liaisons plus nombreuses ou de nature différente.

SUMMARY

Hexachlorocyclohexane isomers can be separated by a glass bead technique with polypropylene glycol Niax 1025 as the stationary phase. The principal isomers separated are the γ-hexachlorocyclohexane (Lindane isomer), the α, β, ε, and δ isomers and γ-heptachlorocyclohexane. The life of the glass bead column is short — about 20 days in constant use. A longer column life can be obtained by pretreatment of the glass beads.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Trennung der Isomeren des Hexachlorocyclohexans durch Gaschromatographie unter Anwendung der Glasperlen-Technik mit Polypropylenglycol als stationärer Phase. Folgende Isomere wurden erhalten: γ (= Lindane Isomer), α, β, ε, δ sowie γ-Heptachlorocyclohexan.

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IDENTIFICATION OF NITRILES IN PETROLEUM PRODUCTS. COMPLEX FORMATION AS A METHOD OF ISOLATION*

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The work described in this paper is a part of a continuing study of the nitrogen-containing constituents in hydrogenated petroleum distillates with particular emphasis on the development of techniques for the separation and characterization of these impurities. Studies in this area were deemed desirable since many catalysts employed in petroleum processing are affected adversely by nitrogen-containing compounds[1]. For this reason, it would be advantageous in many respects to know the nature of the nitrogen compounds in a distillate before processing.

In earlier studies it was shown that nitrogen bases could be separated from a hydrogenated distillate by extraction with hydrochloric acid and that indoles, carbazoles, and phenazines could be isolated as their perchlorates[2]. Analysis of the oil after this treatment showed that considerable nitrogenous material remained unidentified. It proved possible to adsorb these remaining compounds together with appreciable amounts of aromatic hydrocarbons on aluminum oxide. Since the presence of aromatic hydrocarbons hampers the identification of these nitrogen compounds, methods for their separation were needed.

This paper reveals a new approach to the problem of isolating nitrogen compounds from petroleum products, namely complex formation between metal salts and the nitrogen compounds. Ferric chloride and zinc chloride were found to be particularly effective and permitted separation of the nitrogen-containing compounds from a hydrocarbon medium. It was also found that these complexes could be thermally decomposed to release a nitrogen concentrate for further characterization. Resolution of this concentrate by a combination of fractional elution from an aluminum oxide column and gas chromatography led to the identification of nitriles, which hitherto have not been isolated from petroleum products. The nitriles were either identified or their presence indicated by ultraviolet spectroscopy and mass spectrometry.

EXPERIMENTAL

Instruments

A gas chromatograph, made in this laboratory and fitted with a Gow-Mac thermal conductivity cell, was employed for the separation work. The chromatograph was operated at a temp. of 290° and a helium pressure of 15 psig. An analytical column (20′ × $^1/_4$″ I.D.) with 20% silicone oil-firebrick packing was used. The outlet of the

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* Dedicated to Professor Eugen Werle, University of Munich, on the occasion of his 60th birthday.

column was maintained at a temperature about 20° higher than the column temperature to minimize condensation of substances in the exit line. A heating wire wrapped around the outlet tube supplied the additional heat required. Test tubes of 10-ml capacity, cooled with water, were used as receivers for the separated compounds. Fractions collected in this manner could be used directly for identification purposes.

A Cary recording spectrophotometer, Model 11, was employed to obtain the ultraviolet absorption spectra of the isolated substances. In all cases methanol (spectrograde) was used as solvent.

A Consolidated Electrodynamics Corporation mass spectrometer, Model 21–103, modified in this laboratory with a high-temperature inlet system, served for mass spectrometric investigation of the nitrogen compounds. Both low and high voltage mass spectra were obtained.

Preliminary investigations

For this study a partially hydrogenated furnace oil was selected; its physical and chemical properties are shown in Table I. The content of aromatics, paraffins, and olefins was determined by the FIA method (ASTM D1319). The total nitrogen content of the oil was determined by the Kjeldahl method and the basic nitrogen by potentiometric titration with acetic acid–perchloric acid. Pyrroles plus indoles were determined colorimetrically with *p*-dimethylaminobenzaldehyde[3] and carbazoles[2] with 2-bromo-2-nitroindandione-1,3.

TABLE I

ANALYSIS OF HYDROGENATED FURNACE OIL

Test	*Result*
°API (gravity)	25.7
Aromatic Hydrocarbons, Vol.-%	60.4
Saturated Hydrocarbons, Vol.-%	37.7
Olefins, Vol.-%	1.9
Total nitrogen, p.p.m.	160
Basic nitrogen, p.p.m.	25
Pyrrole + Indole nitrogen, p.p.m.	5.7
Carbazole nitrogen, p.p.m.	40

Concentration and separation of nonbasic nitrogen compounds on aluminum oxide

To obtain a nonbasic nitrogen concentrate for this study, 500 ml of the hydrogenated furnace oil was extracted with three 500-ml portions of 1 *N* hydrochloric acid to remove the basic components. The oil was then washed with water and dried over sodium sulfate. The resulting oil had a nitrogen content of 120 p.p.m. indicating that 25% of the total nitrogen had been removed. The finding that 25% rather than 15.6% of the nitrogen was removed by hydrochloric acid extraction was expected, since it had been shown by earlier studies that the acid treatment removed some indoles as indole polymers[4,5].

The oil was then passed through a column, 90 cm × 2.0 cm I.D., containing 200 g of activated aluminum oxide (Alcoa, grade F-20) (column I)[6]. Oil entrained on the column was removed by elution with 500 ml of isohexane. A Kjeldahl analysis of the effluent oil showed that approximately 95% of the nonbasic nitrogen remained on the column. The nitrogen compounds were recovered by eluting the column with 500 ml of methanol. After removal of the methanol on a steam bath, the residue contained 1.8% nitrogen. This concentration step was repeated several times to obtain sufficient material for study.

To determine whether the nonbasic nitrogen compounds could be further separated on aluminum oxide, approximately 0.1 g of the concentrate was mixed with 5 g of aluminum oxide and the impregnated adsorbent transferred to the top of a column (130 cm × 0.9 cm) containing 50 g of the aluminum oxide (column II). The column was then eluted successively with 100-ml portions each of carbon tetrachloride, carbon tetrachloride containing 1, 2, 3, 4, 6, 8, and 10% by volume of methanol, and finally with pure methanol. The solvent was removed from each fraction on a steam bath and each residue was dissolved in 4 ml of methanol. The resulting fractions were designated 0, 1, 2, 3, 4, 6, etc., fraction 0 being obtained with pure carbon tetrachloride.

Examination of the individual fractions by ultraviolet spectroscopy revealed that each contained many compounds and that this technique alone would not give the desired separations. Nevertheless, some indication of the presence of carbazoles in fractions 1 and 2 was noted, and the spectra of fractions 3 and 4 agreed closely with that of pure 1,2-dicyanonaphthalene shown in Fig. 1.

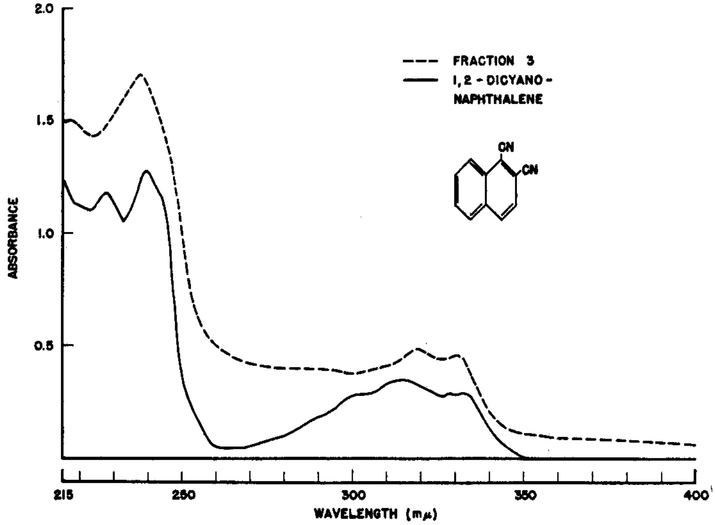

Fig. 1. U.V. absorption spectrum indicating the presence of 1,2-dicyanonaphthalene in fraction 3 from Al_2O_3 column II.

Since some indication of the presence of nitriles had been obtained in fractions 3 and 4 from the aluminum oxide column, it appeared worthwhile to determine whether the nitriles could be detected by saponification and titration of the liberated ammonia. For this purpose, a portion of the nonbasic nitrogen concentrate from aluminum oxide column I was extracted with 72% perchloric acid to remove the indoles, carbazoles, and phenazines. The resulting concentrate contained 1.1% nitrogen.

To conduct the test, a 10-mg portion of this concentrate was transferred to the bottom of a glass tube (50 cm × 0.5 cm I.D.). One ml of 75% sulfuric acid and

100 mg sodium chloride were added and the tube was heated in a sand bath for 3 h at 150°. After cooling, the contents were carefully diluted with 5 ml of water[7]. The aqueous solution obtained was transferred to a Conway vessel for the determination of ammonia by a microdiffusion method[8]; 4 ml of concentrated sodium hydroxide was added to the sample and the liberated ammonia absorbed in 3 ml of 0.01 N sulfuric acid. Titration of the sulfuric acid after reaction revealed that 0.35 ml of the acid had been neutralized. This indicated the formation of ammonia in the reaction and suggested the presence of nitriles. Other unidentified nitrogen compounds, however, might also form ammonia under these conditions. This test, although useful as a check for the presence of nitriles identified by other methods, would be meaningless as the sole test for nitriles.

Precipitation and recovery of nitrogen compounds as metal complexes

From previous experience it was known that condensed aromatic hydrocarbons would be adsorbed with the nitrogen compounds on aluminum oxide; hence, a method was needed which would provide a separation of the 2 types of compounds and also permit recovery of the nitrogenous material.

The unshared pair of electrons on the nitrogen atom, present in many types of nitrogen compounds, coordinates with certain salts to form complexes. To evaluate this approach as a method for removing nitrogen compounds from the oil, 25 g of each of the following salts were shaken with 250-ml portions of the oil for 3 h at room temperature: $CoCl_2.6H_2O$; $P_2O_5.24WO_3.xH_2O$; $P_2O_5.24MoO_3.xH_2O$; $NH_4Cr(NH_3)_2(SCN)_4.H_2O$; $CuCl_2.2H_2O$; $HgCl_2$; $FeCl_3.6H_2O$; and $ZnCl_2$ (not dried). After shaking, the salts were removed from the oil by filtration through filter paper. Only $FeCl_3.6H_2O$, $ZnCl_2$, and a mixture of the 8 salts were effective in lowering the nitrogen content of the oil. The data obtained with these salts are shown in Table II.

TABLE II

RESIDUAL NITROGEN CONTENT OF HYDROGENATED OIL AFTER TREATMENT WITH $FeCl_3$, $ZnCl_2$, AND A MIXTURE OF 8 SALTS

Salt	*p.p.m. N*
$FeCl_3.6H_2O$	80
$ZnCl_2$ (not dried)	110
Mixture of 8 salts	0.2

Since $FeCl_3$ and $ZnCl_2$ were the most effective salts for removing nitrogen compounds from the oil, their combined effect was also tested. Table III shows the data obtained with the combined salts when 250 ml of oil and the reaction conditions stated above were used.

On the basis of the data in Tables II and III, a mixture of $FeCl_3$ and $ZnCl_2$ was more effective for nitrogen removal than the individual iron and zinc salts. A comparison of the data also shows that a mixture of 50 g each of $FeCl_3 + ZnCl_2$ is nearly as effective as the mixture of the 8 salts.

To illustrate the selectiveness of the separation technique relative to nitrogen removal, 500-ml portions of the hydrochloric acid extracted oil were shaken with varying amounts of single portions of $FeCl_3$ and $ZnCl_2$ for 3 h in closed bottles at room temperature (Fig. 2). The precipitates were removed from the oil by filtration, the oil was washed repeatedly with water to remove entrained salts, and finally dried. A portion of each of the treated oils was reserved for nitrogen determination. The second salt was then added to the treated oil and the extraction procedure repeated. Finally, a mixture of ferric and zinc chlorides was added to each pretreated sample of oil and this blend handled as described previously. Fig. 2 shows the quantities of each of the components used as well as the resulting nitrogen contents of the samples. It can be seen that ferric chloride removed approximately 80 p.p.m. of the nitrogen whereas zinc chloride removed only 10–25 p.p.m. This finding suggests a certain selectivity of each salt for different types of nitrogen compounds. Moreover, the lowering of the nitrogen content from 19 or 25 p.p.m. to 2.5 p.p.m. by the combined salt treatment, after exposing the oil to each salt separately, indicates a synergistic effect between ferric and zinc chloride.

TABLE III

RESIDUAL NITROGEN CONTENT OF HYDROGENATED OIL AFTER TREATMENT WITH INCREASING QUANTITIES OF $FeCl_3 + ZnCl_2$

$FeCl_3 + ZnCl_2$ (g)	p.p.m. N
5 + 5	11.1
10 + 10	11.0
15 + 15	9.3
20 + 20	8.5
25 + 25	6.4
30 + 30	5.4
50 + 50	0.6

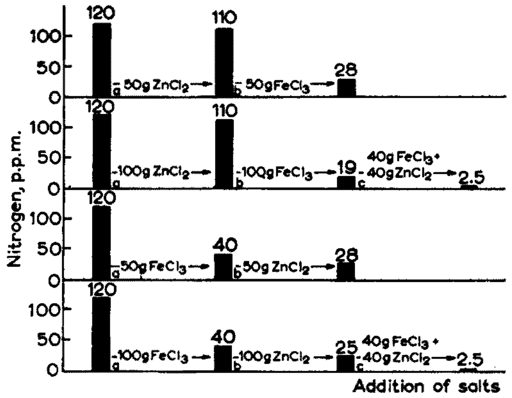

Fig. 2. Selective precipitation of nitrogen compounds in hydrogenated furnace oil with meta salts. Synergistic effect between $FeCl_3$ and $ZnCl_2$. a = 500 ml oil; b = 450 ml oil; c = 400 ml oil

Liberation of nitrogen compounds from the metal complexes by thermal decomposition

Since it had been shown that complex formation was an effective means of isolating nitrogen compounds from a petroleum distillate, the next step was to determine if the nitrogen compounds could be liberated from the complexes. Thermal decomposition was used for this purpose since in some cases the metal to nitrogen bonds are broken upon heating with fragmentation of the complexes into salts and organic material[9-11].

Before decomposition, the complexes, obtained by the reaction of 250 ml of hydrochloric acid extracted oil with 50 g each of ferric and zinc chlorides, were freed from entrained oil by extraction with isohexane in a Soxhlet apparatus. Instead of a paper thimble, which is destroyed by the salts, a glass frit (13 cm × 3.5 cm) of medium porosity was used. The metal complexes were dried at about 80°, pulverized in a mortar, and finally rubbed between sheets of hard paper further to reduce the size of the salt particles. After several such treatments, the complexes were considered to be free from hydrocarbons.

For thermal decomposition of the complexes, a glass apparatus consisting of 3 glass tubes A, B, and C, inserted one inside the other, was assembled as shown in Fig. 3. Approximately 15 cm of the left-hand portion of tube A was surrounded with steel tubing which was wrapped with 15 feet of resistance wire (2.5 ohms per foot). A thermocouple, inserted under the heating tape, was employed for temperature measurements. A small plug of glass wool, 24 cm from the left end of the tube, prevented salt particles from being blown into the cold part of the tube during the heating. A glass spiral trap, attached to tube B and cooled by liquid nitrogen, served to collect volatile compounds not condensed by the dry ice in tube C.

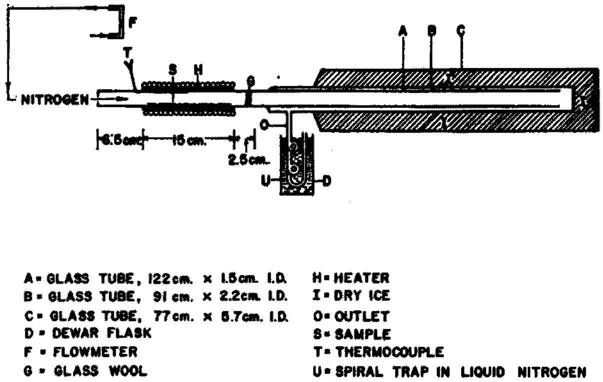

Fig. 3. Apparatus for the thermal decomposition of the $FeCl_3$ and $ZnCl_2$ complexes.

The pyrolysis was conducted by placing 3 g of the pulverized and washed metal complexes of the nitrogen compounds in the portion of tube A wrapped with the heating wire. A nitrogen source was attached at tube A and a nitrogen flow of about 145 ml per min maintained. The temperature was raised at a rate of 7–8° per min up to 450°. At this point, the heater was turned off and the unit allowed to cool to room temperature The apparatus was then dismantled and tube A cut at the plug of glass wool. The condensate was washed out with methanol and methylene chloride, the solutions combined with the condensate from the liquid nitrogen trap, and dried over sodium sulfate. After filtration, the solvents were removed on a steam bath, leaving a concentrate which contained 1.1% nitrogen.

Since ultraviolet spectra and saponifiable nitrogen compounds had previously indicated the presence of nitriles in the oil, it was of interest to determine whether a typical nitrile could be recovered from the oil with the mixed metal chlorides and would withstand the thermal decomposition of its complexes; 1 g of 1-cyanonaphthalene was dissolved in 500 ml of hydrogenated oil previously freed of inherent nitrogen compounds by the $FeCl_3$-$ZnCl_2$ treatment, 45 g each of $FeCl_3$ and $ZnCl_2$ were then added and the mixture shaken for 3 h at room temperature. This treatment lowered the nitrogen content from 220 p.p.m.–70 p.p.m. N, confirming that nitriles can be removed from a petroleum distillate by complex formation with metal salts. These complexes were isolated and decomposed as described above. 1-Cyanonaphthalene was identified as a product of this reaction proving that nitriles can be recovered unchanged from complexes with $FeCl_3$ and $ZnCl_2$ by thermal decomposition.

Adsorption and elution of several pure nitriles, such as benzonitrile, *p*-tolunitrile, 1-cyanonaphthalene, 2-cyanonaphthalene, 9-cyanonaphthalene, 4-biphenylcarbonitrile and terephthalonitrile, on aluminum oxide, as well as treatments with hydrochloric and perchloric acids under the conditions described in this paper, did not result in any structural changes of the nitriles. Therefore, these techniques may be used for the purposes described here. Whether the same stability of all nitriles is found in the process of pyrolysis of metal complexes has to be investigated in the future.

Separation and identification of nitriles

Since the concentrate from the thermal decomposition, which contained 1.1% nitrogen, was a composite of nitrogen types, additional separation methods were needed. After indoles, carbazoles, and phenazines were removed by treatment with 72% perchloric acid, the residue contained 1.0% nitrogen. Fractional elution of an aluminum oxide column and gas chromatography were used for the separation of the remaining compounds.

Aluminum oxide

A 20-mg portion of the nonbasic nitrogen concentrate, remaining after treatment with perchloric acid, was mixed with 2 g of activated aluminum oxide and this

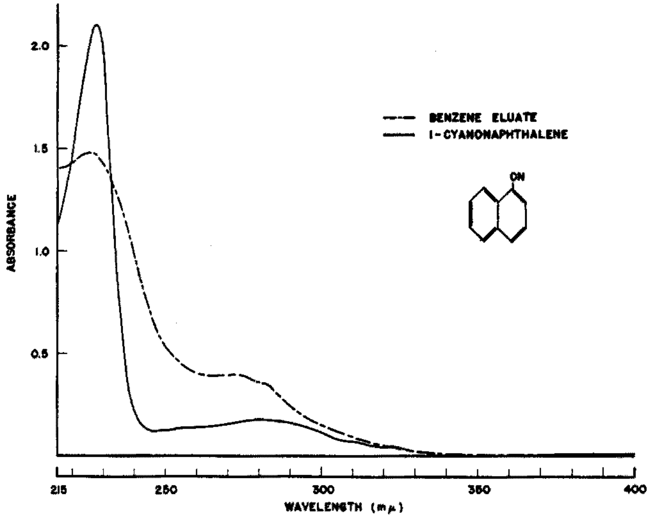

Fig. 4. U.V. absorption spectrum indicating the presence of 1-cyanonaphthalene in the benzene eluate from Al_2O_3 column III.

mixture transferred to the top of a column (70 cm × 1.2 cm I.D.) packed with aluminum oxide (column III). The nitrogen compounds were eluted with 100 ml each of carbon tetrachloride, benzene, chloroform, acetone, methanol, and methylene chloride in the order given. Following the addition of each solvent, 100 ml of isohexane were passed through the column, the isohexane eluate combined with the preceding eluate, and the separate fractions concentrated on a steam bath. Each residue was dissolved in 4 ml of methanol and ultraviolet spectra were obtained. In Fig. 4, the similarity between the spectrum of the material eluted with benzene and that of 1-cyanonaphthalene suggests that the latter may be present in the eluate.

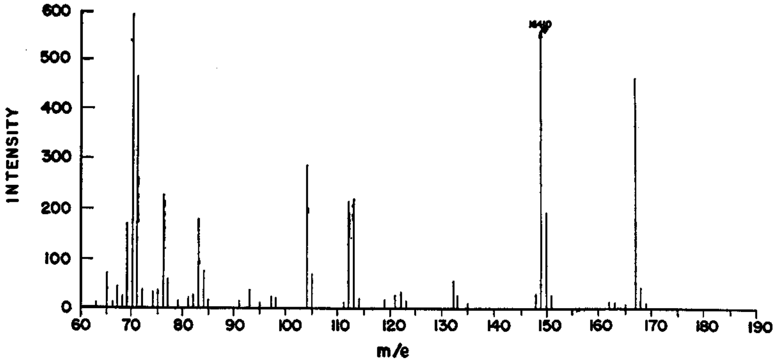

Fig. 5. High voltage mass spectrum of the benzene eluate from Al_2O_3 column III.

The fractions were also investigated by mass spectrometry. The mass spectrum of the residue from the benzene eluate is shown in Fig. 5. This spectrum shows an intense peak of *m/e* value of 167 which can be attributed to a methylcyanonaphthalene. Since the U.V. absorption spectrum of this eluate also indicated an alkylcyanonaphthalene, its presence, therefore, was reasonably assured. The most intense *m/e* value in the mass spectrum was 149 which suggests the presence of dihydroxytolunitrile. This, however, was not confirmed by other data.

The ultraviolet and the mass spectra of the remaining fractions obtained from aluminum oxide column III did not contribute to the identification of the nitriles and are not presented here.

Gas chromatography

Gas chromatography was also used to resolve the nonbasic nitrogen compounds recovered from the metal complexes. The concentrate, blended with a small amount

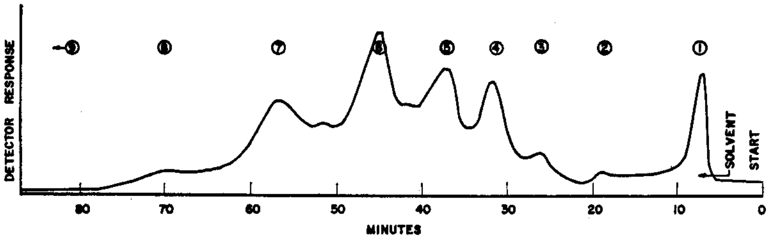

Fig. 6. Gas chromatographic separation on silicone oil-firebrick of compounds liberated from $FeCl_3$ and $ZnCl_2$ complexes.

of benzene, gave a chromatogram with nine peaks (Fig. 6). The separation was repeated a number of times and the individual fractions were collected in water-

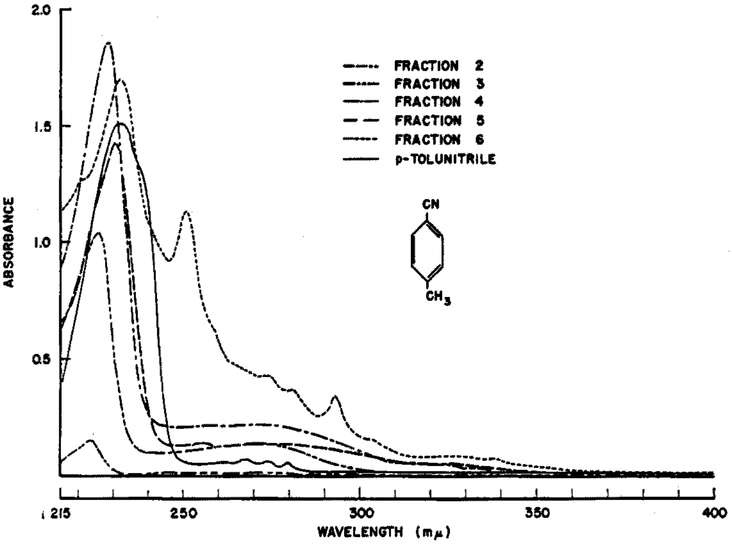

Fig. 7. U.V. absorption spectra of *p*-tolunitrile and of compounds separated by gas chromatography.

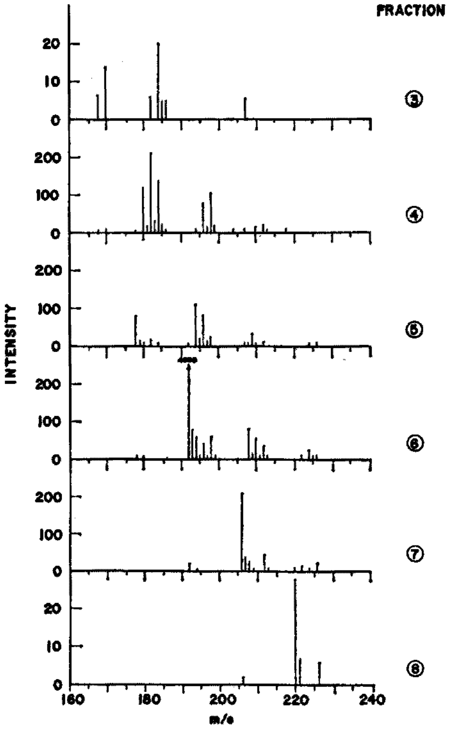

Fig. 8. Low voltage mass spectra of gas chromatographic fractions.

cooled 10-ml glass tubes. An intense odor similar to that of benzonitrile was noted in several of the fractions. 4 ml of methanol were added to each tube and the resulting solutions were examined by ultraviolet spectroscopy.

The U.V. spectra of fractions 2, 3, 4, and 5 showed an intense absorption peak between 224 and 232 mμ similar to that of *p*-tolunitrile (Fig. 7). The spectra of fractions 7, 8 and 9, on the other hand, showed intense absorption peaks at about 254 mμ comparable with that of phenanthrene. This was surprising, particularly since phenanthrenes were not expected to form complexes with ferric or zinc chloride. However, it is possible that the phenanthrenes were not completely removed from the complexes by extraction with isohexane in the Soxhlet apparatus. Mass spectral data also indicated the presence of alkylphenanthrenes in these fractions (*m/e* 178, 192, 206, and 220 in Fig. 8).

Fractions 3 through 8 obtained from the gas chromatographic separation of the nonbasic nitrogen compounds were investigated by low voltage mass spectrometry. The resulting spectra are shown in Fig. 8. Fractions 1, 2, and 9 did not contain sufficient material for mass spectrometry. The mass spectra indicated that each fraction contained many individual compounds. The longer the retention time of a particular fraction, the higher also was the average molecular weight of the compounds it contained. Since this rule applies for series of homologous compounds, the observation actually indicates that such series are present. On the basis of the molecular weights, the compounds listed in Table IV are believed to be present in the individual fractions. The molecular weights of the nitriles and their homologs are expressed as *m/e* ratios in the low voltage mass spectra and are listed together with the corresponding gas chromatography fractions.

It was mentioned previously that the ultraviolet absorption spectra of fractions 2, 3, 4, and 5 were similar to that of *p*-tolunitrile (Fig. 7). In addition the mass spectral data indicated the presence of C_3- and C_4- dicyanobenzene (*m/e* 170 and 184) in fractions 3 and 4 and C_1-dicyano-2,3-dihydroindene (*m/e* 182) in fraction 4 as the major components. These 2 types of compounds as well as *p*-tolunitrile have similar ultraviolet absorption spectra because of their structural similarities. In this paper, C_1-, C_2-, C_3-, etc. refer to methyl-, ethyl-, propyl-, or any combination of these alkyl groups.

From the ultraviolet absorption and the mass spectra it appears, therefore, that gas chromatography fractions 2, 3, 4, and 5 contain those compounds of Table IV which have structures similar to those of *p*-tolunitrile. These are alkylated dicyanobenzenes, cyano-, and dicyano-2,3-dihydroindenes.

Since an indication for the presence of dihydroxytolunitrile, cyano- and dicyanoindenes, cyanobiphenyl, and dicyanooctahydronaphthalene was obtained only from mass spectral data, the actual presence of these compounds in the hydrogenated oil has not been confirmed. Moreover, since no differentiation of isomers was possible with low voltage mass spectrometry, it is possible that more than one compound could be assigned to a given molecular weight. In such cases, as is shown below, only one compound was included in Table IV: cyano-2,3-dihydroindene (MW 143) or cyanotetralin; C_1-cyanoindene (MW 155) or cyanodihydronaphthalene; C_2-cyanoindene (MW 169) or diphenylamine; C_1-dicyano-2,3-dihydroindene (MW 182) or dicyanotetralin.

It is also possible that some lower members of the different homologous series of

TABLE IV

INTERPRETATION OF LOW VOLTAGE MASS SPECTRA

Type of Nitrile			$+CH_2$		$+2CH_2$		$+3CH_2$		$+4CH_2$		$+5CH_2$		$+6CH_2$		$+7CH_2$	
	m/e	*Fr*	*m/e*	*Fr*	*m/e*	*Fr*	*m/e*	*Fr*	*m/e*	*Fr*	*m/e*	*Fr*	*m/e*	*Fr*	*m/e*	*Fr*
Dicyanobenzene (U.V.)	128	—	142	—	156	—	170	3,4	184	3,4,5	198	4,5,6	212	4,5,6,7	226	5,6,7,8
Dicyanocyclohexane	134	—	148	—	162	—	176	—	190	3,4	204	4	218	4		
Cyanoindene	141	—	155	—	169	—	183	4	197	4,5,6	211	6	225	6		
Cyano-2,3-dihydroindene (U.V.)	143	—	157	—	171	—	185	3,4	199	4,6	213	4,6,7				
Cyanonaphthalene (U.V.)	153	—	167	—	181	4	195	5,6	209	5,6,7						
Dicyanoindene	166	—	180	4,5,6	194	4,5,6	208	5,7	222	6,7						
Dicyano-2,3-dihydroindene (U.V.)	168	3,4	182	3,4,5	196	4,5,6	210	4,5,6	224	5,6,7						
Dicyanonaphthalene (U.V.)	178	4,5,6	192	5,6,7	206	7	220	7,8								
Cyanobiphenyl	179	5	193	6	207	3,4,5,7	221	8								
Dicyanooctahydronaphthalene	186	3,4	200	4												

(U.V.) = Indicated also by U.V. spectrum nitriles are present in the nitrile concentrate. This was indicated by the small peaks 1 and 2 shown on the gas chromatography curve (Fig. 6).

DISCUSSION

This study shows that ferric chloride and zinc chloride form complexes with nitrogen compounds present in a petroleum distillate permitting their isolation in a relatively pure form. This was expected since metal salts are frequently used in analytical investigations for the formation of complexes with nitrogen bases[12]. The melting points of such complexes are occasionally used for the identification of these bases; *e.g.* 2,8-dimethylquinoline which was isolated from a crude kerosene distillate[13]. Zinc chloride has also been used to purify pyridine and quinoline isolated from petroleum distillates[10]. Furthermore, the thermal decomposition of the zinc chloride complexes of those 2 bases had been investigated[9,11] and is reported to occur at temperatures above 320°[10]. In addition, mercuric chloride complexes have been used for the purification of pyridines and quinolines from petroleum distillates[14] as well as for the isolation and purification of alkaloids[15].

In this investigation, the nitrogen compounds were liberated from the metal complexes only by thermal decomposition. Liberation of nitrogen compounds from metal salt complexes on heating had been observed in several other investigations. Ethylenediamine, for example, evolved from *tris*(ethylenediamine) chromium(III) chloride 3 $^1/_2$ - hydrate at 245°, and 1,2-propylene diamine was liberated above 350° by heating of the corresponding chromium complex[16]. The formation of complexes of beryllium chloride with varying amounts of iso-capronitrile, propionitrile, and *p*-tolunitrile has been shown[17] by thermal analyses, while beryllium chloride complexes of cyanonaphthalene and acetonitrile could not be thermally analysed because of their ease of charring. However, in the present work, 1-cyanonaphthalene was recovered from its iron- and zinc chloride complexes by heating. Cuprous chloride is also known to form complexes with 1- and 2-cyanonaphthalene[18].

Pyrolysis of such complexes may not be the most desirable method for recovery, as indicated above, since certain types of nitrogen compounds may decompose or rearrange. Also, certain of the complexes may be very stable and may not decompose into the salt and the nitrogen compound on heating. The high stability, *e.g.* of vanadium and nickel complexes of porphyrins at elevated temperatures is well known[19,20], and such complexes are found even in high boiling petroleum distillates. Since decomposition of the metal complexes with acids[21], bases, or hydrogen sulfide[22] is less drastic, these treatments could possibly be used to isolate other types of nitrogen compounds from petroleum products.

The identification of phenanthrene and some of its alkyl derivatives among the nitriles was unexpected as stated previously. It is known that antimony (V) chloride[23], antimony(III) chloride, stannic chloride and aluminum chloride[24] react at room temperature forming precipitates with aromatic hydrocarbons such as indene, anthracene, and diphenylmethane. Such a reaction, if possible with ferric and zinc chlorides, would also explain the presence of phenanthrenes. This study indicated that pure phenanthrene can be completely extracted from a mixture of ferric and zinc chlorides using hexane as solvent. However, it is difficult completely to extract phenanthrene from this mixture when mixed with nitriles; this indicates a greater degree of entrainment of phenanthrene when the metal complexes are also present.

Applying complex formation to the nonbasic nitrogen fraction of a hydrogenated oil led to the isolation and identification of several nitriles in this work. Previously, nitriles such as benzonitrile, 2-methyl-, and 3-methyl-benzonitrile had been identified in shale oil by mass spectrometry[25], and nitriles in general were also detected as hydrolyzable nitrogen compounds in shale oil[26-28]. To our knowledge, however, the presence of nitriles in petroleum has not been reported previously.

In the present study, ultraviolet and mass spectra indicated the presence of dicyanobenzene, cyano-2,3-dihydroindene, cyanonaphthalene, dicyano-2,3-dihydroindene, and dicyanonaphthalene, whereas the presence of dicyanocyclohexane, cyanoindene, dicyanoindene, cyanobiphenyl, dicyanooctahydronaphthalene, and/or several of their alkyl derivatives was detected only by mass spectrometry. It is evident that these compounds resisted catalytic hydrogenation, but this study did not reveal whether they were originally present in the crude oil, or if they were formed in the process of refining and hydrogenation. Since the nitriles reacted with ferric and zinc chlorides, they may also have an affinity for metal-containing catalysts. The need for a study of the conditions for removal of nitriles from petroleum process streams is apparent. The application of analytical methods different from those described here for the qualitative and quantitative determination of nitriles may give information beyond that obtained in this study[27,29-33].

ACKNOWLEDGEMENTS

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SUMMARY

Nitrogen compounds were completely removed from a hydrogenated furnace oil by shaking with a mixture of ferric chloride and zinc chloride. The resulting complexes were separated from the oil and thermally decomposed to liberate the nitrogen compounds. After removal of nitrogen bases with hydrochloric acid and indoles, carbazoles, and phenazines with perchloric acid, the nitrogen compounds remaining in the concentrate were separated by fractional elution from an aluminum oxide column and gas chromatography. The following compounds were identified or their presence was indicated in the resulting fractions by their ultraviolet and/or mass spectra: dicyanobenzene, dicyanocyclohexane, cyanoindene, cyano-2,3-dihydroindene, cyanonaphthalene, dicyanoindene, dicyano-2,3-dihydroindene, dicyanonaphthalene, cyanobiphenyl, dicyanooctahydronaphthalene, and/or several of their alkyl derivatives.

RÉSUMÉ

Une méthode est proposée pour l'identification des nitriles dans le pétrole. On procède comme suit: formation de complexes métalliques. Après élimination des bases azotées (par l'acide chlorhydrique), des indoles, carbazoles et phénazines (par l'acide perchlorique), les composés azotés qui restent sont séparés par élution fractionnée d'une colonne d'alumine et chromatographie gazeuse, et identifiés par leurs spectres dans l'ultra-violet et par leurs spectres de masse.

ZUSAMMENFASSUNG

Beschreibung einer Methode zum Nachweis und Identifizierung von Nitrilen in hydriertem Heizöl. Nach Isolierung der Stickstoffverbindungen und Abtrennung der Stickstoffbasen werden die Nitrile mit Hilfe von Säulen- und Gaschromatographie getrennt und durch Ultraviolett- und Massenspektren identifiziert. Die nachgewiesenen Nitrile werden angegeben.

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PHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF MAGNESIUM IN ROCKS*

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INTRODUCTION

The classical scheme of analysis of silicate rocks and related materials[1-3] has been partly replaced in recent years by a number of so-called "rapid methods"[4-11]. These methods generally involve photometric determination of alumina, silica, iron, manganese, phosphorus, titania, etc., flame photometric determination of sodium and potassium, and compleximetric titration of calcium and magnesium.

The "rapid methods" used at the Geological Survey of Canada are modified versions of those described by SHAPIRO AND BRANNOCK[5,7]. For the determination of magnesium an aliquot of the sulfuric acid master solution, containing 100 mg of sample, is treated with ammonium hydroxide to precipitate the R_2O_3 group. The suspension is then diluted to volume in a volumetric flask and filtered through a dry paper. Two aliquots of the filtrate, each containing 20 mg of sample, are titrated with standard EDTA solution, one at pH 10 with Eriochrome Black T as indicator, the other at pH 12.5 with Cal-Red[12]. The magnesium content is represented by the difference between the two titrations.

With samples containing less than 1% MgO (corresponding here to about 120 μg of magnesium), results by the titrimetric method tend to be uncertain. A photometric method is now proposed, in which the sample preparation and chemical separations remain unchanged.

COLORIMETRIC DETERMINATION OF MAGNESIUM

A method based on the thiazol yellow lake[13] was tried but results were erratic, as was expected from earlier experience[14].

The superiority of reactions which form soluble colored complexes, rather than lakes, has been pointed out by SANDELL[15]. Thus Eriochrome Black T[16] and bis-salicylidene-ethylenediamine[17] have been applied as colorimetric reagents for magnesium, although calcium interferes in both cases.

MANN AND YOE[18,19] have described 2 reagents which form soluble reddish complexes with magnesium at pH 8.95 in the presence of ethanol. One of these (Fig. 1. A) is available commercially under the trivial name "Magon". We propose the name "Magon Sulfonate" for the other; the chemical name is sodium 1-azo-2-hydroxy-3-

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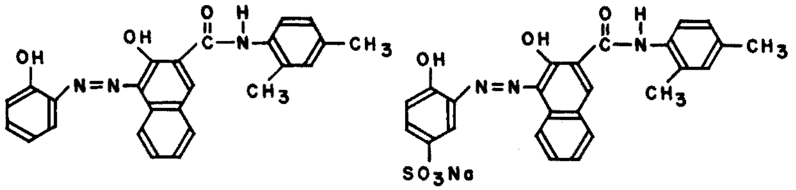
(2,4-dimethylcarboxanilido)-naphthalene-1'-(2-hydroxybenzene-5-sulfonate). SATO AND TAKEUCHI[20] have applied Magon Sulfonate while OGATE AND HOROI[21] have used Magon for traces of magnesium in sodium chloride.



A

MAGON

(REF. 19)

B

MAGON SULFONATE

(REF. 18)

Fig. 1. Mann and Yoe reagents for magnesium.

In the proposed procedure an aliquot of the ammoniacal filtrate, representing 0.8 mg of sample, is evaporated to dryness after the addition of a solution containing 20 μg of calcium and 1 ml each of concentrated hydrochloric and nitric acids. This treatment decomposes ammonium sulfate and the sulfuric acid liberated is removed by fuming. The residue is dissolved in a small volume of water. An ethanolic solution of Magon Sulfonate is then added, followed by triethanolamine and borax buffer. The quantity of Magon Sulfonate is the same as that recommended by MANN AND YOE, but the quantity of borax is double that used by them. The solution is diluted to 25 ml with ethanol, and absorbance is measured at 510 mμ after 1 h.

APPARATUS AND REAGENTS

Photometric measurements were made on both the Beckman DU and the Beckman B Spectrophotometers.

Magon and Magon Sulfonate were obtained from the La Motte Chemical Products Co., Chestertown, Md. The triethanolamine was Eastman No. 1599. All other reagents were of analytical reagent grade. All water used was both distilled and de-ionized.

PROCEDURE

Reagents

Standard magnesium solution. Dissolve 0.060 g of magnesium ribbon by heating with 5 ml of water and 2 ml of hydrochloric acid. Cool and make up to 1 l in a volumetric flask. Store in a polyethylene bottle. Just before use, transfer a 10-ml aliquot to a 250-ml volumetric flask, add 1 ml of sulfuric acid (1:1), and make up to volume (1 ml contains 4 μg MgO).

Acid blank solution. Dilute 1 ml of sulfuric acid (1:1) to 250 ml.

Acid calcium solution. Dissolve 0.25 g of calcium carbonate by heating with 5 ml of water and 2 ml of hydrochloric acid. Cool and make up to 500 ml in a volumetric flask. Store in a polyethylene bottle. Transfer a 10-ml aliquot to a 1-l beaker. Add, with stirring, 290 ml of water, 100 ml of hydrochloric acid and 100 ml of nitric acid. Store in a polyethylene bottle.

Reagent solution. Weigh 0.015 g of Magon Sulfonate into a 150-ml beaker. Add 100 ml of 95% ethanol. Cover and dissolve by gentle warming and magnetic stirring. Prepare fresh daily.

Triethanolamine solution. Mix 15 ml of triethanolamine with 60–70 ml of water and dilute to 100 ml.

Borax buffer (0.08 *M*). Dissolve 3.05 g of $Na_2B_4O_7 \cdot 10H_2O$ in 80–90 ml of water and dilute to 100 ml.

Method

Weigh 0.4000 g of sample (100-mesh or finer) into a 90-ml platinum crucible. Add 1–2 ml of water, and, with caution, 10 ml of hydrofluoric acid and 3 ml of sulfuric acid. Cover the crucible and digest on a steam bath overnight. Remove the cover and heat on a sand bath until the volume of liquid is reduced to about 3 ml. Cool, add 1 ml of nitric acid, and continue heating until sulfur trioxide fumes are evolved. (If there is any sign of charring at this point, repeat the nitric acid treatment and evaporation to fumes.) Cool and transfer the solution to a 400-ml Vycor beaker. Dilute to 100 ml and boil to complete solution. (A persistent white residue, if present, is likely barium sulfate.) Cool, filter if necessary, and make up to 200 ml in a volumetric flask. (Aliquots of this solution are also used in the determination of iron, titanium, phosphorus, manganese, sodium and potassium.)

Transfer a 50-ml aliquot (*i.e.* 100 mg of sample) to a 250-ml volumetric flask and dilute to about 200 ml. Add 10 ml of 25% w/v ammonium chloride solution and a drop of methyl red indicator. Add ammonium hydroxide, dropwise with swirling, until the indicator turns yellow, then 2 or 3 drops in excess. Make up to volume, mix, and set aside for 30 min. Filter through a dry, 9-cm. Whatman No. 40 filter paper into a dry 300-ml. Erlenmeyer flask. Stopper the flask. (Aliquots of this solution are also used for the determination of calcium and magnesium by EDTA titration.)

For samples where the EDTA titrations indicate a MgO content under 2%, transfer a 2-ml aliquot of the above filtrate (*i.e.* 0.8 mg of sample) to a 20-ml beaker. Into another 20-ml beaker, pipette 2 ml of acid blank solution, for use as a blank. One or more standards may be prepared, approximating the expected compositions of the samples, by pipetting appropriate volumes of standard magnesium solution into 20-ml beakers. (Each ml of standard magnesium solution corresponds to 0.5% MgO.)

Add 5 ml of acid calcium solution to each of the 20-ml beakers. Evaporate to the appearance of sulfur trioxide fumes, and continue heating until fumes are no longer evolved. If necessary, warm each beaker gently over a burner to evaporate any sulfuric acid which may condense on the beaker walls. Allow to cool. Add 5 ml of water to each beaker, cover, and warm to dissolve all residue, boiling if necessary. Allow to cool.

Transfer to 25-ml volumetric flasks, rinsing each beaker twice with 3–5-ml volumes of ethanol. To each flask, add 5 ml of reagent solution, 0.5 ml of triethanolamine solution and 1 ml of borax buffer. Dilute to volume with ethanol, mix, and set aside for 1 h.

Fill a 1-cm absorption cell with water, place in the spectrophotometer, and adjust the instrument to zero absorbance at 510 mμ. Fill another cell with the blank and measure its absorbance immediately. Measure the absorbances of all the standards, then of all the samples, and finally on fresh portions of the blank and standard solutions from the volumetric flasks. Measure each absorbance immediately after filling the absorption cell. Keep the volumetric flasks stoppered.

Subtract the mean blank reading from all the other readings. Calculate the MgO content of each sample solution by linear interpolation of absorbances between the 2 standards giving readings closest to that of the sample.

DISCUSSION AND RESULTS

The concentration of ammonium sulfate in the sample aliquot is sufficient to prevent attainment of pH 8.95 on addition of the borax buffer, and also sufficient to produce a calcium sulfate turbidity in the ethanolic medium. The nitric–hydrochloric acid treatment, followed by the removal of the liberated sulfuric acid, eliminates both of these effects.

Effect of calcium

According to MANN AND YOE[18], calcium increases the absorbance of the magnesium complex of Magon Sulfonate, but the effect is nearly constant over the range of 0.4–12 p.p.m. of calcium. They report no calcium effect on the Magon complex[19], up to 20 p.p.m. Above the limiting concentrations, they state that calcium forms a red precipitate with both reagents.

To study this effect, varying amounts of calcium and magnesium were carried through the procedure of MANN AND YOE[18]. The results (Table I) showed that calcium enhances the absorbance of the blank (*i.e.* the solution containing no magnesium) to an extent equivalent to about 1 μg of magnesium, but there is very little effect on the solutions actually containing 5 μg of magnesium. Thus, on subtracting the absorbance of the blank from that of the sample, the result is a net *decrease* in the magnesium absorbance. The data in Table I were obtained with Magon, but the same effect was observed with the sulfonated reagent.

TABLE I

EFFECT OF CALCIUM

Ca present (μg)	*Mg found (μg)*	
	none present	*5 μg present*
50	1.1	5.2
100	0.7	4.6
150	0.9	4.6
200	1.0	5.1
250	1.1	4.8

The calcium addition in the proposed procedure assures that all samples containing up to about 40% CaO fall within the range of constant calcium effect.

Effect of aluminum

The MANN AND YOE procedure, when applied in our scheme without modification, gave high results on analysed samples, even though some magnesium might have been lost in the R_2O_3 separation. It is also possible, however, that aluminum is not completely separated in this step, and this could cause high results[18,19]. Triethanolamine was therefore investigated as a possible masking agent for any aluminum present in the filtrate from the R_2O_3. Aliquots of several samples were taken through the proposed procedure, with varying amounts of triethanolamine. The results (Table II) demonstrated the efficacy of triethanolamine. The one sample which gave high results with the larger triethanolamine addition contained much more aluminum than that found in silicate rocks. A still higher triethanolamine addition might bring that sample into line. Since triethanolamine has a slight effect on sensitivity and color stability, a constant amount must be used with blanks, standards and samples.

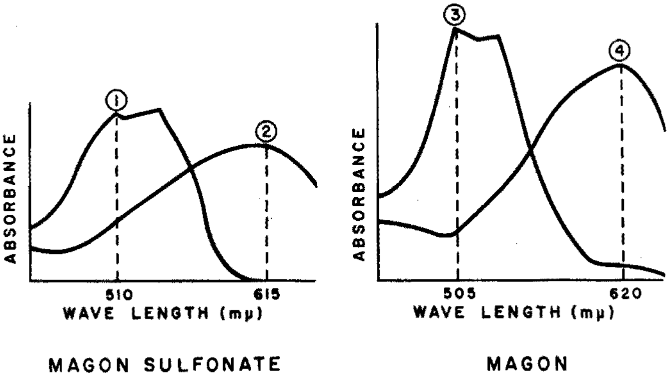
TABLE II

EFFECT OF TRIETHANOLAMINE

Present (%)		*MgO found (%)*		
			Triethanolamine added	
Al_2O_3	*MgO*	*none*	*27 mg*	*80 mg*
14.9	0.20	0.87	0.38	0.21
14.8	0.35	0.79	0.50	0.35
16.3	0.53	1.74	1.32	0.63
7.4	0.63	1.43	0.79	0.69
17.6	0.76	1.76	1.18	0.94
33.9	0.93	—	—	1.44

Color stability

According to MANN AND YOE, maximum absorbance is attained by the Magon Sulfonate complex about 30 min after mixing, and by the Magon complex immediately after mixing. Both complexes are reported to be stable for at least 1 h.



MAGON SULFONATE MAGON

(COURTESY OF "ANALYTICAL CHEMISTRY")

Fig. 2. Absorption spectra (after Mann and Yoe). 1. Magnesium complex (excess magnesium). 2. Free reagent[18]. 3. Magnesium complex (excess reagent). 4. Free reagent[19].

Figure 2 shows that the colored systems produced with magnesium by both reagents involve mixtures of the pink of the complex and the blue of the excess reagent. Since excess of reagent is always present in a magnesium determination, absorbance measurements made at the peak wavelength of the complex will include a variable component due to excess reagent. The magnitude of that component will decrease with increasing concentration of magnesium. Thus the sensitivity of the reaction could be enhanced, theoretically, by correcting for the absorbance due to excess reagent. Such correction can be accomplished by measuring the absorbance of the mixed color system at the peak wavelength of the reagent, where the absorption of the complex is negligible. There is a linear relationship between the absorbances of the reagent at the 2 wavelengths, a relationship which can be established by measuring the 2 absorbances in a series of solutions containing varying concentrations of reagent, but no magnesium.

In our work, an attempt to construct such a "correction curve" revealed a new effect not mentioned by MANN AND YOE. A solution containing Magon, but no magnesium, was taken through the procedure. After a one-h wait, an absorption cell was filled with the final solution and a series of absorbance measurements made, alternately at 620 and at 505 mμ, without refilling the cell. Table III shows the effect observed.

TABLE III

INSTABILITY OF COLOR

Min after filling cell	*Absorbance*	
	620 mμ	*505 mμ*
1	0.652	—
2	—	0.274
4	0.651	—
5	—	0.274
6	0.642	—
7	—	0.278
8	0.639	—
9	—	0.281
11	0.638	—
12	—	0.282
13	0.635	—
14	—	0.283

Clearly, the absorbance at 620 mμ appears to diminish steadily (after the first 5 min) while that at 505 seems to increase, roughly in inverse proportion. On refilling the absorption cell with fresh solution from the volumetric flask (which had been stoppered in the interval) the reading at 620 was restored to a slightly *higher*, and that at 505 to a slightly *lower*, value than the initial readings. Further readings on the new portions showed the same patterns of change as before.

In a series of tests with both reagents, with varying concentrations of magnesium, triethanolamine and borax, no means could be found to eliminate this effect. However, it was found to be less pronounced with increasing magnesium content, suggesting that the effect is a property of the excess reagent. Further, it can be diminished by using Magon Sulfonate in preference to Magon, and by increasing the concentrations of borax and of triethanolamine.

Because of this instability effect, it is not advisable to attempt to correct for that component of the absorbance due to excess reagent. The absorbance should be measured immediately after filling each absorption cell. Two or three standard solutions can be analysed with each batch of samples, and the results calculated by linear interpolation of absorbances.

Results

Table IV gives a comparison of results obtained by the proposed method with those obtained by other methods.

TABLE IV

RESULTS ON ANALYSED SAMPLES

Sample		*MgO (%)*		
No.	*Type*	*Proposed method*	*Titrimetric EDTA*	*Gravimetric pyrophosphate*
NBS-177	cement	2.48	—	2.45[a]
NBS-1A	limestone	2.28	—	2.18[a]
NBS-198	refractory	0.06	—	0.07[a]
G-1	granite	0.35	—	0.37[b]
R-1875	granite	0.63	—	0.53
R-1873	granite	0.14	0.04	0.17
R-1874	granite	0.70	0.73	0.75
R-1893	rock	1.16	1.10	1.10
A-973	sandstone	1.59	1.39	—
A-966	sandstone	0.40	0.20	—
A-918	sandstone	1.28	1.22	—
A-919	sandstone	1.09	1.20	—
A-970	sandstone	1.13	1.07	—

[a] Certificate value.
[b] Ref. 22.

CONCLUSIONS

The method of MANN AND YOE can be adapted to existing systems of "rapid" rock analysis, with slight modification. Although the magnesium percentages involved are too high to be considered as traces, the absolute quantities of magnesium are of the order of a few micrograms. With slight further modification, the method should be applicable to much lower percentages of magnesium.

Note: After this work was completed, the authors' attention was drawn to a paper by APPLE AND WHITE[23], in which Magon Sulfonate, unfortunately referred to as "Magon", was used in the determination of traces of magnesium in beryllium oxide. In a personal communication, one of those authors mentioned observing an instability effect somewhat similar to that described in this work.

SUMMARY

The method of MANN AND YOE has been adapted to the determination of small amounts of magnesium in a "rapid method" scheme of rock analysis. The effect of calcium is found to be different from that described by the original authors. Triethanolamine is introduced as a masking agent for aluminum. Anomalous instability of the color system requires a revised photometric technique.

RÉSUMÉ

Les auteurs ont adapté la méthode photométrique de MANN ET YOE au dosage de faibles teneurs en magnésium dans des roches. L'aluminium est masqué par la triéthanolamine.

ZUSAMMENFASSUNG

Beschreibung einer Modifikation der photometrischen Methode von MANN UND YOE zur Bestimmung kleiner Mengen von Magnesium in Gesteinen. Aluminium wird mit Triäthanolamin maskiert.

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SPEKTROPHOTOMETRISCHE BESTIMMUNG VON SCANDIUM MIT 4-2(-PYRIDYLAZO)RESORCIN

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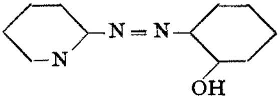
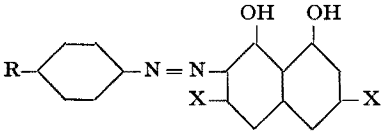
(Eingegangen den 5. Februar, 1962)

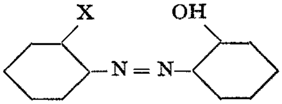
2-Pyridylazofarbstoffe bewährten sich als ausserordentlich empfindliche Reagentien für viele Metallionen und erlauben den Nachweis und die spektrophotometrische Bestimmung von Spuren von Bi^{3+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, UO$_2$$^{2+}$, Y^{3+}, Ga^{3+}, In^{3+}, Tl^{3+}, Sc^{3+}.[1] Für eine Reihe von Metallionen sind diese Azofarbstoffe mit der Donoratomgruppe (I) empfindlicher als die Azofarbstoffe mit den Gruppierungen (II, III), weil im allgemeinen die Reaktionen jener Metallionen, die eine Bindung an Stickstoff bevorziehen, stärker ausgeprägt sind:



(I)



(II)



(III)

Inzwischen hat sich 4-(2-Pyridylazo)resorcin als Indicator bei Titrationen von Pb^{2+},[2] Er^{3+},[3] In^{3+},[4] Bi^{3+} und mehreren zweiwertigen Metallionen mit ÄDTA[5,6] gut bewährt. Es sind auch spektrophotometrische Bestimmungen von Co^{2+}, Pb^{2+} und UO$_2$$^{2+}$ [7] beschrieben und Chelate einer Reihe von Me(II), und Bi^{3+} spektrophotometrisch untersucht worden[6,8].

4-(2-Pyridylazo)resorcin gibt mit Sc^{3+} in schwach saurem Medium intensiv rote Färbungen. In dieser Arbeit wird auf Grund der Untersuchungen der Chelate in Lösungen eine spektrophotometrische Bestimmung kleiner Mengen von Sc^{3+} beschrieben.

EXPERIMENTELLER TEIL

Reagentien und Apparate

Zur Herstellung der Reagenslösung wurde das Mononatriumsalz des 4-(2-Pyridylazo)resorcins aus eigener Synthese[5,6] oder das Präparat der Fa. Merck verwendet nach Feststellung des Gehaltes an Wasser und Verunreinigungen (Na$_2$CO$_3$)[6]. Die Standardlösungen von Sc(ClO$_4$)$_3$ und ScCl$_3$ wurden aus Sc$_2$O$_3$ bereitet und gravimetrisch mittels 8-Hydroxychinolin kontrolliert oder chelatometrisch auf Xylenolorange[9] eingestellt. Alle Chemikalien namentlich Puffer und Salze für die Einstellung der Ionenstärke waren analytisch rein; zur Herstellung der Lösungen wurde bidestilliertes Wasser verwendet.

Die Extinktion wurde mit einem Spektrophotometer SF-4 (Küvette, 1–10 mm), das pH mit dem Röhren-pH-Meter PHM 22, Radiometer gemessen.

Chelate von 4-(2-Pyridylazo)resorcin (PAR) mit Sc^{3+}

In den Lösungen mit Sc^{3+}-Überschuss bildet sich von pH $\geqslant 2$ an ein Chelat der Zusammensetzung $Sc:R = 1:1$, dessen Bildung bei pH $\geqslant 5$ praktisch quantitativ ist (Abb. 1, Kurve 1). In äquimolaren Lösungen von PAR und Sc^{3+} ist der pH-Bereich der Bildung dieses Chelates nur wenig beeinflusst; bei pH 5.2 steigt aber die Extinktions–pH-Kurve steil an und erreicht keinen horizontalen Teil (Abb. 1, Kurve 3), da sich ausserdem noch ein Chelat $Sc:R = 1:2$ bildet und die Existenz–pH-Bereiche beider Chelate sich überlagern. Der Übergang des Chelates $Sc:R = 1:1$ in das Chelat $Sc:R = 1:2$ ist am deutlichsten an einer Extinktions–pH-Kurve der Lösungen mit Reagensüberschuss ($p = c_R/c_{Sc} = 5$) bemerkbar (Abb. 1, Kurve 2). Die Zusammensetzung der beiden Chelate wurde auch nach der Variationsmethode in äquimolaren Lösungen[10] bestätigt. Bei pH = 2.81 liegt das Maximum der Jobschen Kurve für $c_0 = 3.92 \cdot 10^{-4}\,M$ und $\mu = 0.1$ bei dem Verhältnis $Sc:R = 1:1$, bei pH = 3.92 entspricht es für $c_0 = 1.34 \cdot 10^{-4}\,M$, $\mu = 0.1$ und 520–560 mμ schon einem Gemisch der Chelate $Sc:R = 1:1$ und $1:2$. Die Gestalt der Kurven weist auf eine erhebliche Dissoziation der Chelate im gemessenen pH-Bereich hin. In dem entsprechenden pH-Bereich bildet sich das Chelat $Sc:R = 1:1$ nach der Gleichgewichtsreaktion:

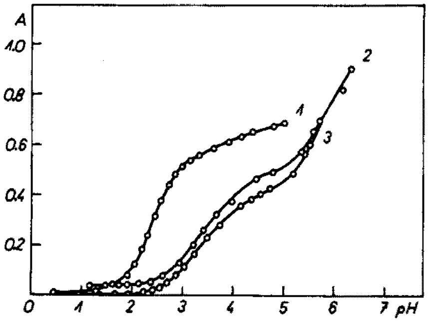


Abb. 1. Extinktions–pH-Kurven den Scandiumchelaten mit PAR. Kurve 1. $[PAR] = 7.46 \cdot 10^{-5}\,M$, $[Sc] = 2.79 \cdot 10^{-3}\,M$, $\mu = 0.1$, 550 mμ; Kurve 2. $[PAR] = 1.73 \cdot 10^{-4}\,M$, $[Sc] = 3.54 \cdot 10^{-5}\,M$, $\mu = 0.4$, 550 mμ; Kurve 3. $[PAR] = [Sc] = 8.94 \cdot 10^{-5}\,M$, $\mu = 0.1$, 560 mμ.

$$Sc^{3+} + H_3R^+ \rightleftarrows ScRH^{2+} + 2H^+$$

Der mol.Extinktionskoeffizient ε_k und die Gleichgewichtskonstante k_1 werden aus Punktpaaren am aufsteigendem Ast der pH-Kurve der Lösungen mit Sc^{3+}-Überschuss bei 560 mμ berechnet, wo das Reagens praktisch nicht mehr absorbiert, und zwar nach dem Verfahren, das schon früher an anderer Stelle veröffentlicht worden ist[6]. Die Resultate wurden mit denen für 520 mμ für den Fall gleichzeitiger Extinktion des Reagenses ergänzt. Es gilten hier folgende Gleichungen:

$$k_1 = [ScRH][H]^2/[Sc][H_3R] \tag{1}$$

$$[R]_0 = [ScRH] + [H_3R] + K_{a_1}[H_3R][H]^{-1} \tag{2}$$

$$[Sc]_0 = \text{const.}$$

$$A = \varepsilon_k\,[ScRH] + \varepsilon_1\,[H_3R] + \varepsilon_2\,[H_2R] = \varepsilon_k\,[ScRH] + \varepsilon_1\,[H_3R] + \varepsilon_2\,K_{a_1}\,[H_3R]\,[H]^{-1} \tag{3}$$

Für das Punktpaar $P_1(H_1,A_1) - P_2(H_2,A_2)$ ist dann

$$\varepsilon_k = \frac{A_1 H_2{}^2 a_2 - A_2 H_1{}^2 a_1}{[\mathrm{R}]_0 H_2{}^2 a_2 - [\mathrm{R}]_0 H_1{}^2 a_1} \tag{4}$$

a_1, a_2 haben folgende Bedeutung:

$$a_1 = [\mathrm{R}]_0 \varepsilon_1 + [\mathrm{R}]_0 \varepsilon_2 K_{a_1} H_1{}^{-1} - A_1 - A_1 K_{a_1} H_1{}^{-1};\ a_2 = [\mathrm{R}]_0 \varepsilon_1 + [\mathrm{R}]_0 \varepsilon_2 K_{a_1} H_2{}^{-1} - A_2 - A_2 K_{a_1} H_2{}^{-1}.$$

Für die Gleichgewichtskonstante k_1 und die Stabilitätskonstante K_1 erhält man folgende Werte:

$$k_1 = a[\mathrm{H}]^2/[\mathrm{Sc}]_0(\varepsilon_k[\mathrm{R}]_0 - A) \tag{5}$$

$$K_1 = [\mathrm{ScRH}]/[\mathrm{Sc}][\mathrm{RH}] = k_1/K_{a_1}K_{a_3} \tag{6}$$

ε_k = mol.Extinktionskoeffizient des Chelates; mol. Extinktionskoeffizient des Pyridiniumkation von PAR (H_3R^+) bei 520 mμ: $\varepsilon_1 = 2.27 \cdot 10^3$; mol. Extinktionskoeffizient von freien PAR (H_2R) bei 520 mμ: $\varepsilon_2 = 1.69 \cdot 10^3$; $K_{a_1} = 10^{-3.08}$ und $K_{a_3} = 10^{-11.92}$ sind die Dissoziationskonstanten der Stufen H_3R^+ und HR^- von PAR. (Über die Dissoziation von PAR siehe[6].)

Das Hydroxyl-proton in *para*-Stellung zur Azogruppe wird bei der Chelatbildung nicht abgespalten[6]. Die Ladungen der Ionen sind in den Gleichungen der besseren Übersicht wegen, nich angegeben.

Von der Gleichung (4) ergeben sich folgende Werte für ε_k:

520 mμ $\varepsilon_k = 1.47 \cdot 10^4$ (Durchschnitt von 7 Werten)
560 mμ $\varepsilon_k = 4.80 \cdot 10^3$ (Durchschnitt von 8 Werten)

Die durchschnittlichen Werte für k_1 und K_1 sind dann:

	k_1	K_1
520 mμ	$10^{-2.17}$	$10^{12.81}$
560 mμ	$10^{-2.11}$	$10^{12.87}$

In der Reihe der Stabilitätskonstanten der von uns bisher untersuchten Chelaten MRH von 4-(2-Pyridylazo)resorcin liegt der Wert für Sc^{3+} zwischen Pb^{2+} und Cu^{2+}:

	Bi^{3+}	Cu^{2+}	Sc^{3+}	Pb^{2+}	Zn^{2+}	Cd^{2+}
log K_1	17.2	16.5	12.8	11.9	11.6	11.5

Die rechnerische Analyse des zweiten steigenden Astes der pH-Kurven 2, 3 in Abb. 1 war ausserordentlich schwierig und gab für die Konstanten des Chelates ScR_2^- infolge gleichzeitiger Hydrolyse von Sc^{3+} keine übereinstimmenden Resultate.

Spektrophotometrische Bestimmung von Scandium

Wie aus den Extinktions-pH-Kurven für äquimolare Lösungen und Lösungen mit kleinen Reagensüberschuss hervorgeht (Abb. 1), kann nur das Chelat $ScRH^{2+}$ (λ max 505 mμ) für die Ausarbeitung einer spektrophotometrischen Methode bei pH 3.5–5 verwendet werden. Da in diesem pH-Bereich das Reagens überwiegend als H_2R, teilweise auch als H_3R vorliegt[6], die bei 505 mμ noch erheblich absorbieren, werden die praktische Messungen bei 530 mμ ausgeführt. Die pH-Kurven zeigen aber keinen ausgeprägten horizontalen Teil für die quantitative Bildung von $ScRH^{2+}$. Die Extinktionsänderung ist bei pH 4.5–4.8 für Lösungen mit 5-fachen Reagensüberschuss relativ klein, aber auch hier beeinflusst schon eine kleine pH-Änderung in nicht gepufferten Lösungen die Extinktion erheblich, sodass die Herstellung einfacher Kalibrationskurven für Scandium schwierig wird.

Die Absorptionskurven der Lösungen mit Scandiumüberschuss (Abb. 2) gehen in Abhängigkeit vom pH nur durch einen unscharfen isosbestischen Punkt in pH-Bereich 1.9–4.8 (3 absorbierende Komponenten: H_2R, H_3R^+, $ScRH^+$); bei pH > 4.9 wird bereits die Bildung des Chelats ScR_2^- bemerkbar. Für die Lösungen mit 5-fachen Überschuss an Reagens haben die Absorptionskurven von pH > 5 ein einheitliches Maximum bei 510 mμ, das dem Chelat ScR_2^- entspricht.

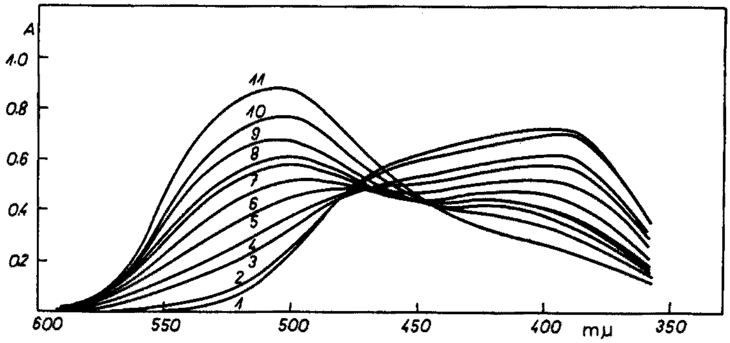


Abb. 2. Absorptionskurven der Lösungen mit Sc und PAR in Abhängigkeit von pH. [PAR] = $3.62 \cdot 10^{-5}$ M, [Sc] = $1.40 \cdot 10^{-3}$ M, $\mu = 0.1$. Kurve 1. pH 1.21; 2. pH 1.93; 3. pH 2.36; 4. pH 2.51; 5. pH 2.73; 6. pH 2.98; 7. pH 3.54; 8. pH 4.09; 9. pH 4.90; 10. pH 5.12; 11. pH 5.43.

Einfluss von Ionenstärke

Mit steigender Ionenstärke der Lösungen (KNO_3, $NaClO_4$) sinkt die Extinktion bei pH 3.75 und für 530–550 mμ schon von $\mu = 0.1$.

μ	0	0.1	0.2	0.3	0.4	0.5
% Extinktion	100	84–86	78–81	73–76	67–71	62–67

Einfluss von Puffern

Die Extinktion vermindert sich ebenfalls erheblich bei pH 3.7–4.5 in Gegenwart

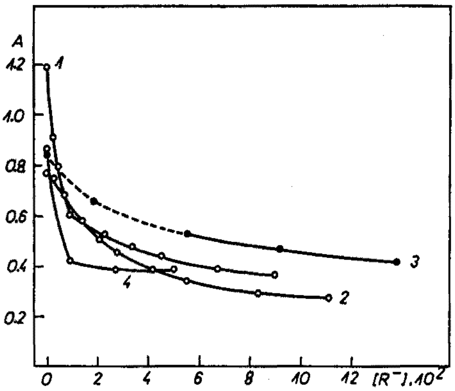


Abb. 3. Einfluss der Puffer auf die Extinktion der Lösungen der Sc–PAR Chelate. 1 Teil = $2 \cdot 10^{-2}$ M als Pufferanion, [PAR] = $1.71 \cdot 10^{-4}$ M. Kurve 1. Acetat, [Sc] = $4.19 \cdot 10^{-5}$ M, $\mu = 0.2$, pH 3.99; Kurve 2. Formiat, [Sc] = $5.03 \cdot 10^{-5}$ M, $\mu = 0.1$, pH 3.76; Kurve 3. Chloracetat, [Sc] = $5.03 \cdot 10^{-5}$ M, $\mu = 0.2$, pH 3.76; Kurve 4. Biphtalat, [Sc] = $5.03 \cdot 10^{-5}$ M, $\mu = 0.2$, pH 3.86.

von Acetat-, Formiat-, Chloracetat- und Kaliumbiphtalatpuffer (Abb. 3). Relativ klein ist der Einfluss von Formiat; das Lambert-Beersche Gesetz wird dann aber schon bei kleinen Konzentrationen von Sc^{3+} nicht mehr befolgt. In Gegenwart von Natriumacetat und bei pH 4.5 erlauben Kalibrationskurven für $\mu = 0.1$ eine einfache Bestimmung von Scandium im Bereich von 0.4–7 μg Sc/ml bei strenger Einhaltung der gleichen Pufferkonzentration in den Mess- und Vergleichslösungen (Abb. 4).

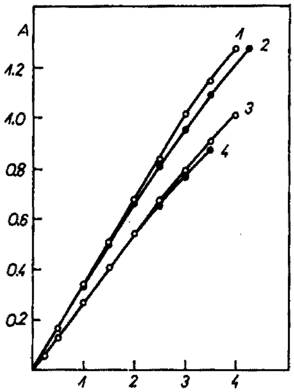


Abb. 4. Kalibrationskurve für Scandium in Gegenwart von Natriumacetat. [PAR] = $3.42 \cdot 10^{-4}$ *M*, 1 Teil = 1.50 μg Sc/ml, $\mu = 0.1$. Die Extinktion des Reagenses abgezogen. Kurve 1. pH 4.5, 530 mμ; 2. pH 4.0, 530 mμ; 3. pH 4.5, 520 mμ; 4. pH 4.0, 520 mμ.

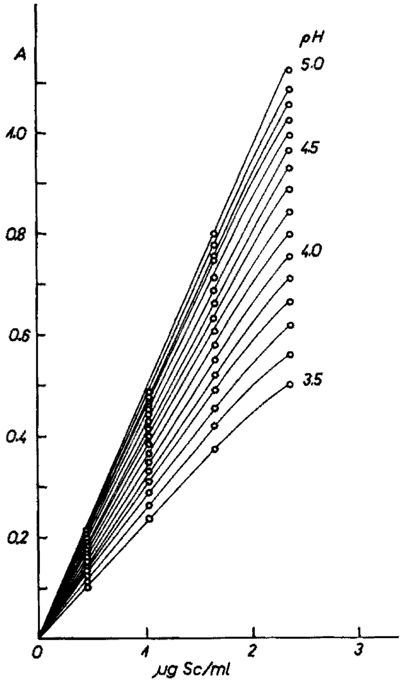


Abb. 5. Kalibrationskurvennomogramm für Scandium für pH 3.5–5.0. [PAR] = $1.92 \cdot 10^{-4}$ *M* $\mu = 0.4$ ($NaClO_4$) 530 mμ.

Diese Bestimmung ist aber weniger empfindlich als die in nicht-gepufferten Lösungen: für $A = 0.01$ 0.044 μg Sc/cm^2.
Scandium wird hier zu relativ stabilen, farblosen Konkurenzkomplexen mit den Anionen der Pufferlösungen als Liganden gebunden.

Für die Bestimmung von Scandium in nicht-gepufferten Lösungen, die empfindlicher ist, wurden bei konstanten μ, λ und Reagensüberschuss Sc : R = 1 : 180 —4 für den pH-Bereich 3–5 (die Bildung von $ScRH^{2+}$) Extinktions-pH-Kurven für verschiedene Konzentrationen von Scandium aufgenommen. Von den pH-Kurven ist dann graphisch ein Nomogramm von Kalibrationskurven für alle 0.1 pH-Einheiten hergestellt worden. Für $\mu = 0.4$ ($NaClO_4$), 0.05–2.4 μg Sc/ml und $c_R = 1.916 \cdot 10^{-4}$ *M* sind diese Kalibrationskurven praktisch linear. Um die unbekannte Konzentration von Scandium zu bestimmen muss man die Extinktion und das pH der Lösung genau messen und den entsprechenden Wert für c_{Sc} in dem Nomogramm zwischen Kalibrationskurven der zwei am nähesten gelegenen pH-Werte interpolieren (Abb. 5).

AUSFÜHRUNG DER METHODE

In einem 50-ml Messkolben werden zur schwach sauren Probelösung, die Scandium als Chlorid, Perchlorat oder Nitrat enthält, 10 ml der PAR-Natriumsalzlösung (228 mg/l) zugegeben, mit Ammoniak oder $HClO_4$ auf ein pH von 3–5 eingestellt, die Gesamtionenstärke mit 1 *M* $NaClO_4$ auf $\mu = 0.4$ reguliert und zur Marke aufgefüllt. Nach 10 Min wird die Extinktion bei 530 mμ gemessen und die eigene Extinktion der Reagenslösung abgezogen. Der optimale Konzentrationsbereich für Scandium ist 0.1–2.4 μg Sc/ml. Die praktische Empfindlichkeit für $A = 0.01$ liegt zwischen 0.044 μg Sc/cm^2 bei pH 3.5 und 0.0206 μg Sc/cm^2 bei pH 5.0. Die Reaktion wird gestört durch Katione, die mit PAR bei pH 3–5 farbige Chelate bilden[5,6] oder durch Anione, die Scandium zu farblosen Komplexen binden. Der Einfluss einiger Ionen ist in der Tabelle I angegeben.

TABELLE I

DER EINFLUSS EINIGER IONEN AUF DIE BESTIMMUNG VON SCANDIUM BEI pH 3.52

($c_{Sc} = 2.35$ μg Sc/ml)

Störendes ion	*µg/ml*	*Fehler, % Sc*
Zr^{4+}	0.92	+ 4
Th^{4+}	0.77	+ 4
Ti^{4+}	21.5	+ 5
Al^{3+}	30.9	+ 3
Y^{3+}	99.6	+ 3
La^{3+}	542	+ 5
Ce^{3+}	227	+ 6
Sm^{3+}	5.7	+ 6
Er^{3+}	18.1	+ 7
F^-	0.1	− 2.5
PO_4^{3-}	0.5	− 7
SO_4^{2-}	46.2	− 6
SCN^-	4080.0	− 3
$S_2O_3^{2-}$	384.0	− 2

Für den Konzentrationsbereich 0.1–1.4 μg F^-/ml ($c_{Sc} = 5.24 \cdot 10^{-5}$ M, $c_R = 1.92 \cdot 10^{-4}$ M) fällt die Extinktion des Chelates $ScRH^{2+}$ praktisch linear ab, sodass die Entfärbung auch zur Bestimmung kleiner Mengen von F^- benutzt werden kann. Fe^{3+} und Fe^{2+} bilden bei $pH > 1$ resp. $pH > 2.5$ rote Chelate mit PAR und stören daher. Die beschriebene Methode ist gut geeignet für die spektrophotometrische Bestimmung von Spuren von Scandium in reinen Lösungen oder nach seiner Abtrennung[11].

Bemerkung: Während des Druckes dieser Arbeit erschien eine Arbeit von A. I. BUSEV und CHANG FAN in *Talanta*, 9 (1962) 101 über das selbe Problem.

DANK

Herrn Prof. Dr. F. PETRŮ, Chemische und chemisch-technologische Hochschule, Prag, danken wir herzlich für analytisch reines Sc_2O_3, der Fa. Merck A.G., Darmstadt (DBR) für das freundliche Überlassen von 4-(2-Pyridylazo)resorcin, Natriumsalz.

ZUSAMMENFASSUNG

4-(2-Pyridylazo)resorcin (PAR) bildet in wässrigen Lösungen mit Sc^{3+} bei $pH \geqslant 2$ und $pH \geqslant 5$ zwei rote Chelate $ScRH^{2+}$ und ScR_2^- wovon das erstere als Grundlage für eine spektrophotometrische Methode zur Bestimmung von Scandium in Mengen von 0.05–2.4 μg/ml herangezogen wurde. Gemessen wird in nicht-gepufferten Lösungen bei 530 mμ in Gegenwart eines Überschusses von PAR bei pH 3.5–4.5 und $\mu = 0.4$. Die Konzentration von Scandium wird mit Hilfe eines Kalibrationskurven-Nomogramms für verschiedene pH bestimmt. Ionen, die mit PAR ebenfalls gefärbte Chelate in dem angegebenen pH-Bereich bilden oder Scandium maskieren, stören.

SUMMARY

4-(2-Pyridylazo)resorcinol (PAR) forms 2 red chelates with scandium in aqueous solution at $pH \geqslant 2$ or 5: $ScRH^{2+}$ and ScR_2^-. The former can be used to determine 0.05–2.4 μg Sc/ml at pH 3.5–4.5 with $\mu = 0.4$; measurement is done at 530 mμ. Many ions interfere and separation is necessary.

RÉSUMÉ

Les auteurs ont mis au point une méthode de dosage spectrophotométrique du scandium au moyen de 4-(2-pyridylazo)résorcine. Deux chélates se forment suivant le pH: $ScRH^{2+}$ et ScR_2^-. Plusieurs ions gênent; une séparation est nécessaire.

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COUNTERCURRENT EXTRACTION SEPARATION OF SOME PLATINUM GROUP METALS. PART II

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(Received March 12th, 1962)

The purpose of this work was to develop further the separation of the platinum group metals by countercurrent extraction first reported by BERG AND SENN[1,2]. The earlier work dealing with the extractive separation of the chloro-complexes of platinum and palladium, platinum and rhodium, and rhodium and iridium clearly demonstrated the ability of countercurrent extraction techniques to separate metals with a very limited number of equilibrium stages.

This present study reports on the extractive separation of several platinum group metals in the form of thiocyanate complexes. The complexes are partitioned between acid thiocyanate solutions and normal tributylphosphate.

EXPERIMENTAL

Apparatus

A Beckman Model DK spectrophotometer with matching silica cells was used for the analysis of the platinum group metals.

The countercurrent distribution apparatus was a device based on the design of CRAIG AND POST[3].

Reagents

A standard platinum (2150 p.p.m.) solution was prepared by dissolving 2.1500 g of platinum thermocouple wire in aqua regia. The solution was taken to dryness and the residue taken up in concentrated hydrochloric acid several times. Finally, the residue was dissolved in 100 ml of concentrated hydrochloric acid and diluted to 1 l with distilled water.

A stock palladium (1960 p.p.m.) solution was prepared by dissolving the pure metal (A. D. Mackay, Inc.) in fuming perchloric acid. The solution was evaporated to dryness and the residue taken up in 100 ml of concentrated hydrochloric acid and diluted to volume. The solution was standardized by precipitation analysis using dimethylglyoxime reagent.

Stock rhodium (1120 p.p.m.) and iridium (1520 p.p.m.) solutions were prepared by dissolving rhodium(III) chloride and iridium(IV) chloride (A. D. Mackay, Inc.) respectively, in 100 ml of concentrated hydrochloric acid and diluting to 1 l with distilled water. The solutions were standardized by the method of GILCHRIST[4].

Buffer solutions (pH 1) were prepared by mixing 48.5 ml of 0.2 *N* hydrochloric acid with 25 ml of 0.2 *N* potassium chloride and diluting the mixture to 100 ml in accord with Clark and Lubs buffer mixtures[5].

Analytical procedures

Extractant and raffinate phases were analyzed separately throughout the study. This necessitated a different pretreatment for each phase before the metal analysis was performed. Aliquots of extract from each sample were evaporated to dryness on a moderately heated hot plate and then fumed with perchloric acid to destroy all organic material before the metal analysis. The large excess of thiocyanate in the raffinate phase was destroyed by heating the sample with nitric acid prior to performing the metal analysis.

After completing the preliminary oxidation steps described above, the samples from raffinate and extract phases were handled alike. Spectrophotometric procedures were used for all analyses. Platinum was determined by the method of AYRES AND MEYER[6], palladium by the method of AYRES AND TUFFLY[7], rhodium by the method of AYRES AND YOUNG[8], and iridium by the method of AYRES AND QUICK[9].

Measurement of distribution coefficients

Distribution coefficients for the extraction of the various metal thiocyanate complexes from buffered media into *n*-tributylphosphate were determined for thiocyanate: metal ratios of 10 : 1 and 200 : 1 at a pH of 1, 2, 3, and 3.8. The procedure was as follows. A 5.00-ml aliquot of the stock metal solution was evaporated to dryness on a steam bath and the residue dissolved in 25 ml of buffer solution. A weighed amount of solid potassium thiocyanate was added to give the desired

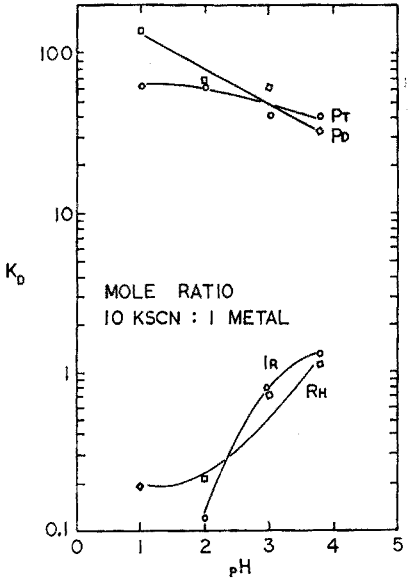

Fig. 1. Distribution coefficients *vs.* pH for platinum metal–thiocyanate complexes distributed between tributylphosphate and hydrochloric acid solution. Mole ratio 10 KSCN: 1 Metal.

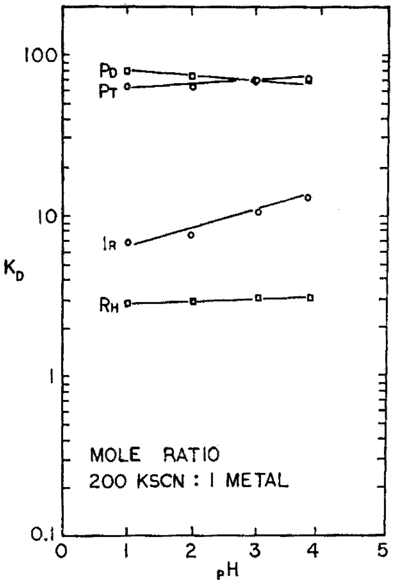

Fig. 2. Distribution coefficients *vs.* pH for platinum metal–thiocyanate complexes distributed between tributylphosphate and hydrochloric acid solution. Mole ratio 200 KSCN: 1 Metal.

thiocyanate to metal ratio and the solution was warmed on a steam bath for 10 min. After cooling this to room temperature, 25 ml of *n*-tributylphosphate previously saturated with potassium thiocyanate were added to the system. The 2 phases were mixed for 1 min in a separatory funnel and allowed to settle. The raffinate was filtered through Whatman No. 1 filter paper and taken for analysis. The distribution coefficient K_d is defined by

$$K_d = \frac{\text{mg metal/ ml of extractant}}{\text{mg metal/ ml of raffinate}}$$

The variation of K_d with pH for the 4 metals at thiocyanate: metal ratios of 10 : 1 and 200 : 1 is given in Figs. 1 and 2 respectively.

Separation technique

10.00-ml aliquots of the appropriate stock solutions were mixed and evaporated to dryness on a steam bath. The residue was dissolved in 30 ml of pH 1 buffer solution. Solid potassium thiocyanate was added to give a 10 : 1 mole ratio of KSCN : metal. The sample was then heated on a steam bath for 10 min, cooled to room temperature, and transferred to the first tube (tube number 0) of the countercurrent extractor. The other tubes of the extractor were filled with an equal volume of pH 1 buffer solution. 25 ml of tributylphosphate previously saturated with potassium thiocyanate were then added to tube 0 and the system was inverted 40 times to allow ample contact between phases. Once the phases had separated the extract was transferred to tube 1 and fresh extractant was added to tube 0. This procedure was repeated up to the point that an effective separation had occurred. Extractant and raffinate phases were analyzed separately for the precious metals as outlined in the analytical procedure.

RESULTS

The results of separations of various binary mixtures of platinum group metals are

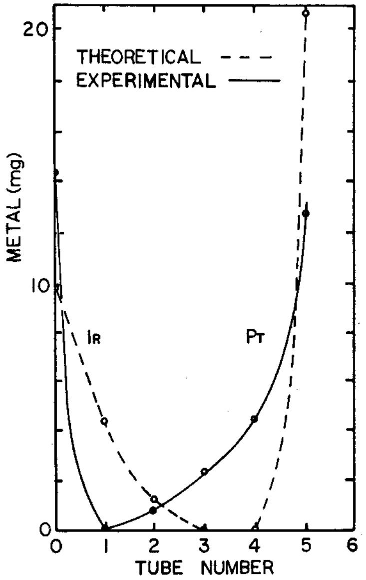

Fig. 3. Separation of thiocyanate complexes of Pt and Ir by distribution between TBP and hydrochloric acid (pH 1). Mole ratio 10 KSCN: 1 Metal.

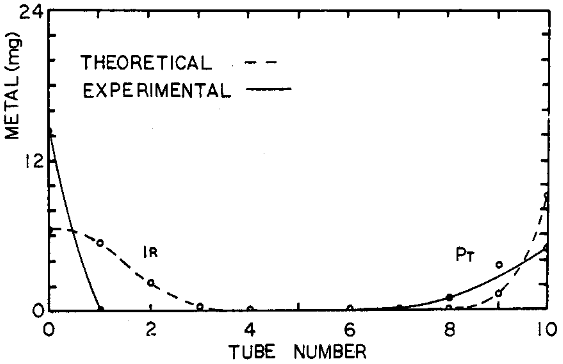

Fig. 4. Separation of thiocyanate complexes of Pt and Ir by distribution between TBP and hydrochloric acid (pH 1). Mole ratio 10 KSCN: 1 Metal.

given in Figs. 3–8 where the amount of metal calculated and found in each tube of the apparatus is plotted *vs.* the tube number. Recoveries of the individual metals ranged from 93–97%.

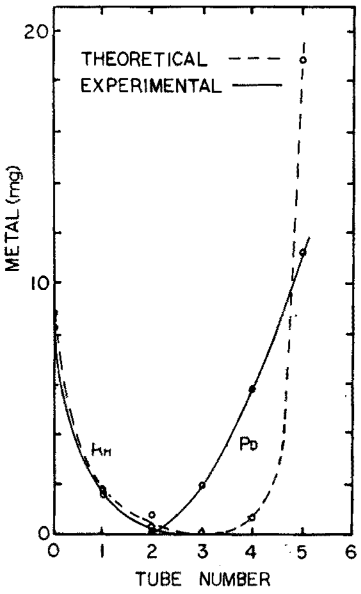

Fig. 5. Separation of thiocyanate complexes of Rh and Pd by distribution between TBP and hydrochloric acid (pH 1). Mole ratio 10 KSCN: 1 Metal.

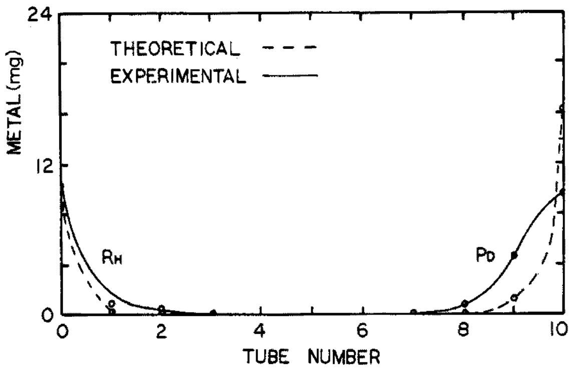

Fig. 6. Separation of thiocyanate complexes of Rh and Pd by distribution between TBP and hydrochloric acid (pH 1). Mole ratio 10 KSCN: 1 Metal.

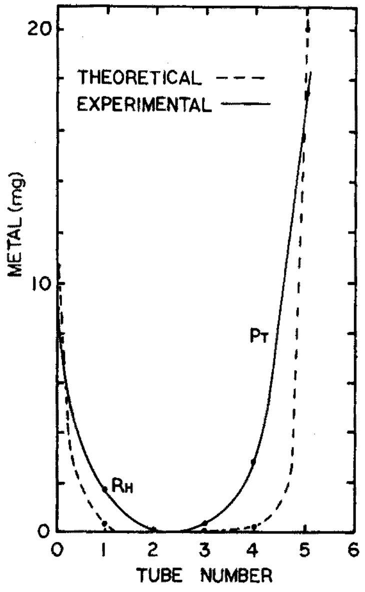

Fig. 7. Separation of thiocyanate complexes of Rh and Pt by distribution between TBP and hydrochloric acid (pH 1). Mole ratio 10 KSCN: 1 Metal.

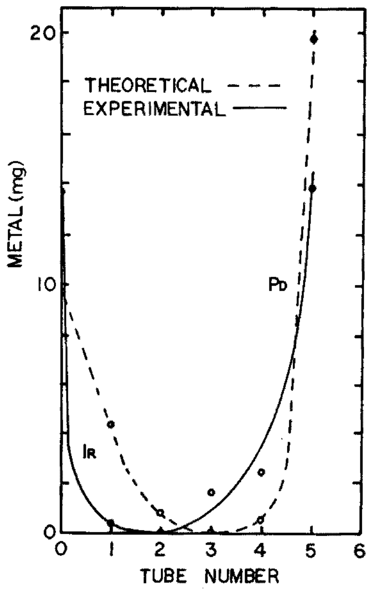

Fig. 8. Separation of thiocyanate complexes of Ir and Pd by distribution between TBP and hydrochloric acid (pH 1). Mole ratio 10 KSCN: 1 Metal.

DISCUSSION

The application of countercurrent distribution techniques to the problems of separations in the platinum group metals is a fresh approach to an old problem. The separations effected here were essentially quantitative, simple and fast with a very limited number of equilibrium stages involved.

The number of equilibrium stages needed for a separation are predictable from the distribution coefficients as evidenced by the great similarity of the theoretical and experimental distribution curves given in Figs. 3–8. The theoretical curves were calculated from the eqn. of CRAIG AND CRAIG[10].

$$T_{n,R} = \frac{n!}{R!\,(n-R)\,!}\,\frac{1}{K_d+1}^{\,n}\,K_d^R$$

where $T_{n,R}$ is the fraction of solute present in the Rth tube after n transfers and K_d is the distribution coefficient.

On the basis of the values of K_d determined for rhodium and iridium with a mole ratio of thiocyanate: metal of 200 : 1, one would expect to be able to effect a separation of these metals with a few equilibrium stages. Unfortunately, the separation does not work. At this time the reasons for the anomalous behavior are not known, but the same problem has been encountered before[1,2].

There is considerable evidence to indicate that further studies in this field will make it possible to resolve mixtures of 4 or 5 platinum metals with something like 25 or 30 equilibrium stages, a worthy accomplishment considering the simplicity of the method.

SUMMARY

Binary mixtures of Pt and Rh, Pt and Ir, Pd and Rh, and Pd and Ir were resolved by a countercurrent extraction technique. The metals were partitioned between an acidic aqueous phase containing potassium thiocyanate and an organic phase, *n*-tributylphosphate. Distribution coefficients were determined for each metal for a thiocyanate: metal mole ratio of 10 : 1 and 200 : 1 at pH values of 1, 2, 3, and 3.8. Optimum conditions for separations were determined to be a thiocyanate: metal mole ratio of 10 : 1 and a pH of 1. Under these conditions the K_d values for Pd, Pt, Rh and Ir were 139, 62.3, 0.19 and 0.09 resp. Effective separations were achieved with each binary mixture on a Craig extraction apparatus utilizing less than 10 equilibrium stages. There was a 95% average recovery of each of the metals.

RÉSUMÉ

Une méthode par extraction à contre-courant est décrite pour la séparation des métaux du groupe du platine, sous forme de complexes thiocyanés, en utilisant le *n*-tributylphosphate comme solvant organique. Les coefficients de partage sont indiqués.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Trennung der Platinmetalle durch Verteilung ihrer Thiocyanat-Komplexe zwischen saurer Thiocyanatlösung und *n*-Tributylphosphat nach dem Prinzip der Gegenstromextraktion nach Craig. Die optimalen Bedingungen für die Trennungen und die Verteilungskoeffizienten werden angegeben.

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SOME THEORETICAL CONSIDERATIONS IN ANALYTICAL CHEMISTRY

PART VII*. THE INFLUENCE OF ABSOLUTE CONCENTRATION ON THE PARAMETERS OF REDOX TITRIMETRY

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Methods have been proposed[1] for the calculation of the incompleteness of redox reactions and for the calculation of data for titration curves making allowance for the reaction deficiency. The influence of absolute reactant concentrations on the reaction deficiency and on certain parameters significant to redox titrimetry may now be examined further.

In discussing redox reactions, it is convenient to classify them into three groups[1,2], inhomogeneous, homogeneous and symmetrical, for which the treatment becomes progressively simpler. Let the oxidising titrant reaction be represented by eqn. (1) and the reducing titrand reaction be represented by eqn. (2). Multiplication of (1) by x and of (2) by y where $n_1x = n_2y$ then gives the balanced general overall eqn. (3),

$$a\mathrm{Ox}_1 + n_1\varepsilon \rightleftharpoons c\mathrm{Red}_1 \qquad (1)$$

$$b\mathrm{Red}_2 \rightleftharpoons n_2\varepsilon + d\mathrm{Ox}_2 \qquad (2)$$

$$ax\mathrm{Ox}_1 + by\mathrm{Red}_2 \rightleftharpoons cx\mathrm{Red}_1 + dy\mathrm{Ox}_2 \qquad (3)$$

An *inhomogeneous* reaction results when $a \neq c$ and/or $b \neq d$: this is the not uncommon general case arising through a change in molecular complexity, of which halogen oxidants afford an example. A *homogeneous* reaction arises when $a = b = c = d = 1$, or when $ax + by = cx + dy$, but $x \neq y$: this is the common case. A *symmetrical* reaction is one in which $a = b = c = d = 1$ and $x = y$: such reactions are fairly common. This classification will be used in the discussion which follows.

Concentration dependence of the potentials and the reaction deficiency

It has been said[1] that when account is taken of incompleteness of reaction, the absolute concentrations of the reactants are called into requisition in the calculation of titrimetric data, instead of the relative concentrations (or percentage of reaction), even in the simplest case of a symmetrical reaction. This is not to say that absolute concentrations influence the resulting potentials in all instances: trial calculations will show that the potentials are independent of absolute concentration for homogeneous and symmetrical reactions. It is obvious that, when the reaction deficiency is represented as a concentration and not as a ratio, it will depend on absolute concen-

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* Part VI see *Anal. Chim. Acta*, 26 (1962) 397.

tration, but the use of absolute concentrations in the calculation of potentials arises through the exigencies of the method, the quickest, most versatile and simplest method[1] involving preliminary calculation of reaction deficiency in terms of absolute concentration.

Using the same notation as before[1], the potential of the titration system at constant anagen and katagen concentration is governed by the variable ratio in the log term of the Nernst equation. Before the equivalence point for reaction (3) this is

$$\frac{[\mathrm{Ox}_2]^{dy}}{[\mathrm{Red}_2]^{by}} \tag{4}$$

In terms of apparent concentrations, corrected for reaction deficiency, this becomes

$$\frac{(C_{\mathrm{ox}_2} - \frac{d}{b}\,\delta_{\mathrm{red}_2})^{dy}}{(C_{\mathrm{red}_2} + \delta_{\mathrm{red}_2})^{by}} \tag{5}$$

If the reagent concentrations are changed by a factor λ then the reaction deficiency (as a concentration) will change by a factor λ_1. Inspection of eqn. (5) will immediately show that if $\lambda = \lambda_1$, the potential remains constant only if $b = d$ (if $a = c$ after the equivalence point).

The actual relationship between λ and λ_1 may be derived from the equilibrium constant[1] at any selected point in the titration, since

$$\begin{aligned}\frac{n_1 n_2 \Delta E_0}{0.00019851T} &= \log \frac{\left\{\frac{cn_2}{dn_1} C_{\mathrm{ox}_2} - \frac{cn_2}{bn_1}\delta_{\mathrm{red}_2}\right\}^{cn_2} \left\{C_{\mathrm{ox}_2} - \frac{d}{b}\,\delta_{\mathrm{red}_2}\right\}^{dn_1}}{\left\{\frac{an_2}{bn_1}\,\delta_{\mathrm{red}_2}\right\}^{an_2} \left\{C_{\mathrm{red}_2} + \delta_{\mathrm{red}_2}\right\}^{bn_1}} \\ &= \log \frac{\left\{\frac{cn_2}{dn_1}\,\lambda C_{\mathrm{ox}_2} - \frac{cn_2}{bn_1}\,\lambda_1 \delta_{\mathrm{red}_2}\right\}^{cn_2} \left\{\lambda C_{\mathrm{ox}_2} - \frac{d}{b}\,\lambda_1 \delta_{\mathrm{red}_2}\right\}^{dn_1}}{\left\{\frac{an_2}{bn_1}\,\lambda_1 \delta_{\mathrm{red}_2}\right\}^{an_2} \left\{\lambda C_{\mathrm{red}_2} + \lambda_1 \delta_{\mathrm{red}_2}\right\}^{bn_1}}\end{aligned} \tag{6}$$

From the two log terms,

$$\frac{\left\{\frac{cn_2}{dn_1}\right\}^{cn_2} \left\{C_{\mathrm{ox}_2} - \frac{d}{b}\,\delta_{\mathrm{red}_2}\right\}^{(cn_2+dn_1)}}{\left\{\frac{an_2}{bn_1}\right\}^{an_2} \left\{\delta_{\mathrm{red}_2}\right\}^{an_2} \left\{C_{\mathrm{red}_2} + \delta_{\mathrm{red}_2}\right\}^{bn_1}} = \frac{\left\{\frac{cn_2}{dn_1}\right\}^{cn_2} \left\{\lambda C_{\mathrm{ox}_2} - \frac{d}{b}\,\lambda_1 \delta_{\mathrm{red}_2}\right\}^{(cn_2+dn_1)}}{\left\{\frac{an_2}{bn_1}\right\}^{an_2} \left\{\lambda_1 \delta_{\mathrm{red}_2}\right\}^{an_2} \left\{\lambda C_{\mathrm{red}_2} + \lambda_1 \delta_{\mathrm{red}_2}\right\}^{bn_1}} \tag{7}$$

Simplification gives

$$\lambda_1{}^{an_2} = \frac{\{\lambda b C_{\mathrm{ox}_2} - d\lambda_1 \delta_{\mathrm{red}_2}\}^{(cn_2+dn_1)}\,\{C_{\mathrm{red}_2} + \delta_{\mathrm{red}_2}\}^{bn_1}}{\{bC_{\mathrm{ox}_2} - d\delta_{\mathrm{red}_2}\}^{(cn_2+dn_1)}\,\{\lambda C_{\mathrm{red}_2} + \lambda_1 \delta_{\mathrm{red}_2}\}^{bn_1}} \tag{8}$$

By setting $\lambda = \lambda_1$ in eqn. (8) a more rigorous delineation is obtained of the conditions under which dilution of the titration system produces a proportional dilution, or diminution, of the reaction deficiency,

$$an_2 + bn_1 = cn_2 + dn_1 \quad \text{or} \quad (b - d)n_1 = (c - a)n_2 \tag{9}$$

Under these conditions, with which homogeneous and symmetrical reactions comply, overall dilution has no effect on the resultant potential.

For inhomogeneous reactions, eqn. (8) is incapable of yielding a simple algebraic solution, and the simplest way of establishing the effect of dilution on the potential is by experimental solution of the master equation (eqns. (11) and (21) in ref. 1).

For example, in a reaction such as the oxidation of mercurous nitrate with bromine, $a = 1$, $b = 1$, $c = 3$, $d = 2$, $n_1 = 2$, $n_2 = 2$, $x = 1$, $y = 1$. Let $\Delta E_0 = 100$ mV, $t = 30°$ and the original titrant and titrand concentrations be 0.05 M. After the addition of 99.9% of the titrant, the following figures result.

λ	λ_1	δ_{red_2}	$E-E_0$
1	1.000	$1.2860 \cdot 10^{-5}$	+54.562 mV
0.5	$6.915 \cdot 10^{-2}$	$1.1194 \cdot 10^{-6}$	+49.830 mV
0.1	$1.517 \cdot 10^{-4}$	$1.9508 \cdot 10^{-9}$	+29.971 mV
0.01	$1.518 \cdot 10^{-8}$	$1.9523 \cdot 10^{-13}$	− 0.005 mV

At first sight these figures present a startling paradox that as the solution becomes more dilute, the reaction rapidly becomes much more complete, but at the same time, according to the potentials, proceeds backwards. This paradox is resolved, however, when it is realised that E_0 refers to the condition [Ox] = [Red] = 1, and since these two quantities appear in the Nernst equation in different orders (2 and 1 in this case) the midpoint potential, E_{50}, where [Ox] = 2[Red] will change with absolute concentration. In the example quoted, the values are as follows, the midpoint potential occurring after addition of 50% of oxidant.

λ	*midpoint potential*	$E_{99.9}-E_{50}$
1	$E_0 - 35.283$ mV	89.845 mV
0.5	$E_0 - 44.314$ mV	94.143 mV
0.1	$E_0 - 65.283$ mV	95.254 mV
0.01	$E_0 - 95.283$ mV	95.278 mV

Clearly, therefore, the potential for inhomogeneous reactions is dependent on absolute concentration. So also, in lesser degree, is the relative change in potential during titration dependent on dilution, asymptotically approaching a maximum as the reagents become more dilute.

For homogeneous and symmetrical reactions, since the potential is independent of concentration it should be possible to calculate the potential without reference to concentration by expressing the reaction deficiency as a ratio such as $\delta_{\mathrm{red}_2}/C_{\mathrm{ox}_2}$ or $\delta_{\mathrm{red}_2}/C_{\mathrm{red}_2}$ before the equivalence point. The latter ratio will become infinity at the equivalence point, and is therefore not helpful in equivalence point calculations.

The ratios may readily be extracted for *symmetrical reactions*. From eqn. (15) of ref. 1:

$$(A-1)\delta_{\mathrm{red}_2}{}^2 + AC_{\mathrm{red}_2}\delta_{\mathrm{red}_2} + 2C_{\mathrm{ox}_2}\delta_{\mathrm{red}_2} - C_{\mathrm{ox}_2}{}^2 = 0 \tag{10}$$

Dividing through by $C_{\mathrm{ox}_2}{}^2$ gives a quadratic in the first ratio, and formula solution gives the value

$$\frac{\delta_{\mathrm{red}_2}}{C_{\mathrm{ox}_2}} = \frac{1}{2(A-1)}\left\{\left[\left(\frac{AC_{\mathrm{red}_2}}{C_{\mathrm{ox}_2}} + 2\right)^2 + 4(A-1)\right]^{1/2} - \left(\frac{AC_{\mathrm{red}_2}}{C_{\mathrm{ox}_2}} + 2\right)\right\} \tag{11}$$

which converges towards the equivalence point.

Division of equation (10) by $C_{\mathrm{red}_2}{}^2$ followed by formula solution of the resulting quadratic evaluates the second ratio, which diverges towards the equivalence point:

$$\frac{\delta_{\mathrm{red}_2}}{C_{\mathrm{red}_2}} = \frac{1}{2(A-1)}\left\{\left[\left(A + 2\frac{C_{\mathrm{ox}_2}}{C_{\mathrm{red}_2}}\right)^2 + 4(A-1)\frac{C_{\mathrm{ox}_2}}{C_{\mathrm{red}_2}}\right]^{1/2} - \left(A + 2\frac{C_{\mathrm{ox}_2}}{C_{\mathrm{red}_2}}\right)\right\} \qquad (12)$$

In eqns. (11) and (12) the ratios $C_{\mathrm{red}_2}/C_{\mathrm{ox}_2}$ and $C_{\mathrm{ox}_2}/C_{\mathrm{red}_2}$ are directly accessible from the percentage of titrant added; no appeal to absolute concentrations is required.

For calculating potentials, the logarithmic term in the Nernst equation is,

$$\frac{C_{\mathrm{ox}_2} - \delta_{\mathrm{red}_2}}{C_{\mathrm{red}_2} + \delta_{\mathrm{red}_2}} \qquad (13)$$

which may be converted into terms of the ratios of eqns. (11) and (12) thus,

$$(13) = \frac{\dfrac{C_{\mathrm{ox}_2}}{\delta_{\mathrm{red}_2}} - 1}{\dfrac{C_{\mathrm{red}_2}}{\delta_{\mathrm{red}_2}} + 1} = \frac{1 - \dfrac{\delta_{\mathrm{red}_2}}{C_{\mathrm{ox}_2}}}{1 + \dfrac{\delta_{\mathrm{red}_2}}{C_{\mathrm{red}_2}}} \cdot \frac{\dfrac{\delta_{\mathrm{red}_2}}{C_{\mathrm{red}_2}}}{\dfrac{\delta_{\mathrm{red}_2}}{C_{\mathrm{ox}_2}}} = \frac{1 - \dfrac{\delta_{\mathrm{red}_2}}{C_{\mathrm{ox}_2}}}{1 + \dfrac{\delta_{\mathrm{red}_2}}{C_{\mathrm{red}_2}}} \cdot \frac{C_{\mathrm{ox}_2}}{C_{\mathrm{red}_2}} \qquad (14)$$

which gives eqn. (15) as the rigorous expression for the potential at a selected point in a symmetrical reaction, and shows that the true potential is always less than the approximate potential calculated by ignoring the reaction deficiency:

$$E = E_{\mathrm{O}_2} + \frac{0.00019851T}{n_2}\left\{\log_{10}\frac{1 - \dfrac{\delta_{\mathrm{red}_2}}{C_{\mathrm{ox}_2}}}{1 + \dfrac{\delta_{\mathrm{red}_2}}{C_{\mathrm{red}_2}}} + \log_{10}\frac{C_{\mathrm{ox}_2}}{C_{\mathrm{red}_2}}\right\} \qquad (15)$$

Analogous equations, symmetrical with the foregoing, may be derived for the oxidant system in the region following the equivalence point.

It is therefore possible to calculate the data for symmetrical titrations directly from the percentage of titrant added without calculating or using absolute concentrations, but the process involves the solution of two complex quadratics and is inapplicable to the equivalence point itself. It does not, therefore, offer any practical advantage over the route via absolute concentration previously proposed[1].

The same ratios may be extracted for *homogeneous reactions* from eqns. (12) or (13) of ref. 1. Division of numerator and denominator by $C_{\mathrm{ox}_2}{}^{(x+y)}$ gives the first ratio,

$$A = \frac{\left(1 - \dfrac{\delta_{\mathrm{red}_2}}{C_{\mathrm{ox}_2}}\right)^{(x+y)}}{\left(\dfrac{\delta_{\mathrm{red}_2}}{C_{\mathrm{ox}_2}}\right)^x \left(\dfrac{C_{\mathrm{red}_2}}{C_{\mathrm{ox}_2}} + \dfrac{\delta_{\mathrm{red}_2}}{C_{\mathrm{ox}_2}}\right)^y} \qquad (16)$$

Similar division by $C_{\mathrm{red}_2}{}^{(x+y)}$ gives the second ratio,

$$A = \frac{\left(\dfrac{C_{\mathrm{ox}_2}}{C_{\mathrm{red}_2}} - \dfrac{\delta_{\mathrm{red}_2}}{C_{\mathrm{red}_2}}\right)^{(x+y)}}{\left(\dfrac{\delta_{\mathrm{red}_2}}{C_{\mathrm{red}_2}}\right)^x \left(1 + \dfrac{\delta_{\mathrm{red}_2}}{C_{\mathrm{red}_2}}\right)^y} \qquad (17)$$

Solution of eqns. (16) and (17) by successive approximation[1] or computer[3] methods gives values for the ratios which may then be applied in eqn. (15) to give potentials, again without the necessity of referring to absolute concentrations; but again the process involves the solution of two high order equations instead of one and is inapplicable to the equivalence point, and has no practical advantage over the route via absolute concentration[1].

The equivalence point potential

Although eqns. (12), (14), (15) and (17) are not applicable to the equivalence point condition because the ratios $\delta_{\text{red}_2}/C_{\text{red}_2}$ and $C_{\text{ox}_2}/C_{\text{red}_2}$ become infinity at this point, eqns. (11) and (16) are still usable. The general route[1] using, but not depending on, absolute concentration is also applicable to the equivalence point and can be used to derive the equivalence point potential, by first calculating δ_{red_2} for the condition $C_{\text{red}_2} = 0$, and then substituting the values in the Nernst equation.

For homogeneous and symmetrical reactions, the general formulation of eqn. (3) is, in terms of n_1 and n_2,

$$n_2\text{Ox}_1 + n_1\text{Red}_2 \rightleftharpoons n_2\text{Red}_1 + n_1\text{Ox}_2 \qquad (18)$$

and from the reacting ratios[1], at the equivalence point,

$$C_{\text{red}_1} = \frac{n_2}{n_1} C_{\text{ox}_2}; \quad \delta_{\text{ox}_1} = \frac{n_2}{n_1} \delta_{\text{red}_2} \qquad (19)$$

At equilibrium, the equivalence point potential, E_{ep}, will be,

$$E_{\text{ep}} = E_{0_2} + \frac{RT}{n_2 F} \log_e \frac{C_{\text{ox}_2} - \delta_{\text{red}_2}}{\delta_{\text{red}_2}} = E_{0_1} + \frac{RT}{n_1 F} \log_e \frac{\delta_{\text{ox}_1}}{C_{\text{red}_1} - \delta_{\text{ox}_1}} \qquad (20)$$

From (19)

$$= E_{0_1} + \frac{RT}{n_1 F} \log_e \frac{\frac{n_2}{n_1}\delta_{\text{red}_2}}{\frac{n_2}{n_1} C_{\text{ox}_2} - \frac{n_2}{n_1}\delta_{\text{red}_2}} = E_{0_1} - \frac{RT}{n_1 F} \log_e \frac{C_{\text{ox}_2} - \delta_{\text{red}_2}}{\delta_{\text{red}_2}}$$

Dividing the middle section of (20) and E_{ep} by n_1 and dividing the right hand section of (20) and E_{ep} by n_2 gives (21) and (22); summation removes the log terms and yields expression (23) for E_{ep} which is independent of concentration.

$$\frac{1}{n_1} E_{\text{ep}} = \frac{1}{n_1} E_{0_2} + \frac{RT}{n_1 n_2 F} \log_e \frac{C_{\text{ox}_2} - \delta_{\text{red}_2}}{\delta_{\text{red}_2}} \qquad (21)$$

$$\frac{1}{n_2} E_{\text{ep}} = \frac{1}{n_2} E_{0_1} - \frac{RT}{n_1 n_2 F} \log_e \frac{C_{\text{ox}_2} - \delta_{\text{red}_2}}{\delta_{\text{red}_2}} \qquad (22)$$

$$\left(\frac{1}{n_1} + \frac{1}{n_2}\right) E_{\text{ep}} = \frac{1}{n_2} E_{0_1} + \frac{1}{n_1} E_{0_2}$$

$$\therefore E_{\text{ep}} = \frac{n_1 E_{0_1} + n_2 E_{0_2}}{n_1 + n_2} \qquad (23)$$

This is not the common form of expression[2], but it answers more logically and directly to experience which places the inflection of the titration curve nearer to the reactant involving the transfer of the larger number of electrons, and requires less thought since the values of n_1 and n_2 are already in mind. Conversion to the common expression may be made through the least common multiple concept[1] from the relationship $n_1 x = n_2 y$,

$$E_{\mathrm{ep}} = \frac{xE_{0_2} + yE_{0_1}}{x + y} \tag{24}$$

For homogeneous and symmetrical reactions, therefore, rigorous derivation of the equivalence point potential is possible without reference to absolute concentrations, and the result confirms the accuracy of the common expression as a weighted mean of the normal potentials[2,4].

When, however, there is a change in molecular complexity on reaction, that is when $a \neq c$ and/or $b \neq d$ as in an inhomogeneous reaction, it is no longer possible to derive an expression for the equivalence point potential without reference to absolute concentration[2,4]. This does not mean that the equivalence point potential cannot be calculated for a specific case, as BARD AND SIMONSEN[4] have already shown, because for a specific case the further factor required[2,5] to permit solution of the equations is provided by the reactant concentration. It is possible to derive a single equation for this purpose[4], but this is inevitably cumbersome, and it is less confusing to conduct the operation in three stages. Using the reductant system, these are:

(*a*) Calculate C_{ox_2} from eqn. (29) of ref. 1, the initial reactant concentrations and the stoichiometry of reaction (3),

$$C_{\mathrm{ox}_2} = \frac{dn_1 M_{\mathrm{O}} M_{\mathrm{R}}}{an_2 M_{\mathrm{R}} + bn_1 M_{\mathrm{O}}} \tag{25}$$

(*b*) Substitute this value of C_{ox_2} and the value $C_{\mathrm{red}_2} = 0$ in the general equilibrium equation (11) of ref. 1 and calculate δ_{red_2}. The substitution and simplification give, in a convenient form for manual computation:

$$(\delta_{\mathrm{red}_2})^{(an_2+bn_1)} = \frac{1}{A}\left\{\left(\frac{b}{a}\right)^a \left(\frac{c}{d}\right)^c \left(\frac{n_1}{n_2}\right)^{(a-c)}\right\}^{n_2} \left\{C_{\mathrm{ox}_2} - \frac{d}{b}\,\delta_{\mathrm{red}_2}\right\}^{(cn_2+dn_1)} \tag{26}$$

$$\text{where } A = \text{antilog}\,\frac{n_1 n_2 \Delta E_0}{0.00019851\ T}$$

A close first approximation (better than 0.1%) can be extracted very simply by neglecting $(d/b)\delta_{\mathrm{red}_2}$ with respect to C_{ox_2}.

(*c*) Substitute this value of δ_{red_2} in the Nernst equation:

$$E_{\mathrm{ep}} = E_{0_2} + \frac{0.00019851T}{n_2}\log_{10}\frac{\left\{C_{\mathrm{ox}_2} - \frac{d}{b}\,\delta_{\mathrm{red}_2}\right\}^d}{\{\delta_{\mathrm{red}_2}\}^b} \tag{27}$$

A similar method may be operated on the oxidant system, by setting $C_{\mathrm{ox}_1} = 0$. In practice the calculations are quite rapid, despite the cumbersome appearance of the equations.

At the equivalence point of the example quoted on p. 255 this process yields the following data, illustrating the marked influence of concentration.

λ	C_{ox_2}	δ_{red_2}	$E_{ep}-E_{0_2}$	$E_{ep}-E_{50}$
1.0	$5\cdot10^{-2}$	$2.2075\cdot10^{-5}$	61.598 mV	96.882 mV
0.5	$2.5\cdot10^{-2}$	$3.9082\cdot10^{-6}$	66.109 mV	110.422 mV
0.1	$5\cdot10^{-3}$	$6.9963\cdot10^{-8}$	76.592 mV	141.876 mV
0.01	$5\cdot10^{-4}$	$2.2126\cdot10^{-10}$	91.591 mV	186.874 mV

It was noted on p. 255 for a similar set of conditions that the relative change in potential during a titration increased asymptotically to a maximum value as the reagents became more dilute. The data above indicate that the relative change in potential from any point in the titration to the equivalence point increases rapidly with dilution, and in conjunction with the data on p. 255 it will be seen that this increase resides in a very small region just before the equivalence point. The titration curve in the equivalence point region therefore rapidly becomes steeper as the reagents become more dilute, as shown in the data below for the last 0.1% of the titration ($E_{ep}-E_{99.9}$). The increase in the relative change in potential between the midpoint (E_{50}) and the equivalence point (E_{ep}) shows a relationship to the relative dilution very close to the logarithm of the dilution ratio, the discrepancy being no more than a few microvolts, as shown below.

λ	$E_{ep}-E_{99.9}$	$\log_{10} 1/\lambda$	$(E_{ep}-E_{50}\ at\ \lambda)$ − $(E_{ep}-E_{50}\ at\ \lambda=1)$	$44.994^{*}\cdot\log 1/\lambda$
1	7.04 mV	0	0	0
0.5	16.28 mV	0.30103	13.541 mV	13.546
0.1	46.62 mV	1.0	44.994 mV	44.994
0.01	91.57 mV	2.0	89.993 mV	89.988

* $44.994 = (E_{ep} - E_{50}$ at $\lambda = 0.1) - (E_{ep} - E_{50}$ at $\lambda = 1)$ mV.

The quantitativeness of the reaction

The quantitativeness of reaction[2,5,6] is given by the ratio of [Ox₂] to [Red₂] at the equivalence point. In terms of reaction deficiency and apparent concentration, for homogeneous and symmetrical reactions, this is,

$$\frac{[\mathrm{Ox_2}]}{[\mathrm{Red_2}]} = \frac{C_{ox_2} - \delta_{red_2}}{\delta_{red_2}} \tag{28}$$

This ratio is directly accessible from eqn. (13) of ref. 1, by using the equivalence point condition that $C_{red_2} = 0$,

$$\frac{n_1 n_2 \Delta E_0}{0.00019851T} = \log_{10} \frac{\{C_{ox_2} - \delta_{red_2}\}^{(n_1+n_2)}}{\{\delta_{red_2}\}^{n_2}\{\delta_{red_2}\}^{n_1}}$$

whence

$$\frac{[\mathrm{Ox_2}]}{[\mathrm{Red_2}]} = A^{\frac{1}{n_1+n_2}} \tag{29}$$

Again, therefore, for homogeneous and symmetrical reactions, rigorous derivation of the quantitativeness of the reaction is possible without reference to absolute concentration, and the result confirms the accuracy of the common expression[2,5,6] as the $(n_1 + n_2)$th root of the corresponding equilibrium constant, and its independence of absolute concentration.

For inhomogeneous reactions it has been shown to be impossible to derive such a relationship without supplying a further known quantity[2,5]. For a specific instance this further quantity is a concentration of one of the reactant species, conveniently[2] C_{ox_2}, at the equivalence point where $C_{\mathrm{red}_2} = 0$. Working from the reductant system, the steps are:

(*a*) Calculate C_{ox_2} from eqn. (25).

(*b*) Calculate δ_{red_2} from eqn. (26). The same first approximation is useful.

(*c*) The quantitativeness of the reaction, to be strictly comparable with other reactions, is given by

$$\frac{b[\mathrm{Ox}_2]}{d[\mathrm{Red}_2]} = \frac{b\left\{C_{\mathrm{ox}_2} - \frac{d}{b}\,\delta_{\mathrm{red}_2}\right\}}{d\delta_{\mathrm{red}_2}} \tag{30}$$

Substitution of the values from steps (*a*) and (*b*) gives the required parameter. It is possible to formulate the extraction of this parameter directly from eqn. (26), but as can be seen in eqn. (31) there is no economy of labour since δ_{red_2} still requires evaluation.

$$\frac{b[\mathrm{Ox}_2]}{d[\mathrm{Red}_2]} = \frac{b}{d}\left\{A\left[\left(\frac{a}{b}\right)^a\left(\frac{d}{c}\right)^c\left(\frac{n_2}{n_1}\right)^{(a-c)}\right]^{n_2}\delta_{\mathrm{red}_2}{}^{[n_1(b-d)+n_2(a-c)]}\right\}^{\frac{1}{cn_2+dn_1}} \tag{31}$$

An analogous method may be applied to the oxidant system by setting $C_{\mathrm{ox}_1} = 0$, and yields the same result. At the equivalence point of the example quoted on p. 255, this process yields the following data which illustrate the profound influence of absolute concentration on the completeness of reaction:

λ	C_{ox_2}	δ_{red_2}	$b[\mathrm{Ox}_2]/d[\mathrm{Red}_2]$
1	$5 \cdot 10^{-2}$	$2.2075 \cdot 10^{-5}$	$1.1315 \cdot 10^{3}$
0.5	$2.5 \cdot 10^{-2}$	$3.90824 \cdot 10^{-6}$	$3.125 \cdot 10^{3}$
0.1	$5 \cdot 10^{-3}$	$6.9963 \cdot 10^{-8}$	$3.573 \cdot 10^{4}$
0.01	$5 \cdot 10^{-4}$	$2.2126 \cdot 10^{-10}$	$1.13 \cdot 10^{6}$

The relevance of this criterion to redox titrimetry can be challenged; if the reaction is stoichiometric and the equivalence point can be evaluated and experimentally located, the quantitativeness of the reaction does not affect the accuracy of the determination. The precision is, however, defined by the sharpness of the potential changes in the equivalence point region and upon this the quantitativeness of the reaction exerts an influence. However, this criterion is restricted to the equivalence point alone, and a much more general and useful concept is that of reaction deficiency (δ_{red_2} or δ_{ox_2}) which, as has been shown, adequately embraces the equivalence point. The partial treatment of quantitativeness in the standard texts[5,6,7] is therefore of limited virtue.

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SUMMARY

Redox reactions are classified into symmetrical, homogeneous and inhomogeneous reactions. Reaction deficiencies when expressed as concentrations are dependent on absolute reactant concentrations, but have been proved to be independent of dilution when expressed as ratios in symmetrical and homogeneous reactions. An expression relating change of reaction deficiency with dilution for inhomogeneous reactions has been derived; dilution of the reactants very rapidly decreases the reaction deficiency.

Expressions for potentials in terms of concentration ratios have been derived for homogeneous and symmetrical reactions and prove to be independent of dilution. For inhomogeneous reactions the absolute potential falls on dilution, although the relative potential change, *e.g.*, from the mid-point of a titration, increases asymptotically to a maximum.

New derivations of the equivalence point potential and of an expression for the quantitativeness, for symmetrical and homogeneous reactions confirm the classical expressions and demonstrate their independence of dilution. For inhomogeneous reactions, methods of calculation of quantitativeness and equivalence point potentials through reaction deficiencies are proposed. For such reactions, the equivalence point potential rises sharply with dilution, giving titration curves of increasing steepness. The dependence of mid-point potentials and relative change of potential during titration upon dilution are also examined.

RÉSUMÉ

L'auteur a effectué une étude théorique au sujet de l'influence de la concentration absolue sur les paramètres de la titrimétrie d'oxydo-réduction. Les réactions redox sont classées en trois catégories: réactions symmétriques, réactions homogènes et réactions non-homogènes. Pour les réactions symmétriques et homogènes, les résultats obtenus confirment les expériences classiques et montrent que la dilution n'intervient pas; pour les réactions non-homogènes, des méthodes de calculs sont proposées. Pour de telles réactions le potentiel du point d'équivalence augmente nettement avec la dilution.

ZUSAMMENFASSUNG

Der Einfluss der absoluten Konzentration bei Redox-Titrationen wird theoretisch behandelt. Verfasser unterscheidet drei Klassen von Redoxreaktionen: symmetrische, homogene und inhomogene Reaktionen. Es wird gezeigt, dass bei symmetrischen und homogenen Reaktionen eine Verdünnung ohne Einfluss auf das Ergebnis ist; für inhomogene Reaktionen wird eine mathematische Lösung beschrieben.

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A STUDY OF SOME FACTORS WHICH AFFECT THE ADSORPTION OF TITAN YELLOW ON MAGNESIUM HYDROXIDE

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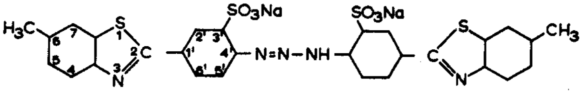
INTRODUCTION

Although many procedures have been described for the determination of magnesium with Titan yellow, there is little agreement on the optimum conditions for carrying out the reaction and the extent to which it is influenced by other ions. In a collaborative study of methods for the determination of magnesium in soil extracts, SHAW[1] found that only 4 out of 10 collaborators reported on the recommended Titan yellow procedure and that two of this number were sceptical of their results because of large differences between replicates.

A previous study[2] has investigated how the reaction is influenced by (*a*) the amount of Titan yellow used, (*b*) the nature and amount of colloid protector employed and (*c*) the presence of other ions in the solutions, and a method for the rapid determination of magnesium in plant material has been developed[3]. Further investigations have now been carried out on these aspects of the reaction and the results are reported in this paper.

THE DYESTUFF

Titan yellow is prepared from dehydrothio-*p*-toluidine sulphonic acid by coupling a diazotised solution with the same acid and is usually given the formula:



in which the sulphonate groups are in the 3′-position. The extensive investigations of SCHUBERT[4] have shown, however, that the technical product is predominantly the 7-sulphonate with a smaller amount of the 5-isomer also present. Variation in the sensitivity of different batches of Titan yellow in their reaction with magnesium hydroxide was first reported by MIKKELSEN AND TOTH[5] and has since been noted by many workers. The nature of the impurities which may be present in commercial samples of dyestuff has been studied by BRADFIELD[2] and the analytical results for four batches of dyestuff are summarised in Table I. Ultraviolet and visible absorption spectra show similar characteristics for different batches of dyestuff and two absorption peaks are observed, one at 405 mμ and one at 330 mμ[2,6]; paper chromatography[2] has shown that these peaks represent two organic compounds, one yellow and the other intensely fluorescent. The component with absorption maximum at 405 mμ is the one that is effective in the reaction with magnesium hydroxide and the ratio of absorption maxima 405 : 330 mμ is a measure of the relative concentrations of the two components. Van Wesemael[6] compared the absorption of an alkaline solution of the dyestuff (measured at 530 mμ) with the sensitivity of that dyestuff in its reaction with magnesium hydroxide but found no relationship between the two values. However, with the 4 dyestuffs investigated here, a relationship was found to exist between the optical density at 405 mμ of an aqueous solution of the dyestuff and the sensitivity of its reaction with magnesium hydroxide.

TABLE I

ANALYSIS OF FOUR SAMPLES OF TITAN YELLOW

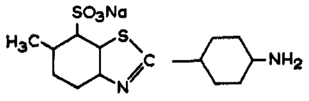
	A	*B*	*C*	*D*
Moisture (%)	7.1	7.3	12.4	7.6
Ash (%)	72.5	56.5	25.0	59.0
Sodium (%)	28.8	20.0	8.1	22.0
Chloride (%)	32.8	4.3	1.6	25.2
Sulphate (%)	4.6	31.9	13.7	7.2
Nitrogen (%)	2.84	4.41	6.37	4.34
Optical Density 330 mμ	0.182	0.320	1.228	0.290
Optical Density 405 mμ	0.365	0.720	0.452	0.674
Ratio 405 : 330	2.03	2.25	0.37	2.32

Sources of dyestuff: A and B from British Drug Houses Ltd, C from Hopkin and Williams Ltd and D from Eastman Kodak Ltd.

Some evidence is also available[7] that the number of sulphonic acid groups present in dehydrothio-*p*-toluidine sulphonic acid and hence in Titan yellow is uncertain and dependent on the temperature and duration of heating during sulphonation. This may affect the adsorption on magnesium hydroxide, since the more sulphonic acid groups which are present, the more hydrophilic the dyestuff and the less readily adsorbed at the surface of a precipitate.

If desired, it is possible to remove inorganic salts from samples of Titan yellow by extracting the dyestuff into a solvent mixture of 1 : 1 methyl cellosolve : diethyl ether, but no satisfactory way of removing the fluorescent organic component has been found. By chromatography on a cellulose column it was possible to obtain a fraction of dyestuff which paper chromatography showed to be almost free of the fluorescent component and the ratio of optical densities at 405 mμ and 330 mμ was then 2.4. With a suitably dilute solution (0.001–0.002%) the ratio of absorbances at these two wavelengths may be used as a screening test in comparing the purity of different batches.

It seemed probable that the fluorescent compound was an excess of the sodium salt of dehydrothio-*p*-toluidine sulphonic acid, resulting from an incomplete coupling reaction:



By reduction with sodium dithionite in acid solution, it was found possible to convert Titan yellow completely to the above compound; an orange-brown solid was isolated from the reaction mixture which was insoluble in water but soluble in sodium hydroxide to give a very pale yellow solution which showed an intense violet fluorescence. This fluorescence is a characteristic of derivatives of dehydrothio-*p*-toluidine[8]. When the sodium salt of this compound was examined by paper chromatography, the R_F value was the same as that of the impurity in the original dyestuff and the absorption spectrum of a dilute solution showed a single peak at 330 mμ.

Effect of light on solutions of Titan yellow

When dilute solutions of Titan yellow are exposed to light, gradual decomposition takes place with the production of a fluorescent compound whose properties are similar to those of the reduction product formed in the reaction between Titan yellow and sodium dithionite. A 0.02% solution of the dyestuff was prepared and exposed to light over a period of 14 days. At intervals, a 0.001% solution was prepared from it and the ratio of optical densities at 405 and 330 mμ was measured, with the following results:

Time of exposure (days)	0	4	7	14
Ratio 405 : 330 mμ	2.28	1.40	1.12	0.17

After 14 days, no absorption maximum was observed at 405 mμ and the Titan yellow had been completely decomposed to the sodium salt of dehydrothio-*p*-toluidine sulphonic acid. The effect of some additives on the photochemical decomposition was also investigated. Solutions were prepared and exposed to light over a period of 10

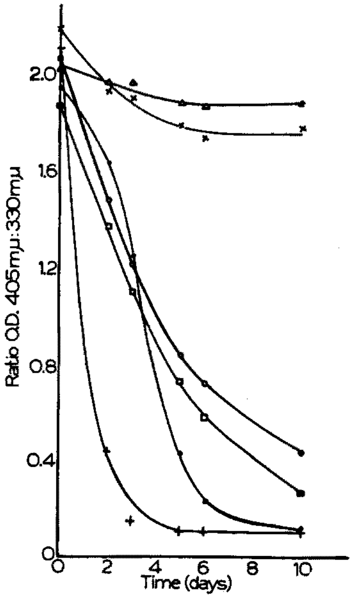


Fig. 1. Effect of additives on the photochemical decomposition of Titan yellow. + 0.005% Titan yellow; × 0.005% Titan yellow + 0.05% polyvinyl alcohol; O 0.005% Titan yellow + 0.05% polyvinyl alcohol + 50% glycerol; △ 0.005% Titan yellow + 0.5% polyvinyl alcohol; ● 0.005% Titan yellow + 1% starch; □ 0.005% Titan yellow + 1% starch + 50% glycerol.

days. At intervals, an aliquot was removed, diluted 5-fold and the ratio of optical densities at 405 and 330 mμ measured (Fig. 1).

The results show that polyvinyl alcohol has a very marked protective action against photochemical decomposition of Titan yellow and confirm the findings of KENYON AND OPLINGER[9]. However, in the presence of glycerol, the effect of polyvinyl alcohol is very much reduced. Its protective action is probably due to the formation of an adsorption compound with Titan yellow which is insensitive to light, since it has been shown (see below) that such a compound is formed in alkaline solutions of polyvinyl alcohol and Titan yellow. It is of interest that the azo compound corresponding to Titan yellow (*i.e.* chloramine yellow) is not decomposed by light, does not form an adsorption compound with polyvinyl alcohol, and does not react with magnesium hydroxide. Nor, according to BOGERT AND BERGEIM[10], is it reduced to dehydrothio-*p*-toluidine sulphonic acid by either acid stannous chloride or sodium dithionite. This suggests that the reactive grouping in Titan yellow is —N=N—NH— and when only —N=N— is present, as in chloramine yellow, no adsorption takes place on magnesium hydroxide.

THE COLLOID PROTECTOR

Protective colloids are now invariably used in methods which employ Titan yellow for the determination of magnesium, their function being to prevent aging of the magnesium hydroxide and to produce a stable colour. Originally, natural gums or starch were used but, more recently, synthetic polymers such as polyvinyl alcohol[11] (P.V.A.), sodium polyacrylate[12] (S.P.A.) and the sodium salt of carboxymethyl cellulose[6] have been preferred. The use of polyvinyl alcohol has been criticised by MITCHELL[13] who found that it reacted with Titan yellow and produced high blank values; MEHLICH[12] has claimed that sodium polyacrylate, and VAN WESEMAEL[6] that carboxymethylcellulose, are superior to any of the stabilising agents previously used. The sensitivity of the reaction has been found to be greatest in the presence of P.V.A. (Table II),

TABLE II

EFFECT OF SOME COLLOID PROTECTORS ON THE SENSITIVITY OF THE REACTION BETWEEN MAGNESIUM HYDROXIDE AND TITAN YELLOW

Colloid protector	*Concentration in final solution (%)*	*ΔA**
Starch	0.2	126
Starch + glycerol	0.2 + 10	218
Gum acacia	0.2	186
Gum tragacanth	0.04	181
Sodium polyacrylate	0.04	124
Polyvinyl alcohol	0.2	290
Polyvinyl alcohol + glycerol	0.2 + 10	395
Starch	0.02	120
Starch + glycerol	0.02 + 10	186
Gum acacia	0.02	102
Gum tragacanth	0.02	141
Sodium polyacrylate	0.02	124
Polyvinyl alcohol	0.02	409
Polyvinyl alcohol + glycerol	0.02 + 10	467

* $\triangle$A = (Optical density of 100 μg Mg — optical density of 0 μg Mg).

provided that its concentration is maintained at the minimum necessary to prevent precipitation of magnesium hydroxide. Glycerol, used with starch or P.V.A., also enhances the sensitivity. Figs. 2, 3 and 4 show the variation, with sodium hydroxide

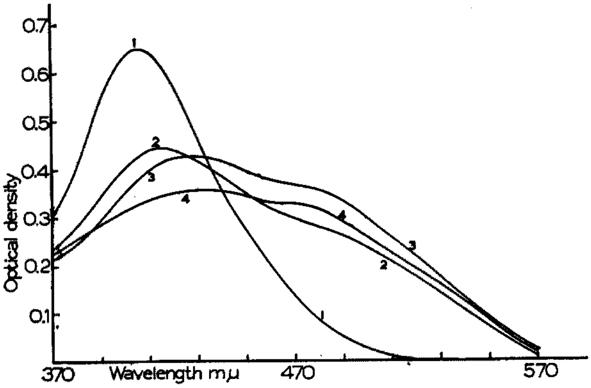


Fig. 2. Variation in Absorption Spectra of Titan yellow with sodium hydroxide concentration. 1. NaOH Nil 2. NaOH 0.2 *M* 3. NaOH 0.4 *M* 4. NaOH 1.0 *M*.

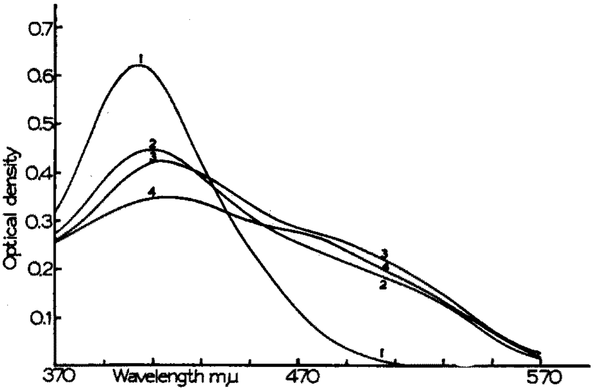


Fig. 3. Absorption Spectra of Titan yellow in the presence of sodium polyacrylate. 1. NaOH Nil 2. NaOH 0.2 *M* 3. NaOH 0.4 *M* 4. NaOH 1.0 *M*.

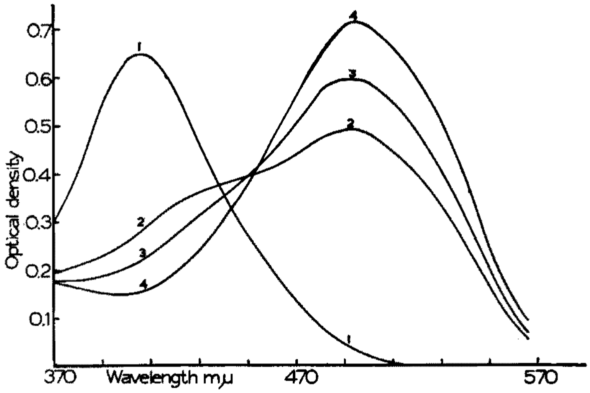


Fig. 4. Absorption Spectra of Titan yellow in the presence of polyvinyl alcohol. 1. NaOH Nil 2. NaOH 0.2 *M* 3. NaOH 0.4 *M* 4. NaOH 1.0 *M*.

concentration, of the absorption spectra of solutions of Titan yellow, Titan yellow + sodium polyacrylate, and Titan yellow + polyvinyl alcohol respectively. In the presence of S.P.A. the absorption spectra are similar to those obtained with Titan yellow alone and no reaction therefore takes place between the colloid protector and the dyestuff. However, in the presence of P.V.A. an absorption maximum is observed at 490 mμ and indicates the formation of an adsorption compound between the colloid protector and the dyestuff. Formation of this compound is favoured by increases in P.V.A. and sodium hydroxide concentrations. In the determination of magnesium with Titan yellow, the amount of dye adsorbed by the hydroxide will be a function of the number of sites on the dyestuff available for reaction. To achieve maximum sensitivity, the amounts of P.V.A. and sodium hydroxide added must therefore be optimal. Sufficient P.V.A. must be present to prevent precipitation of magnesium hydroxide, but any large excess will compete for adsorption sites on the dyestuff and the sensitivity of the reaction will be reduced. This has been previously noted by MITCHELL[13]. Table III shows the values of $\triangle$A (optical density of 100 μg Mg — optical density of 0 μg Mg) obtained using various concentrations of P.V.A. and sodium hydroxide. Solutions containing 0.005% P.V.A. gave, on standing, precipitates of magnesium hydroxide and the $\triangle$A values for these are unreliable. The optimum concentration of P.V.A. is therefore 0.01% in the final solution. At this concentration, the effect of sodium hydroxide on $\triangle$A was investigated in more detail. It was found that a maximum plateau region for $\triangle$A existed between 0.6 and 0.8 *N* sodium hydroxide and a concentration of 0.7 *N* was therefore selected for use.

TABLE III

VARIATION OF $\triangle$A WITH P.V.A. AND SODIUM HYDROXIDE CONCENTRATIONS

NaOH	*P.V.A. (%)*				
	0.005	0.01	0.02	0.04	0.08
0.5 *N*	0.569	0.530	0.475	0.464	0.443
0.8 *N*	0.569	0.510	0.430	0.420	0.365
2.0 *N*	0.412	0.370	0.325	0.325	0.328

THE EFFECT OF OTHER IONS IN THE SOLUTION

Reports in the literature about the effects of other ions on the reaction between magnesium hydroxide and Titan yellow are extremely conflicting and indicate that their influence may be dependent on the protective colloid system employed and on the relative amounts of magnesium and interfering ion present. To test this supposition, the effect of phosphate, calcium, aluminium, iron and manganese on the reaction was investigated using 3 different protective colloid systems: (*a*) sodium polyacrylate (S.P.A.) at 0.02% in the final solution as recommended by MEHLICH[12], (*b*) polyvinyl alcohol (P.V.A.) at 0.01% in the final solution, (*c*) polyvinyl alcohol at 0.01% and glycerol at 10% in the final solution. These conditions give the maximum sensitivity attainable for the determination of magnesium in the presence of P.V.A.[14].

Phosphate

Previous workers have reported that phosphate may increase[15,16] or decrease[6,7,17] the adsorption of Titan yellow on magnesium hydroxide. Some have found[11,12,13,18] no effect from phosphate while others[17,19] have noted that solutions become turbid from formation of colloidal calcium phosphate under the alkaline conditions employed in the reaction. In these experiments it was found that when S.P.A. is used as colloid protector, phosphate has no effect on the recorded optical densities but that when P.V.A. is used, either in the absence or presence of glycerol, then phosphate reduces optical densities and its effect becomes more pronounced as the concentration of magnesium increases. It has also been confirmed that interference may arise from formation of calcium phosphate in solutions high in calcium, producing turbidity and erratic values for the recorded optical density. This effect is most apparent in the presence of high concentrations of phosphorus or calcium; in many Titan yellow procedures the latter condition is realised from the addition of extra calcium to the sample to compensate for the effect of this element on the reaction.

Calcium

The effect of this element is comprehensively reported in the literature and, with a few exceptions, is to increase the optical density of solutions containing magnesium. Some workers, however, have found a decrease in optical density[13,20] while others[9,21] have found no interference. GOFFINET[22] found that an initial increase in colour was followed by a decrease in the presence of larger amounts of calcium. VAN WESEMAEL[6] investigated the influence of calcium in the presence of different batches of dyestuff and found that its effect was dependent on the source of Titan yellow used. In the experiments reported here, calcium increased the optical density when S.P.A. or P.V.A. was used as colloid protector, except at low concentrations of magnesium when no effect was observed. The enhancing effect of calcium became more pronounced as the concentration of magnesium was increased. When glycerol was incorporated with P.V.A., calcium produced very little effect and this can probably be attributed to complex-formation with glycerol at the high alkali concentration.

Aluminium

Most workers[9,17] have found that aluminium reduces the optical density but GLEMSER AND DAUTZENBERG[23] reported that it reduced or enhanced the colour dependent on the relative concentrations of magnesium and aluminium. The latter findings were confirmed in these experiments; the effect was also dependent on the protective colloid system employed. When S.P.A. was used as colloid protector, small amounts of aluminium produced a large increase in optical density which reached a maximum value and then began to decrease. In the presence of P.V.A., aluminium reduced the optical density of solutions containing small amounts of magnesium; with larger concentrations of magnesium, small amounts of aluminium produced an increase in colour intensity but as the concentration of aluminium was further increased, the optical density reached a maximum value and then began to fall. The results obtained with a mixture of P.V.A. and glycerol as protective colloid were qualitatively similar to those obtained with polyvinyl alcohol alone. According to WELLS[24], the arrangement of hydroxyl groups in the layer lattice structures of aluminium and magnesium hydroxide is similar and, when the latter is formed in the presence of aluminium, structures containing mixed layers of magnesium and aluminium atoms are possible. The incorporation of small amounts of aluminium in the magnesium hydroxide lattice seems to increase the surface area, so that more magnesium atoms become available for reaction with Titan yellow and an increase in dye adsorption occurs. This effect is more pronounced in the presence of large amounts of magnesium where the hydroxide is initially less dispersed (and hence has a lower surface: weight ratio) than at lower concentrations. As the aluminium concentration is increased, the optical density reaches a maximum value and then begins to decrease, presumably because more and more magnesium atoms in the surface layer are replaced by aluminium so that, although the surface area of the solid phase has been increased, fewer magnesium atoms are available for reaction with Titan yellow. This results in a decreased adsorption of dyestuff and the optical density, after passing through a maximum value, begins to fall. In the presence of small amounts of magnesium (*i.e.* 25 μg in 20 ml of solution) the only observed effect was a reduction in optical density; probably at these low concentrations the surface area of the solid phase is already at a maximum and is not increased in the presence of aluminium atoms. Their only effect is to replace magnesium atoms in the surface layer and hence reduce the amount of Titan yellow adsorbed. A steady decrease in optical density is therefore observed as the aluminium concentration increases. The effect of aluminium appears to depend on the initial surface area of the magnesium hydroxide, hence it is to be expected that different results will be obtained in the presence of different colloid protectors because these will influence the initial surface area of the solid phase.

Iron

Most investigators[6,9,21,22,23] have reported that iron decreases the optical density of solutions containing magnesium, although BUSSMAN[17] found an initial increase followed by a decrease at higher concentrations of iron. In these experiments it was found that the effect of iron was very variable and dependent on the protective colloid system used and the relative concentrations of iron and magnesium. The results were very similar to those obtained in the presence of aluminium and a similar explanation can be proposed.

Manganese

This element is reported to interfere in three ways; first, by formation of manganous hydroxide in alkaline solution followed by atmospheric oxidation to give a brown coloration[20], secondly by reaction with Titan yellow to give a colour similar to that formed with magnesium[22,25], and thirdly by interference with the formation of the magnesium-dye compound[15,20]. Although most authors have reported that manganese increases the optical density of solutions and yields high results for magnesium, some[16,23] have obtained low results. With S.P.A. or P.V.A. as colloid protector, the observed effects were very similar to those obtained with iron and aluminium. The presence of small amounts of manganese produced a marked increase in optical density which reached a maximum value and was then followed by a rapid decrease, the effect being more pronounced at the higher concentrations of magnesium. The interference probably arises from incorporation of manganese atoms in the magnesium hydroxide lattice — since the hydroxides have similar structures — which alters the amount of dye adsorbed. With solutions containing only manganese, an identical increase in optical density was observed both in the presence and absence of Titan yellow. No reaction occurs, therefore, between manganous hydroxide and the dyestuff and the small increase in optical density observed in the absence of magnesium is due to atmospheric oxidation of manganous hydroxide with the production of a pale yellow, slightly turbid solution. This increase is much too small to account for the observed changes in optical density in the presence of magnesium. When P.V.A. was used in the presence of glycerol as colloid protector, the effect of manganese was less marked; under these conditions and at the high sodium hydroxide concentration employed, manganese formed a pinkish water-soluble complex. Manganese ions were therefore removed from solution and were not incorporated to the same extent in the magnesium hydroxide lattice.

It appears from the above experiments that the extent to which phosphate, calcium, aluminium, iron and manganese influence the reaction is dependent on the protective colloid system used and on the relative concentrations of magnesium and interfering element. Under each set of reaction conditions the effects will be different and it is not surprising that conflicting reports appear in the literature. Since calcium, aluminium, iron and manganese hydroxides all have lattice structures similar to that of magnesium, it seems probable that interference from these elements is caused by their incorporation in the magnesium hydroxide lattice with a resultant change in the nature of the surface and the amount of dye adsorbed. Interference from these elements may easily be overcome by complex formation in alkaline solution and suitable reagents have been described for this purpose[3,14].

SUMMARY

A study is made of factors which influence the adsorption of Titan yellow on magnesium hydroxide. Variation in composition of different dye samples is investigated and the photochemical decomposition of the dyestuff studied. Polyvinyl alcohol is the best of colloid protectors examined. The effects of phosphate, calcium, aluminium, iron and manganese on the reaction depend on the protective colloid system employed and the relative concentrations of interfering element and magnesium present.

RÉSUMÉ

L'auteur a effectué une étude sur les facteurs influençant l'adsorption du jaune titane sur l'hydroxyde de magnésium. L'action du phosphate, du calcium, de l'aluminium, du fer et du manganèse sur la réaction dépend du colloïde protecteur utilisé et des concentrations relatives de l'ion gênant et du magnésium.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung, über die Faktoren, welche die Adsorption von Titangelb an Magnesiumhydroxyd beeinflussen. Es wird gezeigt, dass der Einfluss von Fremdionen von deren Konzentration und von der Wirkung des Schutzkolloids abhängt.

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DETERMINATION OF TRACES OF HYDROGEN IN FLUORO-ORGANIC COMPOUNDS

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The determination of traces of hydrogen is of great importance in studies of highly fluorinated organic compounds; if only a few hydrogen atoms are present in a polyfluoride, the weight percentage will obviously be very low (below 2%), but the hydrogen will almost certainly have a decisive influence on the properties of the compound. It is therefore most desirable to have a reliable direct method for the determination of this hydrogen, which is a most important substituent from the viewpoint of fluorocarbon chemistry. Microcombustion procedures for carbon and hydrogen in fluoro-compounds do not give sufficiently accurate figures for hydrogen when less than 1% is present, no matter which particular modification is used. Very little information has been published on this problem.

SIMONS *et al.*[1] passed volatile liquids and gases over magnesium turnings *in vacuo* at 650–700° and oxidized the hydrogen produced by passing through hot copper oxide; the water formed was weighed after absorption in phosphorus pentoxide. The method is unattractive in that solids and small amounts of materials are not easily dealt with, and that two pumping systems are required.

Pyrolytic method

In the Manhattan Project work, a method was developed[2] in which the samples are pyrolysed in a platinum tube at 1300° in a nitrogen stream, and the hydrogen fluoride produced is titrated with alkali; when the H:F ratio is greater than one, chlorine is added to the nitrogen stream and an iodometric finish is applied in addition to the above titration, an appropriate correction being made. This modified finish is also necessary when the sample contains a halogen other than fluorine. The original method required samples of about 300 mg but satisfactory accuracy (± 0.02% absolute) can be achieved with smaller amounts[3].

The behaviour of elements other than carbon, hydrogen and halogens in the pyrolytic procedure was unknown and extensive investigations were therefore made. Current research programmes made the behaviour of nitrogen and sulphur of particular interest, but insufficient amounts of suitable compounds necessitated the use of non-fluorinated compounds for preliminary tests, in which the samples were pyrolysed in nitrogen as above and the effluent gases were examined. The results of these tests are summarized below.

Nitrogenous compounds produced no acidic substances in the pyrolysis. Compounds containing nitro or amino groups were tested and qualitative and quantitative tests confirmed the absence of nitric oxide and nitrogen peroxide in the effluent gases. Cyanogen was found, especially with amino groups in the sample. Several pure aromatic sulphonic acids, obtained by ion exchange of the commercial sodium salts, were also pyrolysed, parallel tests being run on the parent hydrocarbons. The hydrocarbons gave completely blank values, while their sulphonic acid derivatives gave acidic substances corresponding to 0.02–0.04% hydrogen. Tests showed that hydrogen sulphide, elementary sulphur and traces of sulphur trioxide were formed. Similar results were found for compounds containing nitrogen and sulphur. Thiourea gave results corresponding to 0.09% hydrogen, and thiocyanate was found in the aqueous absorbent.

TABLE I

Compound	*% H theor.*	*% H found*	*Error %*
Octafluoroadipic diamide	1.39	1.41, 1.38	0.02, 0.01
1-Amino-3-imino-2,4,4,5,5,6,6-hepta-fluorocyclohexene	1.28	1.26, 1.28	0.02, 0.00
2-Nitro-5-trifluoroacetamidobenzotrifluoride	1.32	1.30, 1.30	0.02, 0.02

Tests on several highly fluorinated materials containing nitrogen and about 1% hydrogen confirmed that nitrogen in the sample did not interfere (Table I). Several other compounds of interest gave low results because the H:F ratio exceeded one; even a 1:1 ratio was not satisfactory. Mixing such samples with a fully fluorinated compound before pyrolysis improved the results only slightly, possibly owing to different rates of volatilization and decomposition of the two components. When both nitrogen and oxygen were present, some compounds gave satisfactory results while others gave slightly high results which could be traced to nitric acid formation.

When fully fluorinated compounds containing sulphur and oxygen were pyrolysed, the amounts of acid formed generally corresponded to 0.02–0.07% hydrogen, the higher values being found for sulphonates. Even larger positive errors arose with hydrogen-containing compounds, *e.g.* $C_3F_6H_2SO_3$. Titration of the fluoride in the absorbent solution with aluminium(III) in the presence of eriochrome cyanine R indicator[4] gave reasonably accurate results for hydrogen. Probably the difficulties found with sulphur-containing compounds and some nitrogenous compounds could be overcome in all cases by titrating the fluoride rather than the hydrogen of the hydrogen fluoride formed in the pyrolysis, though this would not be satisfactory for compounds containing halogens other than fluorine.

However, in the course of these tests, it became clear that the pyrolytic method is ill-suited to routine work. The principal drawback is that the very expensive platinum tube deteriorates rapidly at the high temperature required for pyrolysis, so that it must be reworked regularly.

Combustion method

At the time that the method of MILLER *et al.*[2] was developed, no really satisfactory procedure existed for the determination of carbon and hydrogen in fluorinated compounds. Since then, several methods have been described: much the best are those in which sodium fluoride[5] or magnesium oxide[6] is used as the absorbent for the fluorinated decomposition products. Magnesium oxide is a particularly efficient and versatile reagent in this type of analysis[7], and allows very accurate determinations of hydrogen even on the micro scale. Accordingly, it was considered feasible to develop a straightforward combustion procedure for the determination of traces of hydrogen. Carbon could probably be determined simultaneously if desired, but this was not done in the proposed method, which would most suitably be applied in conjunction with a procedure for the simultaneous determination of carbon and fluorine[8]. Many of the compounds containing only small amounts of hydrogen are low-boiling liquids which are rather difficult to analyse for fluorine by non-combustion methods.

In the proposed method, a sample of 50–100 mg is burned in oxygen through a long layer of magnesium oxide at 900°. Fluorine is retained in this layer and other halogens and sulphur oxides are retained on a layer of silver at the end of the combustion tube. The water formed is then determined, while carbon and nitrogen oxides are allowed to go to waste.

Determination of water

Gravimetric determination of the water formed in the combustion after absorption in a Pregl tube containing anhydrone was reasonably satisfactory, but the accuracy was slightly less than that of the pyrolytic method. Attention was therefore turned to titrimetric methods, which would, if relatively straightforward, be more convenient for routine use. Several studies have been made in recent years of the titrimetric determination of water using acid chlorides, the hydrogen chloride formed being swept into an absorber and titrated. Succinyl chloride was found to be an improvement on previous reagents of this type, but when it was used to determine water formed in a combustion process the errors were much larger than could be tolerated in elemental analysis[9]. However, β-methyl-β-ethylglutaryl chloride is a better reagent, giving an error of $\pm$ 1% relative over the range 3–15 mg of water in inorganic analysis[10]. Moreover, it has the advantages that no special cooling trap is required between the reaction vessel and the absorber for hydrogen chloride, and that blank values are comparatively low and constant. Accordingly, this reagent seemed promising for the trace hydrogen method.

The reaction vessel and the absorption system previously described[10] were found satisfactory for inorganic hydrated salts at flow rates of about 15 ml/min when oxygen was used as the sweeping gas; in the previous work on the reagent[10], nitrogen was used. The method was then applied to the determination of water from combustion of organic samples and again satisfactory results were obtained.

EXPERIMENTAL

Apparatus

A line diagram of the combustion train and the system for the titrimetric finish is shown in Fig. 1.

The combustion train consists of the oxygen inlet with a pressure head of mercury leading to a flowmeter, a preheater containing platinized asbestos at 600° and a large scavenging U-tube packed with anhydrone. The combustion tube is of clear grade A silica; the volatilization section is 22.5 cm in length and 0.9–1 cm in inner diameter with a conventional side arm. The combustion chamber is 42 cm long and 2.4 cm inner diameter narrowing to a ground glass B 10 cone joint. The combustion tube is packed with a 7 cm layer of silver gauze or electrolytic silver and then with a 25 cm layer of magnesium oxide pellets held in position with silica wool; for the preparation of magnesium oxide, see CAMPBELL AND MACDONALD[7]. The whole magnesium oxide layer must be in the hot part of the furnace. For smooth volatilization, especially of volatile liquids, it is advisable to place a small roll of platinum foil from the narrow section of the tube up as far as the magnesium oxide.

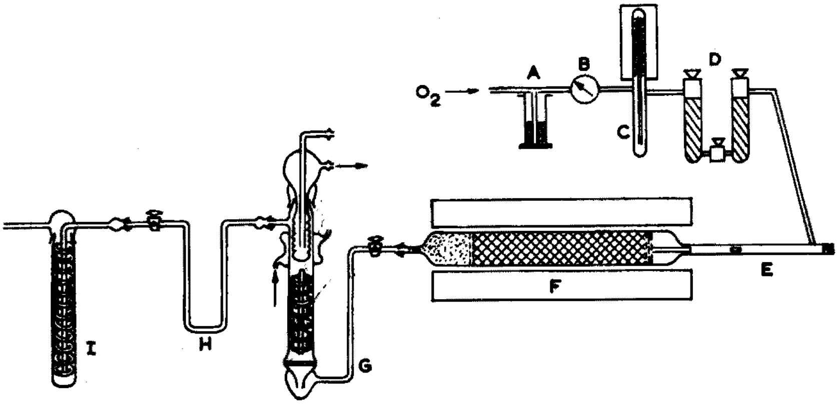

Fig. 1. Combustion train with apparatus for titrimetric finish. A Pressure head, B Flowmeter C Preheater, D Scavenging tube, E Combustion tube, F Furnace, G Reaction vessel, H Spray trap, I Absorption vessel.

The furnace has a length of 40 cm with an inner diameter of 3 cm. The temperature should be 900° over a length of about 25 cm. In the present work, a platinum–rhodium wound model from Johnson Matthey & Co. Limited, Type K25A was used.

The apparatus for the titrimetric finish is exactly the same as that described previously[10]; a heating tape is wrapped round the inlet capillary tube and switched on during determinations[10].

For the gravimetric finish, a Flaschenträger absorption tube containing Anhydrone was attached to the combustion tube via a drawn-out B 10 socket through which silver wire was threaded to prevent condensation of moisture. This tube was then attached through a guard tube to a Marriotte bottle.

β-Methyl-β-ethylglutaryl chloride. For preparation, see BELCHER *et al.*[10].

PROCEDURE

(*a*) *Preparation*

Connect the apparatus and adjust the furnace temperature to 900° and the oxygen flow to 14–15 ml/min. Flush the system thoroughly to remove water. For the titrimetric finish, charge the reaction vessel with 5 ml of the reagent and seal the top joint with Krönig glass cement. Seal the exit arm to the spray trap with glass cement and attach the entry arm to the combustion tube with spring clips. Flush the system with oxygen until blank values become constant.

(*b*) *Combustion*

Weigh a sample of 20–50 mg depending on the expected hydrogen content (0–2%), in a platinum boat or a capillary tube. Insert the sample to a position about 10 cm from the furnace while a rapid flow of oxygen passes out through the mouth of the tube. Stopper the tube and burn off the sample in the conventional way, using a first combustion time of 6–7 min and a second combustion of 6–7 min. Sweep for 16–18 min, making a total time of 30 min for the decomposition.

(*c*) *Gravimetric finish*

Before the first combustion, sweep the Anhydrone tube for 10 min, detach, clean in the conventional way and weigh on the 4th min after releasing the pressure. Reattach the tube and burn the sample. After the decomposition has been completed, detach the tube, clean and weigh as before on a microanalytical balance.

(*d*) *Titrimetric finish*

Charge the absorption vessel for hydrogen chloride with about 8 ml of distilled water and insert the sample into the combustion tube, while the taps on each side of the reaction vessel are closed and while the heating tape around the entry tube is warming up. Open the taps and, if necessary, adjust the flow rate. Burn the sample as described above. After 30 min, close the taps, switch off the heating tape, detach the absorber, and rinse the contents into a flask with about 20 ml of distilled water. Titrate with 0.02 *N* sodium hydroxide using methyl red screened with methylene blue as indicator.

Blank values

Blanks should be determined with an empty boat and with a fully fluorinated sample. Perfluorodicyclohexylethane was found suitable in the present work, provided that it was rigorously dried beforehand. Polytetrafluoroethylene is not a suitable compound for use as a standard or in blank determinations.

RESULTS AND DISCUSSION

The combustion system seems to be quite satisfactory even for very stable fully fluorinated materials, although in micro methods involving similar reagents it is generally necessary to burn such samples in moist oxygen to achieve complete decomposition[5,7]. The high temperature (900°) and the very large amount of magnesium oxide are probably responsible for this success. In early work on the procedure, a 4-cm layer of platinum was placed centrally in the tube filling but later work showed that equally successful results could be obtained without this catalyst. Magnesium oxide alone effectively promotes complete decomposition of fluorinated materials[7].

Representative results obtained by the gravimetric and titrimetric methods are shown in Table II. The same accuracy of ± 0.03% was achieved by both methods. This accuracy is slightly less than that obtained by the pyrolytic method (± 0.02%), but it should be noted that the difference between duplicate results is generally less than the difference from the theoretical value. In all cases the materials examined were research compounds whose absolute purity was uncertain. For occasional determinations, the gravimetric procedure would be the more convenient but for series analysis, the titrimetric method is preferable.

Blank values tended to vary for different batches of the acid chloride reagent; and when the apparatus is first set up, the blank may take some time to settle to a constant value. However, once the apparatus is in use, the reagent is serviceable for many determinations, having a capacity for about 700 mg of water[10].

TABLE II

COMBUSTION METHOD

Compound	*% H theor.*	*% H gravim. finish*	*Error*	*% H titrim. finish*	*Error*
Decafluorocyclohexane	0.76	0.75, 0.75	0.01, 0.01	0.78, 0.78	0.02, 0.02
4 H/5 H-Octafluorocyclohexene	0.89	0.91, 0.90	0.02, 0.01	0.91, 0.92	0.02, 0.03
1-Amino-3-imino-2,4,4,5,5,6,6-heptafluorocyclohexene	1.28	1.25, 1.26	0.03, 0.02	1.29, 1.30	0.01, 0.02
Pentafluoroaniline	1.10	1.12, 1.07	0.02, 0.03	—	—
1,2,3,4-Tetrachloro-1H-heptafluorocyclohexane	0.29	—	—	0.31, 0.30	0.02, 0.01
1,2,2-Trichloro-1,1-difluoroethane	0.60	—	—	0.60, 0.62	0.00, 0.02
1,1,1-Trifluoro-2-chloro-2-bromoethane	0.51	—	—	0.51, 0.53	0.00, 0.02
Trifluoroethyl trifluoromethane sulphonate	0.87	—	—	0.87, 0.85	0.00, 0.02
Perfluorodecanesulphanilide	0.90	—	—	0.89, 0.92	0.01, 0.02
1-Amino-2,4,4,5,5,6,6-heptafluorocyclohexene-3-one	0.85	—	—	0.87, 0.87	0.02, 0.02

Other halogens and sulphur in the sample have no effect on the results, because they are removed in a layer of silver at the beak end of the tube. Rolls of silver gauze are satisfactory but electrolytic silver has a higher capacity[11], which is important because the silver layer must not be allowed to extend into the very hot part of the furnace.

Nitrogen in the organic sample did not interfere in either method. This was expected in the case of the gravimetric method where nitrogen oxides are usually removed in an external absorber after the absorption of water. Nitrogen oxides were, however, expected to interfere in the titrimetric method; it was checked by semiquantitative tests with Griess reagent that these oxides passed straight through the system without causing release of hydrogen chloride from the reagent and without affecting the titration. This would appear to be an additional advantage of β-methyl-β-ethylglutaryl chloride over succinyl chloride[9].

In conclusion, the proposed method gives results of sufficient accuracy for normal estimates of the purity of fluorinated materials and it can be applied without modification to all the usual types of sample. It is much more convenient in use than the earlier pyrolytic method, and the amount of sample required is less.

ACKNOWLEDGEMENT

We are grateful to Mr. G. TURTON for carrying out routine checks of this procedure.

SUMMARY

The determination of traces of hydrogen in highly fluorinated compounds has been studied. Nitrogen and sulphur in the sample interfere slightly in the pyrolytic method of MILLER *et al.* A straightforward combustion method is proposed in which the sample is burned in oxygen over magnesium oxide at 900° and the water formed is determined either gravimetrically or titrimetrically.

RÉSUMÉ

Les auteurs ont étudié le dosage de traces d'hydrogène dans les composés organiques fluorés. Une méthode est proposée consistant à brûler l'échantillon à analyser dans l'oxygène, sur de l'oxyde de magnésium, à 900°. L'eau formée est dosée soit par gravimétrie, soit par titrage.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Spuren von Wasserstoff in hochfluorierten organischen Verbindungen. Die Substanz wird im Sauerstoffstrom über Magnesiumoxyd verbrennt und das gebildete Wasser entweder gravimetrisch oder durch Titration bestimmt.

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THE DETERMINATION OF MICROGRAM QUANTITIES OF SULPHIDE IN BIOLOGICAL MATERIALS

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The determination of small amounts of sulphide in biological materials requires a sensitive method. The well known volumetric methods which depend upon the reduction of iodine in acid conditions[1,2] or iodate in alkaline conditions[3] are insufficiently sensitive, though the latter technique is reliable for standardizing stronger sulphide solutions (see below). LEWIS[4] has described a procedure involving oxidation with iodine in carbon tetrachloride and colorimetric determination of the excess iodine. The method, which is rapid and convenient, did not prove reliable in our hands, probably because iodine reacts with the alkali of the strongly alkaline sulphide solution. Neutralization of the sulphide solution before addition of the iodine led to erratic results presumably because of loss of sulphide. The strongly alkaline sulphide solutions were obtained by the technique used to separate the sulphide from reaction mixtures (see below); substitution of other sulphide absorbents such as cadmium chloride was not successful. Similar findings have been reported by BETHGE[1] who points out that the critical point in all iodometric methods for sulphide is the mixing of the sulphide and the iodine solutions; he also notes the inadvisability of using absorbents which produce sulphide precipitates.

The formation of methylene blue by the reaction of *p*-aminodimethylaniline with sulphide in the presence of ferric chloride[5] has been widely used as a method of sulphide estimation. Various modifications have been recommended[6–11] and because of the intensely coloured product the method has obvious advantages. This reaction, when performed under carefully controlled conditions as described below, was found to be very satisfactory for the determination of microgram quantities of sulphide in biological materials.

The separation of sulphide

The most widely used technique is to acidify the mixture containing sulphide and sweep the hydrogen sulphide with air into some suitable absorbent[7,8,12]; but this is not very convenient if many samples have to be analysed. Moreover, if an alkaline absorbent were used, sulphide would probably be oxidized unless oxygen-free gas were employed.

POSTGATE[13], LEWIS[4], and ANDERSON[14] have used Warburg flasks to separate

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sulphide from reaction mixtures, the sulphide being swept into an absorbent in the central well of the flask. However, it was not easy to obtain satisfactory recoveries by this method probably because of the difficulty of achieving quantitative transfer of the absorbent from the constricted central well, while keeping the total volume of the solution reasonably low.

Isothermal distillation of sulphide using Conway microdiffusion units[15] has also been recommended by previous workers. The recovery of sulphide from 1.0 ml quantities of a $4 \cdot 10^{-3}$ *M* solution of sodium sulphide was tested with 0.5 ml of 40% sodium hydroxide in the central well of the Conway units; 1.0 ml of 4 *N* hydrochloric acid was added to the sulphide solution in the outer chamber and the units were left at room temperature for various periods of time. The alkali from the central well was then transferred to a suitable titration vessel with a Pasteur pipette and the inner well was washed out with four 0.5 ml portions of distilled water. The sulphide was determined by the iodate method[3] and the recovery was compared with direct determinations on 1.0 ml quantities of the same sulphide solution. There was no significant increase in the sulphide recovery if diffusion was continued for more than 165 min. If diffusion were allowed to continue for longer than about 17 h, rather low sulphide recoveries were sometimes obtained, possibly owing to oxidation of sulphide. Bethge[1] recommends that alkaline sulphide solutions should not be stored for long in contact with air. However, no marked losses of sulphide were noted during the present work when sulphide solutions in 40% sodium hydroxide were stored at room temperature for up to 16 h, though it appears that there is little to be gained by prolonging the diffusion process beyond 3 h at room temperature.

In other experiments 20% sodium hydroxide was tried as an absorbent but markedly lower recoveries were obtained after a 3 h diffusion period; 0.5 ml of 40% sodium hydroxide proved satisfactory. Tests of sulphide recovery in three separate experiments each consisting of 4 replicate determinations showed 100.1, 92.6 and 103.2 mean percentage recoveries with mean deviations of 1.8, 1.4 and 1.2% respectively. In the final procedure 0.2 ml of 40% sodium hydroxide gave good recoveries; this amount was governed by the decreased size of the central well (see below) and by the smaller amounts of sulphide taken.

Determination of sulphide by the methylene blue reaction

The practical details used in the preliminary tests of this method were essentially those recommended by Kuratomi *et al.*[12]. The optical densities of the methylene blue were measured in a 1-cm cuvette using a SP 500 Unicam Spectrophotometer. Kuratomi *et al.*[12] recommend 630 mμ as the wavelength for measurements. An examination of the absorption spectrum of the colour produced shows 2 absorption maxima, one at 670–672 mμ and one at 740 mμ. The specific absorption is greater at 740 than at 670 mμ. Fogo and Popowsky[8] recommend measurement at 670 mμ. A check of the variation of optical density at the 670 mμ maximum with sulphide concentration showed a rectilinear relationship and confirmed that Beer's law was obeyed up to optical densities of 2.0 per 1.0 cm light path. The greater sensitivity which results by optical density measurement at 670 mμ has obvious advantages and this wavelength was used for all further optical density measurements.

The methylene blue reaction is known to be pH dependent[8]. With the microdiffusion technique for separation of sulphide, the addition of the strongly alkaline absorbent to the reaction mixture might be expected to affect the colour development. Addition of 0.5 ml of 40% sodium hydroxide caused a slight increase in the intensity of the colour produced and did not affect the linearity of a calibration curve.

It was found that colour formation was complete at room temperature after 15 min and that the colour then remained stable for at least 24 h.

After the Conway units had been in use for several months, the surface of the inner wells showed considerable etching owing to the strong alkali. At the same time troublesome turbidities started to appear during colour formation. Attempts to clarify the solutions by centrifuging before the optical density was read were not successful. Furthermore, the suspended material interfered with the formation of the colour; the methylene blue formation was incomplete even after 3 h. Various devices were tried to protect the central well of the Conway units. Small polythene cups fitting into the central well proved most satisfactory (Fig. 1). The hydrophobic nature of these cups made it difficult to achieve quantitative transfer of the sodium hydroxide and the wash water with a Pasteur pipette. The cup and contents were therefore transferred to a 50-ml wide-necked glass-stoppered flask and the colour was formed in these vessels.

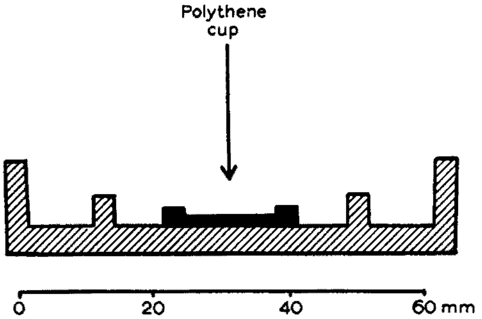

Fig. 1. Polythene inserts for use with Conway units.

The sensitivity of the method was markedly reduced by this technique and low recoveries were obtained, compared with direct determinations on identical aliquots of the sulphide solution. The direct determinations were made in 10-ml stoppered graduated cylinders and the low recoveries were traced to the widely different volumes of the gas phase in the two types of reaction vessel. When the colour was formed directly in 50-ml stoppered flasks and in 10-ml stoppered cylinders, the optical densities with the 50-ml flasks (volume of gas phase about 40 ml) were 65–70% of those obtained with the 10-ml cylinders (gas phase about 2 ml). Since the methylene blue formation seemed to be inversely related to the volume of the gas phase, special tubes were designed. The tubes were fitted with B 24 stoppers and cones which were sufficiently wide to take the polythene cups, and had a minimal gas space above the reaction mixture. The tubes had an external diameter of 27 mm and their volume with the stopper in place was 12.0 ml. Differences in volume of

± 0.25 ml were permissible but greater differences caused significant variation between replicates.

When the reproducibility of the recommended procedure was tested, a series of 6 replicate determinations showed a mean percentage deviation of 1.98. When identical quantities of the same sulphide solution were carried through the recommended microdiffusion procedure and colour formation, the mean percentage sulphide recovery from 6 replicate determinations was 93 with a mean percentage deviation of 2.2.

EXPERIMENTAL

Reagents

p-Amino-N,N-dimethylaniline sulphate. Dissolve 0.5 g of reagent in about 700 ml of distilled water and 200 ml of concentrated sulphuric acid and dilute to 1 l with distilled water.

Ferric ammonium sulphate. Dissolve 31 g of ferric ammonium sulphate in distilled water, add 6.3 ml of concentrated sulphuric acid and dilute to 250 ml with distilled water.

Potassium iodide. 1.65 g of analytical quality potassium iodide dissolved in 500 ml distilled water.

Standardization of sulphide solution

The procedure used was essentially that recommended by BETHGE[3] scaled down to determine 10 μmole amounts of sulphide. Sodium starch glycolate was used as an indicator. Standardized sulphide solutions at pH values about 7 cannot be stored even in stoppered flasks and must be used immediately; except in quite alkaline solutions hydrogen sulphide is quickly lost.

Procedure for determination

Standard No. 1 Conway units are recommended. Place a polythene cup in the central well and measure 0.2 ml of 40% (w/v) sodium hydroxide into it. In the outer chamber place a 1-ml sample (containing up to 1.0 μM sulphide). Grease the covers with vaseline, place in position and acidify the contents of the outer chamber with 1.0 ml of approximately 4 N hydrochloric acid, using the technique recommended by CONWAY[15] to avoid losses. Seal the units and leave at room temperature for 3 h. Then open the units and transfer the polythene cups with their contents to the stoppered tubes described above, containing 3.8 ml of distilled water. Add 5 ml of *p*-amino-N,N-dimethylaniline sulphate and 1.0 ml of ferric ammonium sulphate solution rapidly, replacing the glass stopper between additions. Then mix the contents by inverting the tubes several times. After 30–60 min, measure the optical density at 670 mμ using a 1-cm cuvette with distilled water in the reference cuvette. Determine a reagent blank on 3.8 ml of distilled water and 0.5 ml of 40% sodium hydroxide in the same manner.

A calibration curve is obtained by carrying out determinations on a series of standard sulphide solutions. Add 1.0-ml aliquots to the special stoppered tubes and dilute to 4.0 ml with distilled water before adding the other reagents. Add an empty clean polythene cup to each tube. The reaction is so sensitive to differences in the volume of the gas phase, that it is important always to adhere strictly to the same conditions, otherwise anomalously high apparent recoveries of sulphide are obtained. After considerable use the polythene cups tend to become discoloured, and low recovery figures are obtained. No satisfactory method of cleaning the cups has been found and at the first sign of discolouration they should be discarded.

APPENDIX

Since the experiments described above were completed GUSTAFSSON[16] has reported a detailed examination of the methylene blue reaction. GUSTAFSSON's results show that the acidity used in the present studies was higher than the optimum, which probably accounts for the increase in yield of methylene blue observed in the presence of the alkali, and for the difference in the relative absorption at the two maxima. We have observed no significant effects due to slight variations in the room temperature at which the reaction was performed, although GUSTAFSSON's results make it clear that for the highest accuracy the temperature of the reaction mixture should be controlled. GUSTAFSSON recommends a special regimen of reagent addition and shaking when the reaction is performed in volumetric flasks.

SUMMARY

Several methods for the estimation of microgram quantities of sulphide in biological material and enzymatic reaction mixtures were investigated. The optimum conditions for separation of sulphide by isothermal distillation are given. The formation of methylene blue is recommended for the spectrophotometric determination of sulphide; modifications are described to improve the reliability and sensitivity of the method.

RÉSUMÉ

Les auteurs ont examiné diverses méthodes pour le microdosage des sulfures en milieux biologiques. Le procédé au bleu de méthylène est recommandé pour leur dosage spectrophotométrique; quelques modifications y sont apportées.

ZUSAMMENFASSUNG

Zur Bestimmung von Mikrogramm-Mengen von Schwefel in biologischem Material wurden verschiedene Methoden untersucht. Schwierigkeiten bei Destillationsverfahren werden beschrieben. Zur spektrophotometrischen Bestimmung wird die Methylenblaureaktion empfohlen.

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MICROANALYSIS WITH THE AID OF ION-EXCHANGE RESINS

PART XX[1]. DETECTION OF NANOGRAM AMOUNTS OF TITANIUM(IV) WITH TIRON

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INTRODUCTION

In the present work the resin spot test[2] was applied to a colour reaction between titanium(IV) and tiron[3,4] (sodium 1,2-dihydroxybenzene-3,5-disulphonate). This reaction is more sensitive and selective than the hydrogen peroxide method, which was previously used in the resin spot test for titanium(IV)[5]. The intensely coloured titanium(IV)-tiron chelate anion is strongly adsorbed on anion-exchange resin beads, and gives the colourless resin phase an intense yellow colour, which allows a very sensitive detection of titanium(IV). Highly sensitive, simultaneous tests for ultramicro amounts of iron(III) and titanium(IV) using tiron and anion-exchange resin beads were also studied.

EXPERIMENTAL

Reagents

The chemicals used were of analytical grade, unless otherwise specified.

Stock solution of titanium(IV): Potassium bis-oxalato-oxo-titanate(IV) dihydrate $K_2TiO(C_2O_4)_2 \cdot 2H_2O$ (Kokusan Kagaku) was treated with concentrated sulphuric acid and ammonium sulphate according to SANDELL[6]. The stock solution was found to contain 3.22 mg of titanium(IV) per ml*. A series of standard titanium(IV) solutions was prepared by diluting the stock solution with 1 *F* sulphuric acid.

Aqueous solution of tiron: 40 mg of tiron (Wako) was dissolved in 10 ml of distilled water.

EDTA: Disodium ethylenediaminetetraacetate (Dojin Pharmaceutical Laboratories) was used to prepare 0.01 *F* and 0.05 *F* solutions.

Buffer solutions: To adjust the pH values , the following solutions were added to the test solution which was about 1 *F* in sulphuric acid; 2 *F* ammonia, 1 *F* sodium acetate and 1 *F* ammonia-ammonium chloride (pH 10) were used.

Hydrochloric acid and nitric acid were redistilled.

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* The content of titanium(IV) was determined by compleximetric titration, excess of EDTA being back-titrated with 0.05 *F* copper(II) solution using Cu-PAN as indicator[7].

Ion-exchange resins

Commercial strongly basic anion-exchange resins conditioned as previously described[1] were used in the chloride form throughout the present work. The following commercial resins were used: Dowex 1-X1, 1-X2, 1-X4, 1-X10 and 2-X2. Dropping capillary pipettes were drawn from a glass tube so as to deliver 0.04 ± 0.002 ml of de-ionized water per drop.

PROCEDURE

To determine the optimum conditions, the following procedure was used. On a white spot plate, a few grains of a colourless or pale-coloured strongly basic anion-exchange resin were mixed successively with 1 drop each of the test solution, of a dilute EDTA solution* and of the reagent solution, and then with a few drops of buffer solution**. After several min, a yellow colour appeared in the resin phase. The colour should be observed under a fluorescent lamp through a magnifying glass of about 20×. An incandescent lamp tends to decrease the sensitivity of the observation.

RESULTS AND DISCUSSION

In the study of the optimum conditions, each test was done in quadruplicate. No appreciable difference in the coloration of the resin phase could be observed for the resins Dowex 1-X1, -X2, -X4, -X10 and 2-X2 in the chloride form. Hence, Dowex 1-X1 in the chloride form was mainly used as a representative of the strongly basic anion-exchange resins.

Since the colour reaction between titanium(IV) and tiron was reported to be influenced by the pH of the solution[3], the limits of identification for the present resin spot test were determined at various pH values of the reaction media.

The optimum sensitivity of the test was displayed at pH values about 5. At lower pH values the sensitivity was less, and at high pH there was apparent oxidation of the reagent with the formation of a masking red colour[8]. The pH values were checked by placing tiny drops of the solution on indicator papers.

The limit of identification was 0.039 μg Ti (in 0.04 ml) after 20 min and 0.026 μg after 50 min under the optimum conditions.

For the study of reagent concentration a sample solution containing 6.4 μg of titanium(IV) per ml was used. Varying the reagent concentration between 0.01 and 4.0% yielded some difference in sensitivity. Optimum results were obtained with a 0.5% tiron solution.

Iron(III) interferes strongly in the test for titanium(IV) with tiron, because the iron(III) chelate is strongly adsorbed by anion-exchange resins[9] forming an intense blue to violet colour. This interference was effectively prevented by EDTA. The addition of 3 drops of 0.05 *F* EDTA to a drop of the sample solution did not depress the sensitivity of the present test, though the colour intensity in the resin phase was somewhat lower than that in the absence of EDTA. One drop of 0.05 *F* EDTA was sufficient to mask 160 μg of iron(III) in the detection of 0.052 μg of titanium(IV). Three drops of 0.01 *F* EDTA was less effective. On the basis of these observations, a drop of

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* EDTA masks the strong iron(III) interference, which may be present in the usual sample solution[4] (See below).

** The order of addition of the reagents is important; if the buffer is added before the reagent, the sensitivity is lowered, because of hydrolysis of titanium(IV).

0.05 *F* EDTA was always added before the test to mask any possible interference by iron(III).

The influence of neutral salts on the sensitivity of the test was studied with a few drops of 5 *F* sodium chloride added to a drop of the sample solution. One drop of sodium chloride solution had no effect on the sensitivity; 2 drops reduced the sensitivity by about 50% and saturating the test drop with solid sodium chloride reduced the sensitivity by one order of magnitude.

From the above results, the resin spot test for titanium(IV) is most efficiently carried out by the application of a colourless strongly basic anion-exchange resin (X1–X10) in the chloride form, with a 0.05 *F* solution of EDTA and a 0.5% solution of tiron. To adjust the pH of the solution phase to about 5, addition of a drop of 2 *F* aqueous ammonia followed by 2 drops of 1 *F* sodium acetate is desirable.

By this recommended procedure, the limits of identification under the optimum conditions were redetermined semi-quantitatively[10] with Dowex 1-X1, -X2, -X4, -X10 and Dowex 2-X2. No difference was observed when the resin species was changed, the limit of identification for the above resins being 0.026 μg of titanium(IV) after 50 min.

TABLE I

EFFECT OF FOREIGN COMPOUNDS

Foreign ion	*Added salt*	*Colour of the resin phase**	*Amount of foreign ion (μg)*	*Amount of detectable titanium(IV) (μg)*	*Limiting proportion*	*Remark*
Mg(II)	$MgCl_2$	cl	1600	0.026	$1:6\cdot10^5$	
Ca(II)	$CaCl_2$	cl	1300	0.043	$1:3\cdot10^4$	
Sr(II)	$SrCl_2$	cl	1300	0.043	$1:3\cdot10^4$	(*b*)
Ba(II)	$BaCl_2$	cl	1800	0.026	$1:7\cdot10^4$	(*b*)
La(III)	$La(NO_3)_3$	cl	360	0.026	$1:1.4\cdot10^4$	
Ce(IV)	$Ce(SO_4)_2$	dk Br Pu	200	0.13	$1:1.5\cdot10^3$	(*c*)
		gry Re	360	0.026	$1:1.4\cdot10^4$	(*b*), (*c*), (*d*)
Zr(IV)	$ZrO(NO_3)_2$	cl	360	0.052	$1:7\cdot10^3$	(*c*)
Th(IV)	$Th(NO_3)_4$	cl	820	0.052	$1:1.6\cdot10^4$	
V(V)	NH_4VO_3	dk Gry	0.72	0.026	$1:2.8\cdot10$	(*e*)
		dk Bl	13	0.086	$1:1.5\cdot10^2$	(*e*), (*f*)
Cr(III)	$KCr(SO_4)_2$	grn Gry	400	0.13	$1:3\cdot10^3$	(*g*)
Cr(VI)	$K_2Cr_2O_7$	dk Ye Or	0.67	0.17	$1:4$	(*e*)
		cl	32	0.026	$1:1.2\cdot10^3$	(*h*)
Mo(VI)	Na_2MoO_4	Ye Or ~ lm Ye	40	0.039	$1:1\cdot10^3$	(*i*), (*j*)
W(VI)	Na_2WO_4	cl	2.6	0.052	$1:5\cdot10^2$	(*c*)
U(VI)	$UO_2(OAc)_2$	dk Ye Or ~ ye Br	2.7	0.17	$1:1.6\cdot10$	(*e*)
		cl	40	0.039	$1:1\cdot10^3$	(*i*)
Mn(II)	$MnSO_4$	Pk ~ Pu	1300	0.043	$1:3\cdot10^4$	
Fe(III)	$FeCl_3$	Vlt	0.11	0.086	$1:1.3$	(*k*)
		ye Gry ~ dk Bl	160	0.052	$1:3\cdot10^3$	
Co(II)	$CoCl_2$	cl	1600	0.052	$1:3\cdot10^4$	(*g*)
Ni(II)	$NiCl_2$	cl	1300	0.086	$1:1.5\cdot10^4$	(*g*)
Cu(II)	$CuSO_4$	lt ol	160	0.052	$1:3\cdot10^3$	(*e*), (*g*)
Zn(II)	$ZnSO_4$	cl	1300	0.043	$1:3\cdot10^4$	
Cd(II)	$CdSO_4$	cl	1600	0.026	$1:6\cdot10^4$	
Hg(II)	$Hg(NO_3)_2$	cl	180	0.026	$1:7\cdot10^3$	
Al(III)	$KAl(SO_4)_2$	cl	1000	0.13	$1:8\cdot10^3$	(*c*)
		cl	160	0.052	$1:3\cdot10^3$	(*c*)

TABLE I (continued)

Foreign ion	*Added salt*	*Colour of the resin phase*[a]	*Amount of foreign ion (µg)*	*Amount of detectable titanium(IV) (µg)*	*Limiting proportion*	*Remark*
Ga(III)	$GaCl_3$	cl	400	0.064	$1:6\cdot10^3$	
In(III)	$In(NO_3)_3$	cl	310	0.026	$1:1.2\cdot10^4$	
Tl(I)	Tl_2SO_4	cl	720	0.026	$1:2.8\cdot10^4$	
Ge(IV)	Na_2GeO_3	cl	94	0.052	$1:1.8\cdot10^3$	(*e*)
Sn(IV)	$SnCl_4$	cl	27	0.086	$1:3\cdot10^2$	(*c*)
Pb(II)	$Pb(NO_3)_2$	cl	1600	0.052	$1:3\cdot10^4$	(*b*)
Sb(III)	$SbCl_3$	cl	270	0.086	$1:3\cdot10^3$	
Bi(III)	$Bi(NO_3)_3$	cl	160	0.052	$1:3\cdot10^3$	
F^-	KF	cl	120	0.026	$1:5\cdot10^3$	
Br^-	KBr	cl	5300	0.086	$1:6\cdot10^4$	
		cl	1600	0.026	$1:6\cdot10^4$	
NO_3^-	KNO_3	cl	1800	0.026	$1:7\cdot10^4$	
SO_4^{2-}	K_2SO_4	cl	1100	0.026	$1:4\cdot10^4$	
HPO_4^{2-}	Na_2HPO_4	cl	1300	0.026	$1:5\cdot10^4$	
$B_4O_7^{2-}$	$Na_2B_4O_7$	cl	800	0.026	$1:3\cdot10^4$	
HCO_2^-	HCOONa	cl	1600	0.026	$1:6\cdot10^4$	
$C_2O_4^{2-}$	$(NH_4)_2C_2O_4$	cl	320	0.026	$1:1.2\cdot10^4$	
$C_4H_4O_6^{2-}$	Rochelle salt	cl	1300	0.043	$1:3\cdot10^4$	
$C_6H_5O_7^-$	Ammonium citrate	cl	1800	0.026	$1:7\cdot10^4$	

(*a*) The coloration of the resin phase by the foreign compound itself. Colour code[2,11]: cl, colourless; dk, dark; lt, light; Bl, blue; Br, brown; grn, greenish; Gry, grey; gry, greyish; lm, lemon; Ol, Olive; Or, orange; Pk, pink; Pu, purple; Re, red; Vlt, violet; Ye, yellow; ye, yellowish.
(*b*) The test was carried out with a drop of supernatant liquid, after the precipitate in the sample solution had settled.
(*c*) A drop of 4% solution of tiron was used.
(*d*) A drop of 2% solution of ammonium oxalate was added to precipitate cerium(IV) and the supernatant liquid was subjected to the test.
(*e*) Values obtained by comparison with a blank test.
(*f*) A drop of 2% solution of ammonium iron(II) sulphate was added to reduce vanadium(V) and the test was carried out in the presence of 3 drops of 0.05 *F* EDTA.
(*g*) If the colour of the titanium(IV)-tiron chelate on the resin is masked by that of the foreign compound in the solution, the resin beads should be observed after the solution has been poured off and the beads have been washed with a few drops of distilled water.
(*h*) Chromium(VI) was reduced to chromium(III) with a drop of formalin before the test.
(*i*) Uranium(VI) and molybdenum(VI) were removed by passing the test solution containing 4–6 *F* hydrochloric acid through a microcolumn[12] of a strongly basic anion-exchange resin in the chloride form conditioned with 4–6 *F* hydrochloric acid[13]. Titanium(IV) was easily eluted with 4–6 *F* hydrochloric acid.
(*j*) 0.12 µg titanium(IV) cannot be detected in the presence of 0.06 µg molybdenum(VI).
(*k*) Values obtained without the use of EDTA.

The effects of foreign substances are listed in Table I. Vanadium(V), chromium(VI), molybdenum(VI) and uranium(VI) interfere as in the detection of iron(III)[9] (see the remarks in Table I).

SIMULTANEOUS DETECTION OF TITANIUM(IV) AND IRON(III)

Simultaneous detection of iron(III) and titanium(IV) was successfully carried out as follows. When the recommended procedure was applied without EDTA, the blue to violet coloration of the iron(III)-tiron chelate was first observed in the resin beads*. The addition of a drop of 0.05 F EDTA to this system allowed the detection of titanium(IV) by the yellow coloration of the tiron chelate in the resin phase. For example, as little as 1.3 μg of iron(III) and 0.052 μg of titanium(IV) in 0.04 ml of the sample solution were simultaneously detected.

SUMMARY

A sensitive test for nanogram quantities of titanium(IV) is proposed. A resin spot test technique is applied to the colour reaction of titanium(IV) with tiron. The limit of identification is 26 ng of titanium(IV) ($1:1.5 \cdot 10^6$) after 50 min standing. Vanadium(V), chromium(VI), molybdenum(VI) and uranium(VI) interfered seriously. Iron(III) could be masked with EDTA, and iron(III) and titanium(IV) were detected simultaneously.

RÉSUMÉ

Une réaction est proposée, permettant de déceler de très faibles quantités de titane(IV) (de l'ordre du nanogramme). On utilise une résine échangeuse d'ions et le tiron comme réactif. Limite d'identification: 26 ng de titane(IV) après 50 min. Gènent: Vanadium(V), chrome(VI), fer(III), molybdène(VI) et uranium(VI). Mais il est possible, par addition d'EDTA, d'identifier le titane en présence de fer(III).

ZUSAMMENFASSUNG

Beschreibung einer Nachweisreaktion für Titan in Mengen von Nanogrammen durch Tüpfelprobe mit Tiron in Gegenwart eines Austauscherharzes. Störende Elemente werden angegeben; der Einfluss von Eisen-(III) kann durch Zugabe von EDTA ausgeschaltet werden.

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* In this case, the spot plate should be covered with a glass plate to prevent any contamination with iron(III).

o-DIAMINES AS REAGENTS FOR SELENIUM

PART I. 4-DIMETHYLAMINO-1,2-PHENYLENEDIAMINE

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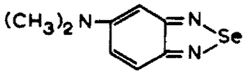
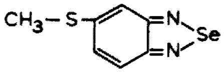
Since HOSTE *et al.*[1,2] proposed diaminobenzidine as a specific reagent for the qualitative and photometric analysis of selenium, this reagent has found numerous applications. CHENG[3] proposed the extraction of the dipiazselenol compound with toluene to avoid interference of foreign ions. The reagent has also been used to determine selenium in arsenic[3], steel and copper[4], organic compounds[5], lead[6], sulphur[7], pyrites[8,9], sulphuric acid[10,11], air and biological materials[12–14]. The use of *o*-phenylenediamine has also been investigated[15].

SAWICKI AND CARR[16] prepared two new selenadiazoles, 5-dimethylamino-2,1,3-benzoselenadiazole (I) and 5-methylthio-2,1,3-benzoselenadiazole (II).



(I)



(II)

These compounds show a maximum optical density at wavelengths of 500 and 572 mμ respectively. The authors suggested that the corresponding diamines might be more interesting reagents than diaminobenzidine, as the wavelengths of maximum absorption are situated in the visible instead of in the ultraviolet region. This communication deals with a systematic investigation of 4-dimethylamino-1,2-phenylenediamine (DAP).

Preparation of the reagent

The reagent is prepared by successive methylation of *m*-nitraniline[17], nitration to 3,4-dinitro-N,N-dimethylaniline[18] and reduction to the diamino compound[16].

(*1*) *Methylation.* 76 g of *m*-nitraniline in 275 ml of water and 187 g of sodium bicarbonate is methylated with three 60-ml portions of dimethylsulphate. After 2 h, the excess of dimethylsulphate is hydrolyzed at 60°. The reaction product is extracted with 300 ml of chloroform and the solvent is evaporated. Part of the reaction product, in the aqueous phase, is converted to the quaternary bromide with *ca.* 50 g of ammonium bromide, and heated *in vacuo* whereby the bromide is decomposed and the nitro derivative collected in the distillate.
Yield: 82.5 g (90%).

(*2*) *Nitration.* 40.5 g of *m*-nitrodimethylaniline is dissolved with thorough stirring

in 420 ml of 60% sulfuric acid containing 42 ml of 30% nitric acid. The solution is diluted after 2 h with 210 ml of water. The precipitate is collected and recrystallized from alcohol.
Yield: 20.5 g (40%).

(*3*) *Reduction.* 41 g of 3,4-dinitro-N,N-dimethylaniline is added gradually to 400 ml of a 12 *N* hydrochloric acid solution containing 400 g of tin(II) chloride dihydrate, the temperature being kept at about 4°. The temperature is raised to 50° and the mixture is stirred for 2 h. The solution is left to crystallize in a refrigerator for 4 days. The crystals are collected, dissolved in 0.1 *N* hydrochloric acid and treated with hydrogen sulphide to obtain complete removal of tin. Tin sulphide is removed by centrifugation. The solution is concentrated *in vacuo* in a stream of carbon dioxide to avoid oxidation of the diamine.

Yield: 14.4 g 4-dimethylamino-1,2-phenylenediamine trihydrochloride (30%).

The trihydrochloride, which was not separated by SAWICKI *et al.*, was analyzed for nitrogen and chlorine after recrystallization and drying over anhydrone. The results found were: nitrogen (micro Dumas) 15.36%, and chlorine (Zacherl-Krainick) 39.0% (Calculated for C_8H_{16}/Cl_3N_3: 16.12% N; 40.83% Cl). The low nitrogen and chlorine contents correspond to 2/3 mole H_2O per mole of diamine. This water cannot be removed by drying over P_2O_5 at 70°, as the product is decomposed.

Stability of the reagent

DAP is rapidly oxidized to a red-purple product in neutral solution or to an orange product in alkaline solution. A selenium determination is only possible in an acidic medium, as this oxidation is then greatly attenuated. The oxidation products have a maximum extinction at 523 mμ, the oxidation being linear as a function of time. The extinction increase in different media for 0.06% DAP solutions is given in Table I. It can be seen that the oxidation rate in acidic medium is sufficiently small so as not to interfere with the selenium determination.

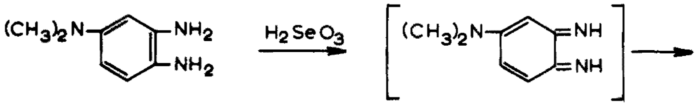
TABLE I

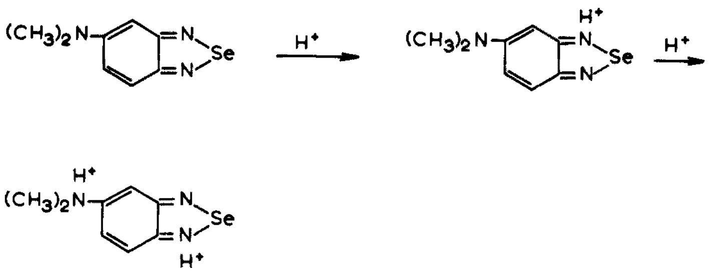
EXTINCTION INCREASE AS A FUNCTION OF ACIDITY

Medium	*ΔE per 10 min*
H_2O	0.230
0.2 *N* HCl	0.014
2 *N* HCl	0.012
4 *N* HCl	0.008

Benzoselenadiazole formation

LUZZATI[19] demonstrated that selenium is bivalent in benzoselenadiazole. According to EFROS[20] an intermediate *o*-quinonediimine is formed, the selenadiazole being able to accept 2 protons[21]:





As the different species have different wavelengths of maximum absorption and different extinction coefficients, the absorption curve of the selenadiazole was investigated as a function of hydrochloric acid concentration for solutions containing 10 μg Se/ml. The results are given in Fig. 1.

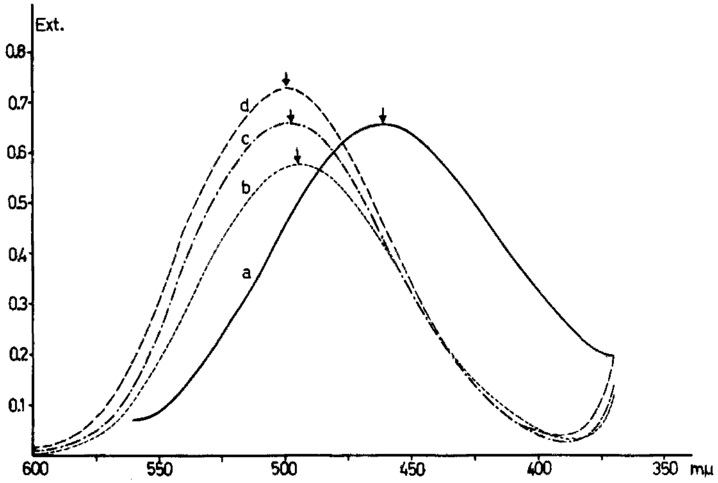


Fig. 1. Absorption curve of 5-dimethylamino-2,1,3-benzoselenadiazole in: a. water; b. 0.196 *N* HCl; c. 1.96*N* HCl; d. 4.00 *N* HCl.

It is apparent that the wavelength of the maximum is not shifted to a longer wavelength from acid concentrations of 2 *N* hydrochloric acid and upwards, whereas the extinction coefficient reaches a maximum at 4 *N* hydrochloric acid. The reaction rate of the selenadiazole formation decreases only slightly with increasing acidity as is apparent from Table II, where the reaction constants are given at different acidities.

TABLE II

REACTION RATE AS A FUNCTION OF ACIDITY

HCl concentration (N)	*Reaction constant* ($l.mol^{-1} . min^{-1}$)
0.2	100
2.0	94
4.0	85

The stability of the color was also measured as a function of time at different acidities. It appeared that in a hydrochloric acid concentration of 0.2 to 5.5 *N* the decrease in the extinction was only 5% after 3 days.

Calibration curve

From the study of reagent stability and benzoselenadiazole formation, 4 *N* hydrochloric acid appears to be the optimum acid concentration, providing the following advantages: a low oxidation rate of the reagent, a wavelength of maximum extinction in the visible region (500 mμ), the highest sensitivity (molar extinction coefficient $\varepsilon = 5.730$), an excellent stability and a sufficient reaction rate. In the conditions given in the procedure, a waiting period of 15 min ensures that the reaction proceeds to the extent of 99.9% as can be computed from the reaction constant at the applied reagent concentration.

Apparatus

Beckman DR spectrophotometer with tungsten lamp and 1 cm corex cells.

Recommended procedure

To 5 ml of the solution under investigation (4 *N* in hydrochloric acid) add 5 ml of a 0.3% reagent solution (4 *N* in hydrochloric acid). Wait 15 min and dilute to 25 ml with 4 *N* hydrochloric acid. Immediate dilution would require a waiting period of 40 min. Measure the extinction in 1-cm cells at a wavelength of 500 mμ *versus* a blank. The final Se concentration should be from 1 to 20 μg/ml.

The reproducibility of the procedure was tested for 10 μg Se/ml giving the following values:

Mean extinction coefficient *k* in g/l : 72.5
Molar extinction coefficient ε in moles: 5730
Standard deviation : 0.49%
Probable error on one measurement : 0.33%
Probable error on the average : 0.17%

TABLE III

CALIBRATION CURVE

Se concentration (μg/ml)	*E*	*k*	*Δk(%)*
2	0.144	72.0	−0.7
4	0.289	72.3	−0.3
6	0.436	72.7	+0.3
8	0.582	72.7	+0.3
10	0.725	72.5	0.0
12	0.874	72.8	+0.4
14	1.033	73.8	+1.8
16	1.169	73.1	+0.8
18	1.336	74.2	+2.3
20	1.477	73.8	+1.8

Table III shows that the reproducibility is satisfactory and that Bouguer-Beer's law is obeyed in the investigated concentration range.

Influence of foreign ions

The influence of a number of foreign ions was investigated. The cations were present as their nitrates or chlorides, the anions as their potassium salts. The foreign ion–selenium ratio was 100:1, except for the sulphate, which was also investigated in a 1000:1 ratio. Se concentration: 10 μg/ml. The results are given in Table IV.

TABLE IV

EFFECT OF FOREIGN IONS ON SPECTROPHOTOMETRIC DETERMINATION

Ion	*E*	% *error*	*Ion*	*E*	% *error*
Al^{3+}	0.731	+ 0.8	Ni^{2+}	0.725	0.0
As^{3+}	0.722	− 0.4	NH_4^+	0.729	+0.6
Ba^{2+}	0.723	− 0.3	Zn^{2+}	0.721	−0.6
Ca^{2+}	0.729	+ 0.6	Br^-	0.726	+0.1
Cd^{2+}	0.731	+ 0.8	Citrate	0.727	+0.3
Co^{2+}	0.830	+14.5	Cl^-	0.721	−0.6
Co^{2+} (corr.)	0.738	+ 1.8	Oxalate	0.726	+0.1
Cr^{3+}	1.407	+94.1	$H_2PO_4^-$	0.726	+0.1
K^+	0.730	+ 0.7	SO_4^{2-} (100)	0.725	0.0
Mg^{2+}	0.724	− 0.1	(1000)	0.727	+0.3
Mn^{2+}	0.724	− 0.1	Tartrate	0.720	−0.7
Na^+	0.720	− 0.7	TeO_3^{2-}	0.722	−0.4

Table IV shows that a number of oxidizing ions as iron(III) and copper(II) interfere, namely by oxidizing the reagent. High extinction values in the presence of cobalt are due to the color of cobalt(II) itself and can be avoided by taking a reading in the absence of reagent. Interference of chromium(III) is due to the formation of a purple complex with the diamine. Attempts to reduce these interferences with complexing agents failed, as they were not active at the high acidity of the medium. Liquid–liquid extraction with benzene or carbon tetrachloride of the selenadiazole was also attempted. Although the distribution constants were favourable no stable extinctions were obtained.

Qualitative analysis

A number of techniques were investigated as a qualitative test for selenium, *e.g.* micro-test tube, spot plate and paper strip. It appeared that the micro-test tube gave the most satisfactory results.

DESCRIPTION OF THE REACTION

Method

To 10 drops of an acid solution in a micro-test tube add one drop of the reagent solution (1% DAP in 3 *N* hydrochloric acid). In the presence of selenium(IV) a red-brown precipitate, or at high dilution a red color, is formed. At the detection limit comparison with a reference blank after 5 min is advisable.

Sensitivity and specificity

Dilution limit: $D = 10^6$ (1 μg Se/ml).

The behaviour of a number of foreign ions was systematically investigated at a selenium concentration of 10 μg/ml. The results are given in Table V.

It appears that most ions do not interfere even in a 100:1 ratio. The following ions should however be absent as they oxidize the reagent or give rise to interfering complexes: Cu(II), Fe(III), V(V), Mo(VI), Au(III), Ru(III), Pd(II), Pt(IV) and Cr(III).

The presence of sulphite also interferes with the selenium detection by benzothiadiazole formation.

TABLE V

EFFECT OF FOREIGN IONS ON THE DETECTION OF SELENIUM

Ion	*Ratio*	*Color*	*Ion*	*Ratio*	*Color*
Cu^{2+}	100	purple-red	Ti^{4+}	100	no interference
Pb^{2+}	100	no interference	Zr^{4+}	100	no interference
Bi^{3+}	100	no interference	Th^{4+}	10	no interference
Cd^{2+}	100	no interference	Be^{2+}	100	no interference
As^{3+}	100	no interference	Ga^{3+}	10	no interference
Sb^{3+}	100	no interference	In^{3+}	10	no interference
Sn^{4+}	100	no interference	Zn^{2+}	100	no interference
Au^{3+}	100	purple-red	Mn^{2+}	100	no interference
Ru^{3+}	10	brown-red	Co^{2+}	100	no interference
Pd^{2+}	100	yellow-brown	Ni^{2+}	100	no interference
Pt^{4+}	10	purple-red	Ba^{2+}	100	no interference
TeO_3^{2-}	100	no interference	Sr^{2+}	100	no interference
Ge^{4+}	10	no interference	Ca^{2+}	100	no interference
Mo^{6+}	100	purple-red	Mg^{2+}	100	no interference
W^{6+}	100	white	Li^{+}	100	no interference
V^{5+}	100	purple-red	Na^{+}	100	no interference
Al^{3+}	100	no interference	K^{+}	100	no interference
Fe^{3+}	100	purple-red	Rb^{+}	100	no interference
Cr^{3+}	100	purple-red	Cs^{+}	100	no interference
UO_2^{2+}	100	no interference	NH_4^{+}	100	no interference
Ce^{2+}	100	no interference	SO_3^{2-}	100	colorless
Y^{3+}	10	no interference	SO_4^{2-}	100	no interference

SUMMARY

4-Dimethylamino-1,2-phenylenediamine is investigated as a photometric and qualitative reagent for selenium. With this reagent selenium(IV) forms 5-dimethylamino-2,1,3-benzoselenadiazole, a red colored compound, with an absorption maximum in the visible region at 500 mμ. Variables such as reagent stability, extinction stability, reaction rate, influence of acidity, foreign ions, validity of Beer's law are discussed. The reagent is highly selective for selenium, has good sensitivity and reproducibility, and is also useful for qualitative purposes.

RÉSUMÉ

La diméthylamino-4-phénylènediamine-1,2 a été examinée en vue de son utilisation comme réactif qualitatif et photométrique du sélénium. Ce réactif donne un composé rouge avec le sélénium(IV); il est très sélectif et présente une bonne sensibilité et une bonne reproductibilité.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Eignung von 4-Dimethylamino-1,2-Phenylendiamin als Reagenz zum Nachweis und zur photometrischen Bestimmung von Selen. Der Einfluss verschiedener Faktoren, wie pH, Fremdionen etc. auf die Reaktion, sowie eine Methode zur Darstellung des Reagenzes werden angegeben.

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Short Communications

The screening of metallofluorescent indicators

It is sometimes found that when a metallofluorescent indicator is being used in a compleximetric titration, a residual fluorescence is present in the solution although the fluorescence of the indicator should have been completely quenched by the excess of metal ions. The quality of the end-point is thus impaired. Several reasons may be given to account for this residual fluorescence, the most likely being the presence of inactive fluorescent impurities in the indicator, arising either as contaminants during the preparation of the indicator, or as a result of deterioration during storage. Weak fluorescent complexes such as those formed between Calcein and alkali metal ions at high pH can also account for residual fluorescence[1].

In studying compounds which show weak metallofluorescent properties, we have found it easier to observe partial quenching of the indicator systems if the residual fluorescence is screened with a "neutral" fluorescent dye of different fluorescence from the residual fluorescence. We have extended this screening of metallofluorescent compounds to conventional metallofluorescent indicators with very satisfactory results.

Thus, in the titration of calcium with EDTA using Calcein or Calcein W as indicator at pH 12 or above, a yellow-green fluorescence is still evident at the end-point of the titration. The addition of a few drops of aqueous 0.01% acridine at the beginning of the titration gives a sharp colour change at the end-point, the fluorescence of the solution changing from bright yellow-green to pure blue.

Similarly, when Calcein Blue is used as indicator in the same titration, the residual blue fluorescence can be effectively screened with Rhodamine B or fluorescein. With the former, the end-point is denoted by a sharp change in the fluorescence of the solution from bright blue to salmon pink.

PROCEDURE

Titration of calcium

a) *Calcein as indicator.* Ten ml of calcium solution (0.02 *M*) is diluted to approximately 50 ml with water. One ml of 5 *N* potassium hydroxide solution, 3 drops of acridine solution (0.01% in dilute hydrochloric acid), and 1–2 drops of Calcein indicator solution (0.1%) are added, and the solution is titrated with 0.02 *M* EDTA to a pure blue fluorescence under ultraviolet light.

b) *Calcein Blue indicator.* Ten ml of calcium solution (0.02 *M*) is diluted to 50 ml with water, and 1 ml of 5 *N* potassium hydroxide solution is added. Three drops of Rhodamine B solution (0.01% in water) and 1 drop of Calcein Blue indicator solution (0.1%) are added, and the solution is titrated with 0.02 *M* EDTA to the appearance of a salmon pink fluorescence.

In the above titrations, the calcium and EDTA solutions were evaluated using Acid Alizarin Black SN as indicator[2]. For ten titrations by each procedure the following average results were obtained for the calcium solution.

	ml of 0.02M EDTA
Screened Calcein	9.98 ± 0.01
Screened Calcein Blue	9.99 ± 0.01
Acid Alizarin Black SN	9.99 ± 0.01

Without the use of screening agents, the error amounted to as much as ± 0.02–0.03 ml of 0.02 *M* EDTA.

We believe that this use of neutral fluorescent dyes as screening agents eliminates much of the uncertainty in the accurate detection of the end-point in titrations involving an apparent incomplete quenching of a metallofluorescent indicator. Although the same principle can be used with metallofluorescent indicators which show complete quenching, little advantage is obtained, unless one prefers a two-colour indicator change to the fluorescent–non-fluorescent change normally exhibited by this type of indicator.

The use of fluorescent screening agents to improve the end-points in the compleximetric titrations of other metal ions using metallofluorescent indicators derived from benzidine is at present being investigated.

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A solvent extraction method for the determination of microgram amounts of chromium

BLUNDY[1] has recently described a method for the determination of micro-quantities of chromium in the presence of iron and nickel, after extraction of chromium(VI) into hexone[2,3]. Back-extraction of chromium(VI) into aqueous solution is followed by a colorimetric finish with diphenylpicrazide. The present work arose out of a study of the extraction of chromium(VI) into basic organic solvents, particularly tri-*n*-butyl phosphate[4]. The species extracted from acid solution has been identified as a solvated chromium(VI) acid: similarly WHITE AND ROSS[5] have reported that in extractions with tributyl phosphine oxide the species in the organic phase is (solvated) $H_2Cr_2O_7$.

It has been shown that tributyl phosphate (TBP) extracts perchromic acid (CrO_5) resulting from the reaction of chromium(VI) with hydrogen peroxide, as well as chromium(VI) itself, from dilute acid solution. Perchromic acid is a Lewis acid which is extracted only by basic solvents[6]; it has been found that the extraction into TBP is quantitative. Furthermore, since TBP extracts hydrogen peroxide from aqueous solution[1], CrO_5 can be formed directly in the organic phase. This solvent extraction of chromium(VI) and CrO_5 has been made the basis of a simple colorimetric method for estimating microgram quantities of chromium. The various methods available for the oxidation of Cr(III) to Cr(VI) have been fully discussed by BLUNDY and were not investigated further. The possible interferences of Cu, Ce, Ni, Th and U (see ref. 1) were examined; the results compare favourably with those of other methods.

EXPERIMENTAL

Materials. Tri-*n*-butyl phosphate was purified as described previously[8].

A standard solution of chromium(VI) was prepared by dissolving 186.4 mg of oven-dried AnalaR K_2CrO_4 in 250 ml. of 1 *N* sulphuric acid: tenfold dilution gave a solution containing 20 μg Cr per ml. A suitable solution of hydrogen peroxide was made by diluting 20 vol. reagent with 1 *N* sulphuric acid to give a *ca.* 1 % solution. Throughout this work, the aqueous phase consisted of AnalaR grade 1 *N* H_2SO_4.

In testing for interference by other metals, suitable solutions were made up in dilute sulphuric acid from the following AnalaR materials; Cu as $CuSO_4 \cdot 5H_2O$, Ce as $(NH_4)_2Ce(NO_3)_6$, Ni as $NiSO_4 \cdot 7H_2O$, Th as $Th(NO_3)_4 \cdot 6H_2O$ and U as $UO_2(NO_3)_2 \cdot 6H_2O$.

Procedure. Pipette suitable aliquots of the standard chromium(VI) solution into calibrated stoppered tubes; dilute to 7 ml with dilute sulphuric acid. Add 1 ml of TBP and equilibrate the contents by gently inverting the tube about 50 times. Add 1 ml of acid peroxide solution and re-equilibrate the solutions. After centrifuging, transfer a suitable volume of the blue (upper) organic layer to the micro-cell of a Spekker Absorptiometer and measure the optical density using OY2 and OG3 filters.

RESULTS AND DISCUSSION

A plot of optical density against the concentration of chromium(VI) is linear over the range 0–100 μg Cr to within $\pm 3\%$, the line passing through the origin.

It is worth noting that CrO_5 is much more stable in TBP solutions than is apparently the case with other solvents[9,10]; the optical density of the separated organic phase was found to be virtually constant for at least 10–15 h.

To examine the possible effects of other elements, 50 mg of cerium(IV), copper(II), nickel(II), thorium(IV) and uranium(VI) were added separately to 60 µg of chromium(VI) and the extraction and colorimetric procedure were carried out as described above. In Table I, the final optical density of the TBP phase is given as a fraction of that resulting from 60 µg of Cr(VI) alone. The method is clearly unaffected by large excesses of Ni, Th and U; in the case of the latter two elements, this is no doubt due to the fact that the extraction into TBP is apparently completely suppressed by working in aqueous sulphuric acid solution. The interference from cerium(IV) was not unexpected but this can presumably be avoided by previous treatment with sodium azide[1]. The marked interference by copper(II), also reported by Blundy[1], is more difficult to explain. Examination of the visible absorption spectra (in the 210–700 mµ region) of solutions of copper sulphate and potassium dichromate, and of an equimolar mixture of the two, revealed no evidence of chemical reaction between them, nor was any precipitate found on allowing such a mixture to stand for some days. Reasonably small quantities of copper do not seem to affect the method however; even 5 mg of copper represents in this case an almost 100-fold excess.

TABLE I

INTERFERENCE FROM OTHER ELEMENTS IN Cr DETERMINATION

Ce(IV)	(50 mg)	0.44
Ni(II)	(50 mg)	1.01
Th(IV)	(50 mg)	0.99
U(VI)	(50 mg)	0.99
Cu(II)	(50 mg)	0.74
Cu(II)	(5 mg)	1.00

This simple technique should be applicable to a variety of systems, both for analysis and for the rapid separation of chromium from other elements which are not extracted by TBP from dilute aqueous sulphuric acid.

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Separation of titanium from other elements with N-benzoyl-N-phenylhydroxylamine

N-Benzoyl-N-phenylhydroxylamine has already been used[1] as a reagent for the gravimetric determination of titanium; aluminium did not interfere but the interferences of iron and of several other metals could not be overcome. The method has now been extended to the determination of titanium in the presence of various interfering metallic ions. Interference from thorium and cerium was avoided by adjustment of the pH of the solution. Titanium and molybdenum were separated by the precipitation of molybdenum with N-benzoyl-N-phenylhydroxylamine, titanium being masked with hydrogen peroxide and EDTA; titanium was then precipitated with the reagent after the metal complex in the filtrate had been decomposed with sodium sulphite and calcium chloride. Titanium was precipitated in the presence of copper, iron, zirconium or vanadium by masking the foreign metal ion with EDTA. A method was also developed for the determination of titanium in bauxite.

Solutions

A solution of titanium sulphate was prepared by fusing titanium dioxide with excess of potassium hydrogen sulphate and dissolving the melt in dilute sulphuric acid (6 *N*). The titanium content was determined gravimetrically with cupferron.

Standard solutions of ferric ammonium sulphate, ammonium vanadate, zirconium nitrate, copper nitrate, ammonium molybdate, thorium nitrate, and ceric ammonium sulphate were also prepared. All the reagents used were of A.R. quality.

DETERMINATION OF TITANIUM IN PRESENCE OF OTHER METALS

Separation from iron, vanadium, zirconium or copper

Known amounts of titanium sulphate solution and foreign ion solution were mixed and diluted to 250 ml. The solution was neutralised with 6 *N* ammonium hydroxide solution, and 4 ml of concentrated hydrochloric acid and 10 ml of aqueous 10% EDTA solution were added. When vanadium was present, the solution was boiled for 2 min in order to reduce the vanadium(V) and then cooled. (Vanadyl ion forms a stable complex with EDTA[2] and if vanadate is present it is first reduced to the vanadyl state[3].) To the cold solution 10 to 15 ml of 2% benzoylphenylhydroxylamine in 95% ethanol were added with constant stirring. The titanium precipitate was allowed to settle for 45 min with occasional stirring, filtered, washed with 0.033 *N* hydrochloric acid solution containing reagent (1 ml of the reagent solution for every 100 ml of the wash-solution), ignited to the oxide and weighed.

Separation of titanium and molybdenum

Known amounts of titanium and molybdenum solutions were diluted to 250 ml with water, neutralised and acidified with 4 ml of acid as described above. To the mixture, 2 ml of 20-vol. hydrogen peroxide were added to complex titanium, followed by 10 ml of 10% EDTA solution. Molybdenum was precipitated by addition of 10 ml of the 2% benzoylphenylhydroxylamine solution, as recommended previously[4]. The precipitate was filtered and washed with 0.02 *N* hydrochloric acid solution and with 10 ml of distilled water. To the filtrate 1–2 g of sodium sulphite was added, and the solution was boiled for 10 min and cooled. A solution containing 1.5–2 g of calcium chloride was added and the organic precipitate formed was filtered off. The pH of the solution was adjusted to 1–2, and titanium was precipitated as described above.

TABLE I

DETERMINATION OF TITANIUM IN PRESENCE OF VARIOUS METAL IONS

(see text for the modifications required)

Foreign ion taken *mg*		*TiO_2 taken* *mg*	*TiO_2 found* *mg*	*Error* *mg*
Fe^{3+}	70.0	9.3	9.3	0.0
	70.0	14.0	14.0	0.0
	140.0	23.4	23.1	−0.3
	140.0	14.0	14.1	+0.1
	210.0	23.1	23.3	+0.2
V^{5+}	60.0	14.0	14.1	+0.1
	60.0	18.7	19.0	+0.3
	60.0	23.4	23.0	−0.4
	120.0	9.3	9.4	+0.1
Zr^{4+}	40.0	14.0	14.4	+0.4
	40.0	18.7	18.8	+0.1
	40.0	23.4	23.4	0.0
	80.0	9.3	9.4	+0.1
	120.0	9.3	9.3	0.0
Cu^{2+}	80.0	14.0	13.8	−0.2
	80.0	18.7	18.7	0.0
	80.0	23.4	23.2	−0.2
	160.0	9.3	9.4	+0.1
	240.0	9.3	9.5	+0.2
Mo^{6+}	5.0	14.0	14.3	+0.3
	5.0	9.3	9.4	+0.1
	5.0	23.4	23.0	−0.4
	10.0	9.3	9.4	+0.1
	15.0	9.3	9.3	0.0
Ce^{4+}	13.0	9.3	9.4	+0.1
	13.0	14.0	14.0	0.0
	13.0	18.7	18.7	0.0
	26.0	9.3	9.3	0.0
	40.0	9.3	9.2	−0.1
Th^{4+}	26.0	9.3	9.5	+0.2
	26.0	14.0	14.0	0.0
	26.0	18.7	18.7	0.0
	40.0	9.3	9.2	−0.1
	52.0	9.3	9.1	−0.2

Determination of titanium in presence of thorium or cerium

Known amounts of titanium and cerium or thorium solutions were diluted to 250 ml. Cerium(IV) was first reduced by hydroxylamine hydrochloride to cerium(III).

The solution was neutralised with 6 *N* ammonium hydroxide solution, and 4 ml of concentrated hydrochloric acid were added. The titanium was then precipitated as described above. Cerium and thorium do not interfere under these conditions. Typical results obtained by the above procedures are shown in Table I.

Determination of titanium in bauxite

A weighed quantity of bauxite (1.5–2.0 g) was mixed thoroughly with 10 ml of concentrated sulphuric acid and 50 ml of water, digested, and evaporated to dryness. The mass was extracted with 3–4 *N* hydrochloric acid. The silica was filtered off and washed, and the solution was diluted to 250 ml. An aliquot (25–50 ml) of this solution was diluted to 300 ml, 10–15 ml of the 10% EDTA solution were added and the pH of the solution was adjusted to 1–2. Titanium was then determined by the addition of benzoylphenylhydroxylamine (10–15 ml) as described above. For a given sample of bauxite, the amount of titanium dioxide found by this method was 8.37 and 8.38%, compared with a content of 8.38% determined by a standard method.

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Determination of carbon and hydrogen in silicon-containing compounds

The formation of extremely stable silicon carbide and/or volatile, stable silanes is reported to be the greatest source of error in the determination of carbon and hydrogen in compounds containing silicon. In slow combustion methods, mixing the sample with a flux of cryolite and red lead (1:5)[1] or with vanadium pentoxide[2], is said to be successful. Strictly controlled volatilization of the sample with combustion at fairly high temperatures has also been recommended[3]. For proper analysis of gaseous materials, mixing with nitrogen before the combustion over a platinum catalyst is beneficial[4]. Siloxanes tend to form clouds of fine silica which pass into the absorption system causing high results; the silica can be retained on a layer of finely divided pumice[5]. A special plug system of silver wool and asbestos has been used to avoid similar effects with the "silver permanganate" combustion catalyst[6].

Korshun *et al.*[7] have studied the behaviour of silicon compounds in detail for their special empty-tube procedure. Apparently, tetra-aryl silanes and unsaturated compounds are most prone to form carbides. This, as well as formation of silane and silica clouds can be prevented by a layer of chromic oxide and asbestos in the special sample capsule; if the sample contains less than 3% hydrogen, addition of water may also be required to avoid carbide formation. In these procedures, silicon can be determined by weighing the special capsule after the combustion. In almost all the above-mentioned methods the necessity of slow and careful volatilization of the sample is stressed, a single analysis requiring a much longer time than is normal for the particular type of procedure involved.

It has recently been shown that the rapid cobalto-cobaltic oxide method of VEČEŘA is very suitable for the determination of carbon and hydrogen in organo-metallic compounds[8]. An attempt was therefore made to extend its use to silicon-containing compounds. Initially quite satisfactory results were obtained, but after a few determinations, it became difficult to obtain a clear picture of what was happening. With some compounds, low carbon results and black residues of silicon carbide were obtained, while in other cases, clouds of silica passed into the absorption system causing high results. Particularly after the combustion of materials containing much silicon, low results were obtained owing to the cobalt oxide pellets being deactivated by a thick coating of fine silica. Additional difficulties were caused by the explosive nature of most of the samples available. Very variable results were obtained even for the same compound.

Sample boat additives were tested for prevention of carbide formation and for retention of silica; tungstic oxide, vanadium pentoxide, chromic oxide, potassium dichromate and asbestos were unsuccessful. A layer of asbestos between the sample and the furnace[7] did not improve the results, nor did increased temperature or slower timing in the analysis. Addition of a platinum roll[4] did not seem effective in encouraging complete deposition of silica before the catalytic layer was reached. Initial pyrolysis in a special insert tube containing a layer of chromic oxide and asbestos[7] was also of little avail. It should be pointed out that these various stratagems would probably be satisfactory under the conditions and for the compounds for which they were designed; in the present work, a much faster procedure was being tested and the samples were of widely different constitutions. Various packings were then placed between the sample boat and the main furnace but again little success was achieved, though improved results were found with a magnesium oxide layer and a higher temperature for the cobalt oxide catalyst. It was finally concluded that no modification of VEČEŘA's method would give satisfactory results on a routine basis without a great loss of simplicity and speed.

Nearly all the previous methods described for silicon-containing compounds involve combustion at fairly high temperatures (800–1,000°) whether or not a combustion catalyst is used. The above results with magnesium oxide as an additional filling therefore indicated that satisfactory results might be obtained with magnesium oxide as the catalytic filling at 850°, as in a rapid method recommended for the determination of carbon and hydrogen in fluorine-containing compounds[9]. In fact, excellent results for a wide variety of compounds were obtained by this procedure; representative results are given in Table I. Under the conditions used, there was no evidence for formation of silicon carbide in the sample boat and no clouds of fine silica appeared beyond the magnesium oxide layer even after about 30 analyses. It is likely that

TABLE I

Compound	*% C theoret.*	*% C found*	*% H theoret.*	*% H found*	*%Si theoret.*
Diphenylsilanediol	66.63	66.75	5.59	5.65	12.99
Triphenyl(1,5-epoxyhexyloxy)silane	76.96	76.89	7.00	7.03	7.50
Hexaphenyldisiloxane	80.85	80.72	5.65	5.74	10.50
Tetramethyldisiloxane	35.76	35.87	10.50	10.45	41.82
Tetramethyltetraphenyl-cyclotetrasiloxane	61.71	61.77	5.92	5.76	20.62
Hexamethyldisilazane	44.65	44.50	11.87	11.92	34.81
Octamethylcyclotetrasiloxane	32.39	32.45	8.15	8.20	37.88
Diphenylmethylchlorosilane	67.07	67.16	5.63	5.85	12.07
Hexa(triphenylsilyl)sucrose	76.12	76.19	5.65	5.73	8.90
Research disiloxane containing P[a]	40.24	40.06	9.12	9.24	18.82

[a] WO_3 added to sample.

magnesium silicate is formed; under the rapid conditions used, a purely mechanical retention of silica is improbable.

The final recommendation is to use the magnesium oxide exactly as described previously[9] except that the furnace temperature should be raised to 900°; the initial volatilization of the sample must be done carefully.

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A simple safety precaution in oxygen flask combustions

The oxygen flask combustion technique presented by SCHÖNIGER in 1955[1] is now generally recognized as a most useful and elegant method for decomposing organic material. Briefly, the technique consists in burning the sample in a conical flask which is filled with oxygen at atmospheric pressure and charged with a suitable absorption liquid. The element sought can usually be determined by titration — after a short interval — in the same flask. The surprising simplicity of the apparatus and procedures has contributed much to the popularity of the technique; the list of elements whose determination by this method has been recommended is quite appreciable and still appears to be growing[2].

Numerous combustions have been carried out in this laboratory using bare flasks, but a few explosions which occurred in isolated cases drew attention to the dangers of using unprotected flasks. Some form of protection was necessary, therefore, but preferably one which would not interfere with the basic simplicity of the technique.

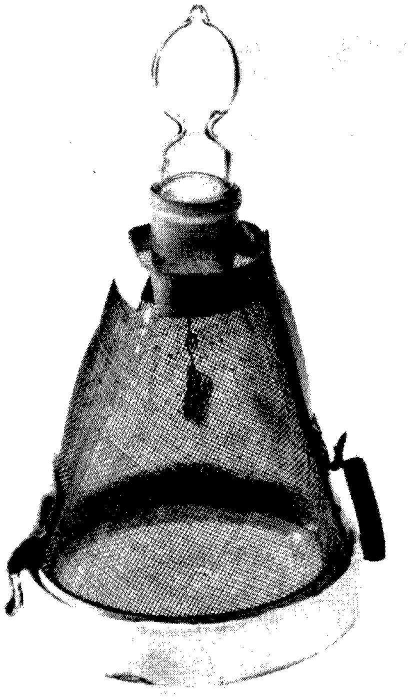

Fig. 1. Schöniger combustion flask with detachable protection jacket.

The detachable wire gauze jacket shown in Figs. 1 and 2 was found to suit the purpose. It is used during the critical combustion step and removed before the titration.

The jacket is made of metal wire gauze and consists of two parts: a circular bottom part and a conical upper part, connected by a leather strip acting as a hinge. The edge of the bottom part is reinforced with a brass strip and all rough edges are covered with adhesive tape. The bottom part is secured to the conical upper part with the aid of a metal spring at a point opposite the leather hinge.

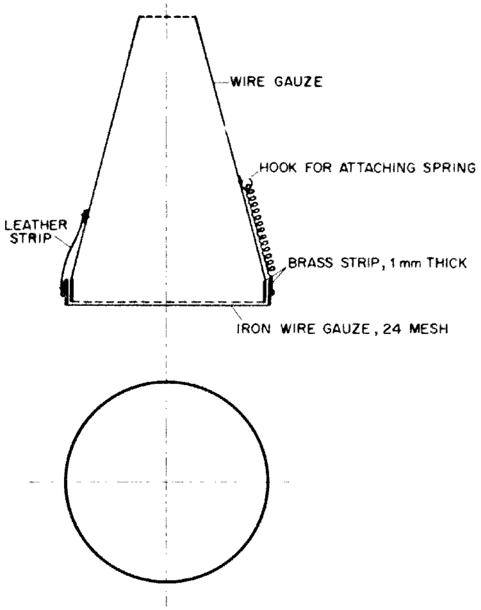

Fig. 2. Schematic drawing of protection jacket.

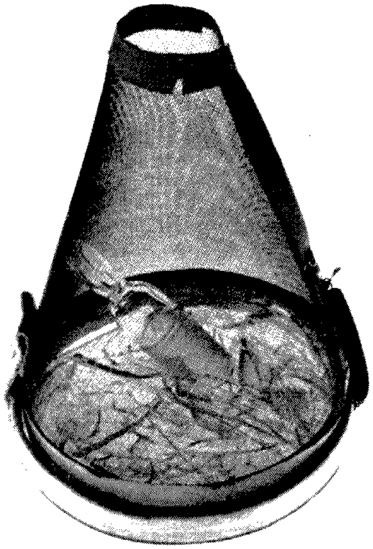

Fig. 3. Flask within protection jacket after accidental explosion.

The jackets can be made to fit any size of flask and are very cheap. They are now in regular use in this laboratory; they present no hindrance whatsoever during the combustion, yet were shown to offer adequate protection to the experimenter and surroundings in case of explosion (Fig. 3).

Koninklijke/Shell-Laboratorium,
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P. GOUVERNEUR
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Received June 12th, 1962

Nitrite as an oxidant for antimony in its spectrophotometric determination with rhodamine B

During an investigation of the occurrence of antimony in sea water, the need arose for a sensitive spectrophotometric method for its determination. The rhodamine B procedure is commonly used, but is of poor precision. In the most frequently used modification of the method[1], antimony is oxidised to the pentavalent state in a hydrochloric acid medium by means of a ceric salt. The excess oxidising agent is destroyed with hydroxyammonium chloride, and any chlorine formed by reaction of the ceric ion with hydrochloric acid is removed with a current of air. Rhodamine B chloroantimonate is subsequently extracted with benzene and the spectrophotometric measurement is made on the extract. The optimum conditions for the determination have been investigated[2,3] and it has been found that a very close control of the timing schedule of all the stages of the process is necessary, if secondary reactions are to be minimised.

The choice of other oxidants to be used in the method is limited; McNULTY AND WOOLARD[4] have oxidised antimony by fuming with perchloric acid before addition of hydrochloric acid and extraction of the complex. FREDERICK[5] has described the use of nitrite as an oxidising agent in a qualitative spot test for antimony. He found that a quantitative test could not be developed because of the mutual interaction of the large excess of nitrite with the rhodamine B. Nitrite has, however, been used as the oxidising agent in the methyl violet and brilliant green photometric methods for antimony[6,7].

This note describes the use of nitrite as an oxidising agent in the rhodamine B method, leading to greater simplicity and a more than doubled sensitivity. The extraction of the rhodamine B complex is carried out with a mixture of chlorobenzene and carbon tetrachloride, which has the advantages of being denser than the aqueous phase and of giving more efficient extraction.

EXPERIMENTAL

Reagents

Rhodamine B–nitrite reagent. Dissolve 0.1 g. of rhodamine B in about 25 ml of water and filter into a 100-ml volumetric flask; add 8.0 ml of 0.1 *M* sodium nitrite solution and dilute to volume.

Extraction solvent. Dilute 125 ml of carbon tetrachloride to 500 ml with chlorobenzene.

Standard antimony solution. Dissolve 0.274 g of potassium antimonyl tartrate hemihydrate in water and dilute to 100 ml. This solution contains 1 mg antimony/ml. The working standard, which is 6 *M* with respect to hydrochloric acid is prepared from this stock solution as required.

Method

Place 20 ml of the sample solution, (not more than 15 μg antimony), which is *ca.* 6 *M* with respect to hydrochloric acid, in a 50-ml separating funnel. Add 2 ml of the rhodamine B–nitrite reagent, mix well and allow to stand for 30 min. Add 10.0 ml of the extraction solvent and shake the funnel for about 1 min. Run the organic phase into a dry centrifuge tube and centrifuge for *ca.* 2 min. Measure the optical density of the solution in a 1-cm cell at 565 mμ against a compensating cell containing the extraction solvent. Carry out a blank run in the same manner using 20 ml of 6 *M* hydrochloric acid in place of the sample. Calibrate the method using known amounts of antimony in the range 1–15 μg. The colour of the extracted solution is stable for at least 2 h.

Under these conditions, the optimum oxidation time was found to be 30 min; after this period, 98 ± 1% of the antimony in the aqueous phase could be extracted with the mixed solvent. The hydrochloric acid concentration is not critical between 5 *M* and 6 *M*, but on either side of this range the efficiency of extraction declines markedly. At lower acid concentrations the extraction of rhodamine B becomes serious.

Beer's Law is obeyed up to at least 15 μg of antimony. The sensitivity of the method is 0.0017 $\mu g/cm^2$, approximately 2.5 times that found when ceric ion is used as the oxidant. Replicate determinations of 10 μg of antimony gave a coefficient of variation of 0.8% for the method.

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R. GREENHALGH
J. P. RILEY

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Received May 25th, 1962

Book Reviews

Absorption spectra in the ultraviolet and visible region, edited by L. LÁNG, Publishing House of the Hungarian Academy of Sciences, Budapest, 1961, (second English edition). Introductory volume, 73 pp., Vol. I, 414 pp., $16.00. Vol. II, 408 pp., $16.00.

Cette publication de l'Académie des Sciences de Hongrie éditée par le Dr. L. Láng comprend, sous cette seconde édition, deux volumes contenant 350 spectres d'absorption visibles et ultraviolets et un fascicule introductif et explicatif de 80 pages.

Il ne s'agit pas d'un travail de compilation dans le domaine de la spectroscopie d'absorption électronique mais plutôt du résultat d'un travail d'équipe d'une quinzaine d'institutions scientifiques et industrielles hongroises et polonaises qui, suivant des directives précises, ont mis en commun le fruit de leur travail dans le domaine des spectres d'absorption visibles et ultraviolets. Ce fait permet de comprendre deux aspects particuliers de ce travail; d'une part, l'uniformité dans la présentation des spectres du point de vue des unités, des symboles, des échelles, d'autre part, la diversité des substances traitées; il est normal que chaque laboratoire ait étudié les substances qui rentraient dans ses activités courantes et pour lesquelles il pouvait garantir une pureté suffisante.

On peut donc dire que de ce double point de vue, le travail constitue un apport non seulement substantiel mais encore de valeur dans le domaine de la spectroscopie d'absorption électronique; cet ouvrage vient très heureusement compléter les publications de Friedel et Orchin, celles du National Bureau of Standards et celles de la Commission des données optiques de l'IUPAC qui est à l'impression.

Pour l'analyste, il s'agit là de documents fondamentaux qui doivent l'aider dans ses travaux d'identification et de dosages élémentaires. Pour le spectroscopiste ou le physico-chimiste moléculaire, cet ouvrage constitue un document intéressant d'autant plus qu'il est précédé d'une introduction faisant le point sur la situation actuelle du point de vue de la théorie des spectres électroniques. Par ailleurs, il est très heureux que les auteurs ne se soient pas contentés de reproduire les spectres mais qu'ils aient également eu le souci de fournir les tableaux avec l'absorbance à des longueurs d'ondes très rapprochées.

Soulignons également que les spectres ont été relevés souvent dans plusieurs solvants et, lorsqu'il s'agit de solutions aqueuses, à plusieurs pH.

G. DUYCKAERTS (Liège)

Anal. Chim. Acta, 27 (1962) 306–307

Analyse Qualitative Rapide des Cations et des Anions, par G. CHARLOT, 3è édition. Dunod, Paris, 1961, pp. 96. Broché 9.50 NF.
Qualitative Schnellanalyse der Kationen und Anionen, nach G. CHARLOT, 3 Auflage, von PFLUGMACHER, W. de Gruyter, Berlin, 1961, S. xv + 112, br. DM 10.80.

Professor Charlot has made very notable contributions to the physicochemical systematization of analytical methods. In qualitative analysis, he has outlined the theoretical bases for the utilization of phenomena such as complex formation, redox reactions, pH effects and solvent extraction, in order to attain sample solutions to which specific confirmatory tests can be applied. The system of qualitative analysis thus developed has undoubted advantages over the classical methods, though its full growth is somewhat hindered by a shortage of suitable specific tests.

In this edition, which is available in both French and German versions, the method is expounded in a format similar to that used previously. For each ion, methods of detection are outlined which can be used in presence of important amounts of other components; the sensitivities of the reactions and the possible interferences are indicated. Methods of eliminating interferences are given and wherever possible, precipitation processes are avoided. Many of the procedures have been modified from the previous editions. The text is clear and concise and gives all the details necessary for practical work.

Anal. Chim. Acta, 27 (1962) 307–308

The method of Professor Charlot lends itself to modification and adaptation in any one of its stages without the general outline of the processes being altered. It is thus much more flexible than the classical methods; it is also a more demanding method, for a knowledge of incompatibilities and interferences is a prerequisite. There is no doubt that the general basis of the procedures represents a great advance in qualitative analysis and the system should be studied carefully by all who are interested in this branch of chemistry.

F. BURRIEL-MARTÍ (Madrid)

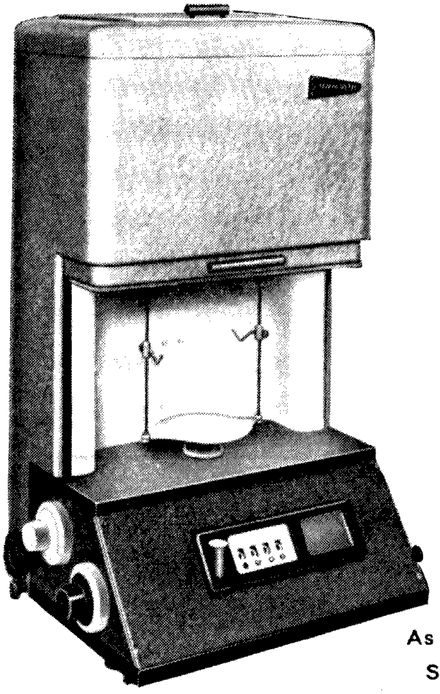
Anal. Chim. Acta, 27 (1962) 307–308

Methoden der Infrarot-Spektroskopie in der chemischen Analyse, von I. KÖSSLER (Bearbeitete und ergänzte Übersetzung des 1960 in tschechischer Sprache erschienenen Werkes "Infracervená spektroskopie v chemické analýza", Prag, 1960) Akademische Verlagsgesellschaft Geest u. Portig K.G., Leipzig, 1961, 227 S. 96 Abb., 29 Tab., D.M. 33.00.

Das Buch gibt eine Einführung in die Anwendung der IR-Spektroskopie auf analytische Probleme und eine Zusammenstellung der hierzu verwendeten Methoden. Dementspechend tritt die Behandlung praktischer Fragen in den Vordergrund während die Theorie nur soweit behandelt wird, als es zum Verständnis unbedingt erforderlich ist. Einem einleitenden Abschnitt über Theorie der IR-Strahlung und der IR-Spektren in elementarer Darstellung folgt ein etwas umfangreicheres Kapitel über IR-Geräte und Präparation der Proben, in dem die Bauprinzipien der verschiedenen Gerätetypen erläutert und Hinweise über Justierung und Eichung gegeben werden; ferner werden die üblichen Methoden zur Vorbereitung gasförmiger, flüssiger und fester Proben beschrieben. Den Hauptteil des Buches bilden die Kapitel über qualitative und quantitative Analyse. Erstere wird nur soweit besprochen, als es sich um die Identifizierung einzelner Stoffe, allein oder in Gemischen handelt. Auf Strukturfragen wird kaum eingegangen. Für die quantitative Analyse werden die verschiedenen bekannten Messmethoden erläutert, wobei auf Fehlermöglichkeiten und anzubringende Korrekturen eingegangen wird. Eine Reihe ausgewählter Analysenbeispiele dürften sich zu Einarbeitung in die Technik als nützlich erweisen. Abgeschlossen wird das Buch mit zwei kurzen Kapiteln über Kombination der IR-Spektroskopie mit Trennungsmethoden und über Dokumentation. Der Stil des Autors ist flüssig, die Darstellung einfach und leicht verständlich. Eine schärfere Gliederung des im wesentlichen durchgehend geschriebenen Textes, auch in drucktechnischer Hinsicht, wäre im Interesse einer besseren Übersichtlichkeit zu wünschen. Wenn das Buch auch an sachlichen Dingen kaum etwas bringt, was in irgendeiner der anderen Monographien über dieses Gebiet nicht auch zu finden wäre, so wird es doch von Vielen, — wegen der auf die besonderen Belange der praktischen Analyse abgestellten Auswahl und Darstellung des Stoffes — für welche die IR-Spektroskopie nur eines von vielen anzuwendenden analytischen Verfahren ist, begrüsst werden.

H. BODE (Hannover)

Anal. Chim. Acta, 27 (1962) 308



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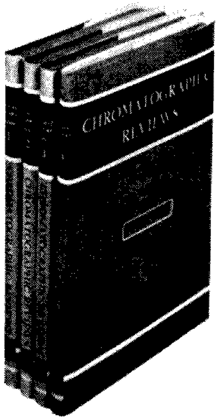
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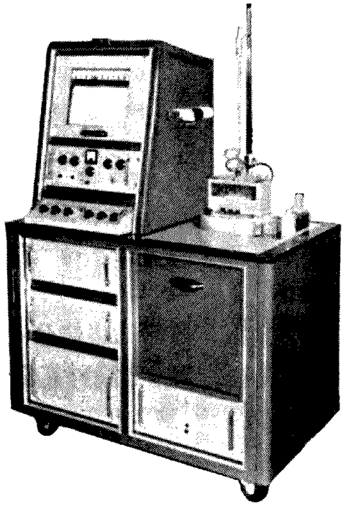

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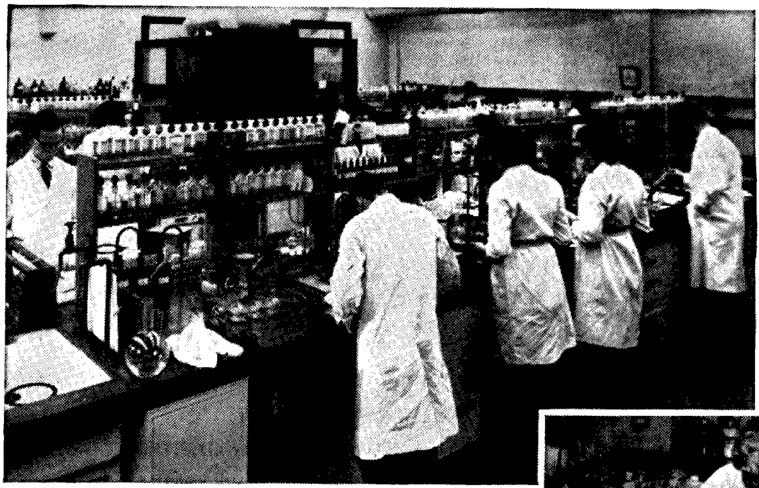

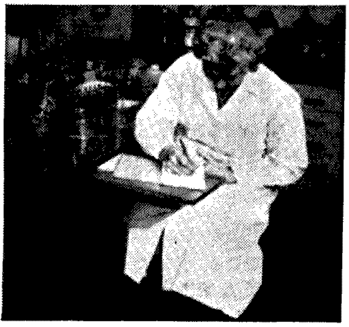

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