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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA
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STATISTICAL TECHNIQUES IN ACTIVATION ANALYSIS

Technical methods involved in activation analysis have received widespread publicity during recent years. Even more recently, various statistical techniques have been employed in conjunction with such technical methods in order to provide a better means of estimating the amounts of various pure chemical elements contained in an unknown mixture. In particular, the method of "least squares" has been employed extensively. However, for the most part, usual least squares applications in activation analysis have utilized the ordinary matrix model $Y = X\beta + e$, under the "error" assumptions (*a*) zero means, (*b*) variances proportional to Y and (*c*) zero covariances. In addition to the fact that assumptions (*b*) and (*c*) may lead to erroneous results, previous applications allow only point estimation, with no provision for confidence intervals and tests for model goodness of fit. The present paper is concerned with a feasible iterative estimation procedure which eliminates the necessity for assumptions (*b*) and (*c*), and which allows construction of confidence intervals and a test for model goodness of fit. A numerical example of the application of the technique is included. Further, an indication is given of how the technique can be extended to apply in the case of "restricted" least squares (quadratic programming).

LEE H. SMITH,
Anal. Chim. Acta, 36 (1966) 149–165

POTENTIOMETRIC TITRATIONS WITH ION-EXCHANGING MEMBRANE ELECTRODES

PART I. THEORETICAL ASPECTS OF SIMPLE PRECIPITATION TITRATIONS

Titration curves were derived for potentiometric titrations with zero electric current, utilizing a membrane electrode as indicating electrode, the membrane consisting of permselective, ion-exchanging material. As a first example, calculations were made for simple precipitation titrations with only $+1$ and -1 charged ions present in the solution to be titrated and in the reagent. For the calculations of the membrane potentials the theory of TEORELL and MEYER AND SIEVERS was used. The influence of several parameters, such as the diffusion coefficients of the ions, the capacity of the membrane and the concentration of the solutions, was examined.

F. P. IJSSELING AND E. VAN DALEN,
Anal. Chim. Acta, 36 (1966) 166–179

PREPARATIVE, INFRARED AND THERMOGRAVIMETRIC STUDIES OF THREE SCANDIUM 8-HYDROXYQUINOLINATES

The preparation of 3 scandium 8-hydroxyquinolinates is reported. Two were prepared by precipitation from homogeneous solution using 8-hydroxyquinoline generated by hydrolysis of 8-acetoxyquinoline, and the third by a solid-phase reaction. The first precipitate was obtained at pH 6.5 as a lemon-yellow compound with the composition $ScQ_3.HQ$ ($Q = C_9H_6NO$). The second chelate was obtained at pH 8.8 as a bright-yellow compound of composition $(ScQ_3)_2.HQ$. The third scandium 8-hydroxyquinolinate was obtained by a solid-phase reaction between the lemon-yellow compound $ScQ_3.HQ$ and 8-hydroxyquinoline. The orange compound has the composition $(ScQ_3)_2.3HQ$. Infrared spectra and pyrolysis curves indicated that the 3 chelates have very similar structures.

T. J. CARDWELL AND R. J. MAGEE,
Anal. Chim. Acta, 36 (1966) 180–188

THE ACCURATE DETERMINATION OF THALLIUM BY DIRECT TITRATION WITH EDTA USING METHYLTHYMOL BLUE AS INDICATOR

After oxidation with bromine, thallium can be determined accurately by titration with EDTA in alkaline tartrate media of pH 7–10 using methylthymol blue as indicator. The end-point in this titration is considerably sharper than that obtained with xylenol orange as indicator in weakly acidic solution, and is considerably less influenced by the presence of bromide, tartrate and acetate. Up to 2.5 g of ammonium or potassium bromide or chloride and up to 5 g of tartrates, acetates, nitrates or sulphates can be tolerated. About 1 mg of thallium in 75 ml can be determined with an error of about 2 μg by spectrophotometric titration. A selective solvent extraction and an anion-exchange procedure are suggested for the separation of Tl(III) from most other titratable elements.

F. W. E. Strelow and F von S. Toerien,
Anal. Chim. Acta, 36 (1966) 189–195

SPECTROPHOTOMETRIC DETERMINATION OF SULPHONYL HALIDES WITH ALKALINE PYRIDINE REAGENT

Two micromethods are described for the determination of sulphonyl halides, which depend on measurement of light absorption at *ca.* 395 and at 550 nm, respectively. These are the absorption maxima of products formed by reaction with pyridine in alkaline solution.

M. R. F. Ashworth and G. Bohnstedt,
Anal. Chim. Acta, 36 (1966) 196–203

THE SPECTROPHOTOMETRIC DETERMINATION OF COBALT IN HIGH-PURITY IRON

(in French)

A spectrophotometric study of the cobalt–β-nitroso-α-naphthol complex between 200 and 350 nm showed the existence of a very sensitive absorption maximum at 308 nm. Utilization of this wavelength allows cobalt in the range 2–20 μg to be determined with good precision. The proposed method is very suitable for the determination of cobalt in high-purity iron.

Tran-Van-Danh, J. Spitz and C. Mathien,
Anal. Chim. Acta, 36 (1966) 204–209

THE SEPARATION OF FISSION PRODUCTS BY ELECTROPHORETIC FOCUSSING OF IONS

Electrophoretic focussing of ions was applied to the separation of the long-lived fission products Zr, Nb, Ru, Y, Ce, Sr and Cs. With hydrochloric acid and nitrilotriacetic acid as the anodic and cathodic electrolytes respectively, a quantitative separation could be obtained, but Zr + Nb + Ru was left as one focus. Detection of the nuclides was by autoradiography or by γ- and β-counting.

M. Pauwels, R. Gijbels and J. Hoste,
Anal. Chim. Acta, 36 (1966) 210–214

THE METHOD OF CONCENTRATION-DEPENDENT DISTRIBUTION IN THE QUANTITATIVE USE OF RADIOISOTOPES

PART III. THE DETERMINATION OF SUBMICROGRAM AMOUNTS OF CAESIUM BY EXTRACTION WITH CALCIUM DIPICRYLAMINATE INTO NITROBENZENE

The dependence of the partition ratio of caesium between a nitrobenzene solution of calcium dipicrylaminate on the total amount of caesium in the system can be used as an analytical calibration curve. An appropriate method of isolating caesium for this determination was worked out using the polyiodide extraction of caesium. The selectivity, sensitivity and accuracy of the method were evaluated.

M. Kyrš and L. Kadlecová,
Anal. Chim. Acta, 36 (1966) 215–219

THE DETERMINATION OF MOLYBDENUM IN NATURAL WATERS, SILICATES AND BIOLOGICAL MATERIALS

Coprecipitation with hydrous manganese dioxide is used for the concentration of molybdenum from natural waters (including sea water) and from solutions prepared from silicate rocks and mineralized biological materials. Molybdenum is determined photometrically with dithiol after dissolving the manganese dioxide precipitate in sulphur dioxide solution. Since only a few elements are coprecipitated by manganese dioxide, separation before photometry is not normally necessary. However, if it is thought desirable, molybdenum can be separated from most other elements by adsorbing it on a cation exchanger and eluting it with hydrogen peroxide. The method was found to have a coefficient of variation of *ca.* 1% with sea water, argillaceous sediments and biological materials at concentration levels of 10.3 µg Mo/l, 7.2 µg Mo/g and 0.9 Mo/g respectively. The U.S. Geological Survey Standard granite (G1) and diabase (W1) were found to contain 6.3 and 0.48 µg Mo/g respectively.

K. M. Chan and J. P. Riley,
Anal. Chim. Acta, 36 (1966) 220–229

VOLATILISATION OF IRIDIUM FROM BOILING PERCHLORIC ACID

(Short Communication)

R. Gijbels and J. Hoste,
Anal. Chim. Acta, 36 (1966) 230–233

DERIVATIVES OF OROTIC ACID AS POTENTIAL REAGENTS FOR ALKALI METALS

(Short Communication)

B. C. Lewis and W. I. Stephen,
Anal. Chim. Acta, 36 (1966) 234–237

SPECTROPHOTOMETRIC DETERMINATION OF TRACES OF THIOUREA IN AMMONIUM THIOCYANATE

(Short Communication)

S. T. Talreja, P. M. Oza and P. S. Rao,
Anal. Chim. Acta, 36 (1966) 238–239

SPECTROPHOTOMETRIC DETERMINATION OF SMALL AMOUNTS OF TITANIUM WITH ADRENALIN

(Short Communication; in German)

L. Jerman and F. Poláček,
Anal. Chim. Acta, 36 (1966) 240–243

AN UNUSUAL EFFECT OF IRON IN THE FLAME-PHOTOMETRIC DETERMINATION OF CALCIUM

(Short Communication)

J. C. van Schouwenburg and A. D. van der Wey,
Anal. Chim. Acta, 36 (1966) 243–245

SPECTROPHOTOMETRIC DETERMINATION OF LANTHANIDES AND YTTRIUM WITH DIANTIPYRYLAZO

(Short Communication)

B. Buděšínský and D. Vrzalová,
Anal. Chim. Acta, 36 (1966) 246–248

THE BOEDEKER REACTION. PART III. THE DETECTION OF SULPHITE ION

(Short Communication)

A. G. Fogg, W. Moser and R. A. Chalmers,
Anal. Chim. Acta, 36 (1966) 248–251

THE USE OF AIR AS CARRIER GAS IN THE ELECTRON CAPTURE DETECTOR

(Short Communication)

G. G. Guilbault and C. Herrin,
Anal. Chim. Acta, 36 (1966) 252–255

REACTIONS OF MERCURY(II) CYANIDE WITH HEAVY METAL SULFIDES

(Short Communication)

F. Feigl, A. Caldas and L. Ben-Dor,
Anal. Chim. Acta, 36 (1966) 255–257

SOME OBSERVATIONS ON THE DETERMINATION OF METALS BY ATOMIC ABSORPTION SPECTROSCOPY COMBINED WITH EXTRACTION

(Short Communication)

T. Takeuchi, M. Suzuki and M. Yanagisawa,
Anal. Chim. Acta, 36 (1966) 258–260

STATISTICAL TECHNIQUES IN ACTIVATION ANALYSIS*

LEE H. SMITH
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(Received January 1st, 1966)

This paper is concerned with the application of statistical methods to estimation of weight proportions of "ingredients" in a "chemical mixture". More specifically, the problem can be described as follows. A chemical mixture is known to be comprised of a number of p "ingredients" which are mixed in unknown proportions. A chemical analysis of the mixture reveals a number, n, of chemical "characteristics" y_i ($i = 1, 2, \ldots, n$) for the mixture. It is required to estimate the unknown weight proportions β_j ($j = 1, 2, \ldots, p$) with which the p ingredients occur in the mixture. Denote by x_{ij} the value of the ith characteristic if a unit weight of the jth ingredient is subjected to the analysis. Then, assuming that the contributions of the ingredients in a mixture are additive, the expected value of the ith characteristic in the mixture should be

$$E(y_i) = \sum_{j=1}^{p} \beta_j x_{ij} \qquad (1)$$

To fix the ideas, let us assume for the time being that the scales in which the y_i are measured are standardized and that the observed values of y_i differ from their expected values by independent residuals e_i of equal variance. Under such circumstances we have a standard regression model and one could estimate the β_j by least squares, *i.e.*, by minimizing the sum of squares

$$Q(\beta) = \sum_{i=1}^{n} (y_i - \sum_{j=1}^{p} \beta_j x_{ij})^2 .$$

The more specific mixture problem with which we are concerned is one arising in activation analysis. A detailed account concerning activation analysis is given by SMITH[1]. For the purposes of this paper, we need only consider the assumptions upon which the entire procedure of activation analysis is based. The assumptions are (*a*) a chemical element, when activated properly, emits a unique γ-ray spectrum which is a function of energy, (*b*) the spectrum of a mixture of chemical elements is a linear combination of the spectra of the chemical elements contained in a mixture, and (*c*) the mass of any chemical element present in a mixture is proportional to the contribution its spectrum makes to the overall mixture spectrum. Thus, we have in this problem that the possibly present "ingredients" are known chemical elements which are activated and for which spectra of γ-ray emission counts are made for a

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series of energy level channels. (In activation analysis the building of such spectra is termed the preparing of "libraries" for the various elements supposed to be in an unknown. It should be noted that, owing to the fact that counts are *very* sensitive to experimental conditions, "libraries" may have to be prepared anew on each occasion that an unknown sample is to be analyzed.) Immediately after the above counts have been made, the corresponding spectrum is recorded for the unknown mixture, so that the problem is a special case of determining the weight proportions β_j in (1), with the x_{ij} representing the counts for the jth pure chemical element made at the ith energy level, while y_i denotes the corresponding count for the unknown sample.

Although the results obtained through use of routine statistical activation analysis procedures (described by SMITH[1]) have often been quite good, there have been some cases in which better results might have been obtained had the procedure been modified. First, consider the usual least squares analysis. It is ordinarily carried out under the usual assumption of uncorrelated errors. However, in most cases there is a dependence between errors observed at various energy level channels. Second, weights (variances) used in the least squares analysis have usually been taken as proportional to the corresponding mixture γ-ray emission counts. It is quite likely that these may be incorrect. Third, consider the selection of a "library" for each element. Each of the samples which is finally selected as a "library" for a given element is used later in the least squares analysis as representing the "true" pure element spectrum. If we are to investigate the dependence described above, sample to sample variations must be used to estimate the variance–covariance matrix of the errors involved in the least squares model. Finally, the routine procedure provides *only* point estimation of the weight proportions, allowing no statement of confidence intervals or tests for model goodness of fit.

The present paper describes a feasible solution to the activation analysis problem which alleviates the above difficulties. The recommended method estimates the variance of the "error variables" directly from repeat activations and resulting repeat sets of counts obtained for each pure element and for the mixture. The covariance problem is dealt with by making r separate estimates of the β proportions, each from a set of q channels ($rq = n$). It is required that r be large enough to allow the assumption that no covariances exist between errors r channels apart, so that we use a weighted least squares estimation of β for each of the r sets, employing as weights the "custom-made variances" estimated directly from the data. The final estimate of β is the average of the r estimates obtained from the r sets. Variances of the estimates as well as confidence intervals are likewise estimated utilizing the r separate estimates. Although most of the discussion in this paper is devoted to "unrestricted" least squares, an indication is given of how the method can be extended in a very straightforward manner to include the use of "restricted" least squares. In fact, one of the outstanding features of the technique developed is the fact that it allows construction of confidence intervals and tests for model goodness of fit *even* in the "restricted" least squares case.

PERTINENT STATISTICAL CONCEPTS

The problem of least squares is treated with various degrees of sophistication throughout statistical literature. For the purposes of this paper suitable treatments are given in GRAYBILL[2] and KEMPTHORNE[3] for the case of uncorrelated errors, and in ANDERSON[4] and SCHEFFE[5] for the case of correlated errors. The following is merely a brief summary of the results derived in the above references.

In least squares we assume a linear relation between some dependent variable and one or more independent variables, *i.e.*, we assume a model of the type

$$y_i = \sum_{j=1}^{p} \beta_j x_{ij} + e_i \quad (i = 1, 2, \ldots, n) \tag{2}$$

where y_i is the ith observation on the dependent variable, x_{ij} is the ith value (known) of the jth independent variable, β_j is the unknown coefficient associated with the jth independent variable, and e_i represents an error associated with the ith observation of the dependent variable. The principal problem in least squares is to estimate the unknown coefficients β_j $(j = 1, 2, \ldots, p)$ and to provide confidence intervals for each β_j. Although the problem can be handled through use of the notation employed in eqn. (2), it can be treated much more succinctly through the use of matrix notation. Hence, we do so in what follows. However, the reader unfamiliar with matrix notation will not be at a complete loss, since the examples will clarify the computations involved. The main purpose of this section is to emphasize the fact that the estimates and resulting confidence intervals for β_j are (possibly) quite different when the errors involved in the model are correlated from when they are not.

The model given by eqn. (2) can be written in matrix form as

$$Y = X\beta + e \tag{3}$$

where Y is an $(n \times 1)$ vector of observations on the dependent variable, X is an $(n \times p)$ matrix of known constants, β is a $(p \times 1)$ vector of unknown parameters, and e is an $(n \times 1)$ vector of unknown errors.

Linear model with uncorrelated errors

Suppose we have the model (3) where $E(e) = 0$ and $E(ee') = \sigma^2 I$, with I representing the identity matrix. That is, suppose we assume the linear model where the errors have equal variances and are uncorrelated. The least squares problem is to find the vector β (where the β_j's may take on any real values) which minimizes the sum of squares (hence, the name least squares)

$$Q(\beta) = (Y - X\beta)'(Y - X\beta) \tag{4}$$

It is shown in GRAYBILL[2] and KEMPTHORNE[3] that $Q(\beta)$ attains its absolute minimum for those and only those values of β which satisfy the "normal equations" $X'X\beta = X'Y$. Under the conditions given above, if the rank of X is p, the unique solution $\hat{\beta}$ to the normal equations is

$$\hat{\beta} = (X'X)^{-1} X'Y \tag{5}$$

The expected value of $\hat{\beta}$ is $E(\hat{\beta}) = \beta$, and the variance–covariance matrix of $\hat{\beta}$ is $\sigma^2(X'X)^{-1}$. We also have as an unbiased estimate of σ^2

$$\hat{\sigma}^2 = \frac{1}{n-p} Q(\hat{\beta}) = \frac{1}{n-p}(Y - X\hat{\beta})'(Y - X\hat{\beta}) \tag{6}$$

Finally as an unbiased estimate of the variance–covariance matrix of $\hat{\beta}$, we have

$$\hat{\sigma}^2(X'X)^{-1} \tag{7}$$

with $\hat{\sigma}^2$ as given in (6). Hence, in the case of uncorrelated errors, we estimate β by (5) and employ (7) to set confidence intervals.

Linear model with correlated errors

Now, suppose we have the same type model (3) where $E(e) = 0$ and $E(ee') = \sigma^2 V$, with V a *known* covariance matrix. In other words, suppose we assume the linear model where the errors are correlated, *i.e.*, V is a full matrix. In this case, if we assume that V is positive definite[3], then we know there exists a non-singular matrix T, such that $TVT' = I$. Using this fact, and the transformation $Z = TY$, it can be shown that the problem becomes one of finding the vector β which minimizes the quadratic form

$$Q^*(\beta) = (Y - X\beta)' V^{-1} (Y - X\beta) \tag{8}$$

The resulting normal equations will become $X'V^{-1}X\beta = X'V^{-1}Y$ from which our estimate of β becomes

$$\hat{\beta} = (X'V^{-1}X)^{-1} X'V^{-1}Y \tag{9}$$

We again have that the expected value of $\hat{\beta}$ is β, but now the variance–covariance matrix of $\hat{\beta}$ becomes $\sigma^2(X'V^{-1}X)^{-1}$. We have as an unbiased estimate of σ^2

$$\hat{\sigma}^2 = \frac{1}{n-p} Q^*(\hat{\beta}) = \frac{1}{n-p} (Y - X\hat{\beta})' V^{-1} (Y - X\hat{\beta}) \tag{10}$$

and, finally, as an unbiased estimate of the variance–covariance matrix of $\hat{\beta}$,

$$\hat{\sigma}^2(X'V^{-1}X)^{-1} \tag{11}$$

where, $\hat{\sigma}^2$ is as given in eqn. (10). Hence, in the case of correlated errors, we estimate β by eqn. (9) and employ eqn. (11) to set confidence intervals. Note that eqns. (9) and (11) may possibly be quite different from eqns. (5) and (7), respectively.

DISCUSSION OF MODEL

Consider now the type model occurring in activation analysis. Suppose we have repeated the activation and counting of an unknown mixture and each of the pertinent pure chemical elements m times. The assumption of a linear relation (*i.e.*, the assumption that there is a linear relation between the counts obtained in given energy level channels when an unknown sample is activated and the counts obtained in these respective energy level channels when the pure chemical elements actually contained in the unknown sample are activated) leads to the model

$$\bar{y}_i = \sum_{j=1}^{p} \beta_j \bar{x}_{ij} + \bar{e}_i \tag{12}$$

with

$$\bar{e}_i = \sum_{j=1}^{p} \beta_j z_{ij} - q_i + Z_i \tag{13}$$

where $\bar{y}_i$ is the average count obtained in the ith energy level channel when the activation and counting of an unknown sample has been repeated m times; β_j is the unknown coefficient (to be estimated) associated with the jth pure chemical element; $\bar{x}_{ij}$ is the average count in the ith energy level channel when m samples of the jth pure chemical element are activated and counted; z_{ij} represents an error due largely to imperfect measurement associated with $\bar{x}_{ij}$; q_i represents an error composed, for the most part, of measurement error associated with $\bar{y}_i$; and Z_i represents a term accounting for failure of the linear model to hold. (The complete development of the model given by eqn. (12) is shown in SMITH[1].) Note that the model (12) very closely resembles the model given by eqn. (2), the model for which ordinary least squares is applicable.

However, inspection of the structure of the compounded error residuals $\bar{e}_i$ in eqn. (13) shows that they contain a component $\sum_{j=1}^{p} \beta_j z_{ij}$ and are, therefore, correlated with the variation of the independent variables $\bar{x}_{ij}$. Therefore, we have a regression model with "errors of measurement on the independent variables" which are correlated with errors in the regression law. Hence, *strictly speaking*, classical least squares estimation would result (see *e.g.* LINDLEY[6] and BARTLETT[7]) in biased estimation. It will be seen that classical theory is used only to suggest appropriate estimators of β_j. We do not rely on the classical theory of linear models for the distribution properties of our estimators. For the latter a special technique of variance estimation has been developed.

FEASIBLE ITERATIVE PROCEDURE

From the previous section we have that the activation analysis model can be written in matrix form as

$$\bar{Y} = \bar{X}\beta + \bar{e} \tag{14}$$

with $E(\bar{e}) = 0$ and $E(\bar{e}\bar{e}') = \sigma^2 V$, where $\bar{Y}$ is an $(n \times 1)$ matrix of average counts obtained at various energy level channels when an unknown sample is activated and counted m times; $\bar{X}$ is an $(n \times p)$ matrix of energy level counts which are "representative" of the counts which can be expected when given masses of pure chemical elements are activated under certain conditions; β is a $(p \times 1)$ matrix of unknown coefficients representing the unknown proportions of the various pure elements which are present in the mixture; and $\bar{e}$ is an $(n \times 1)$ matrix of unknown errors. Note that although the model appears very similar to the general least squares model (eqn. (3)), there is one very significant difference, *i.e.*, here, we do not know V, the variance–covariance matrix. In such a case our problem of estimating β is not even as straightforward as is the usual least squares problem where we assume correlated errors, for recall that in the general problem we assume V known.

The problem is further complicated by the fact that it is not feasible to make m very large. That is, it is not feasible to repeat the counting experiment a very large number of times. Hence, the application of least squares to the activation analysis problem is made even more difficult by the fact that the number of observations on each vector (number of repeats of counts) is much smaller than the number of components in the vectors (number of energy level channels). This violates an important assumption commonly made in development of multivariate theory[4]. For these reasons we are forced to iteration in order to obtain a feasible procedure.

Although we are forced to assume that our variance–covariance matrix is of the form $\sigma^2 V$, rather than of the form $\sigma^2 I$, we have reason to believe that the elements of $\sigma^2 V$ reduce in magnitude as we move from the main diagonal of $\sigma^2 V$ toward either the lower left-hand corner or upper right-hand corner. This is equivalent to saying that the covariance between errors in counts made at two different channels becomes smaller as the distance between the pertinent channels increases. In fact, it is reasonable to assume that this covariance becomes negligible rather rapidly as the distance between the pertinent channels increases. This fact has been used to great advantage in the theoretical development of the iterative procedure.

We shall not discuss in this paper the theory and rationale leading to the method selected as a feasible solution to the activation analysis problem. Rather, we present in this section a *verbal* summary of the steps involved in the procedure as finally developed. (A detailed summary of the steps involved is given in SMITH[8].) The summary is followed by an example of the application of the procedure. We must reiterate that, because of previously mentioned departures from classical assumptions, classical least squares estimation theory as applicable to linear models has been used only to suggest appropriate estimation of β. We do not rely on classical theory of linear models for the distribution properties of our estimates. Theory and rationale related to the investigation of the estimation of β, as well as the setting of confidence intervals on β and testing for model goodness of fit are given in SMITH[1].

We assume that we begin our analysis with fairly good knowledge of the elements which are present, and are, hence, primarily interested in determining the amounts of these elements which make up the unknown mixture. We shall assume that we have selected p elements to be included in the analysis. Further, we shall assume that the total mass of the unknown mixture is known. Hence, we shall be dealing with the estimation of the proportions, β_j $(j = 1, 2, \ldots, p)$, of each element present in the mixture. In cases when the total mass of the unknown mixture is not known, the procedure can be modified easily to allow for estimation of masses rather than proportions.

Estimation procedure

Suppose we have repeated the activation and counting of the unknown mixture and each of the pertinent pure chemical elements m times. From this procedure we obtain m repetitions of the vectors $Y, X_1, X_2, \ldots, X_p$, where Y is the matrix of counts for the mixture and X_j is the matrix of counts for the jth pure chemical element. Next, suppose we randomly order the mY vectors and call them $Y^{(1)}$, $Y^{(2)}, \ldots, Y^{(m)}$, and randomly order the mX_j $(j = 1, 2, \ldots, p)$ vectors and call them $X_j^{(1)}, X_j^{(2)}, \ldots, X_j^{(m)}$. Finally suppose we divide the n energy level channels into r sets, each set containing q channels (we restrict r and q to be such that $rq = n$) as follows: Let Channel Set 1 be the set composed of channels $1, r+1, \ldots, (q-1)r+1$; Channel Set 2 be the set composed of channels $2, r+2, \ldots, (q-1)r+2; \ldots$; Channel Set r be the set composed of channels $r, 2r, \ldots, qr$. (We further require that r be large enough to allow us to assume that the covariance between errors on counts made at two channels is negligible as long as the channels are at least r channels apart. On the other hand, r cannot be too large, because a very large r would give us too few sets of data to allow reasonable establishment of confidence intervals.) Then, for what follows, let us re-number the channels, so that the channels within each set are numbered consecutively from 1 to q. Now, let us divide all the observed y's and x's into r sets as follows: let Set 1 be the set of all y's and x's observed in channels belonging to Channel Set 1; Set 2 be the set of all y's and x's observed in channels belonging to Channel Set 2; . . .; Set r be the set of all y's and x's observed in channels belonging to Channel Set r. Henceforth, we shall designate the set to which an observation (count) belongs by a left superscript. That is, we shall let ${}^{(t)}y_i^{(k)}$ be the count obtained in the ith channel of set t ($t = 1, 2, \ldots, r$) on the kth repetition of the activating and counting of an unknown sample (it should be noted that i now has only the range $i = 1, 2, \ldots, q$) and ${}^{(t)}x_{ij}^{(k)}$ be the standard count obtained in the ith channel of set t on the kth repetition of the activation and counting of the jth pure chemical element. Through this procedure we shall have for each data set m repeats of vectors corresponding to $(Y^{(k)})$ and $(X_j^{(k)})$ ($j = 1, 2, \ldots, p$). We shall denote these for the tth set by $({}^{(t)}Y^{(k)})$ and $({}^{(t)}X_j^{(k)})$. We can thus assume for each set a model of the form

$$({}^{(t)}\bar{Y}) = ({}^{(t)}\bar{X})\beta + ({}^{(t)}\bar{e}) \tag{15}$$

where the left superscript (t) indicates that we are considering data from set t. (Actually, this assumption is really no different from our assumption that $\bar{Y} = \bar{X}\beta + \bar{e}$ (eqn. (14)). We are now merely looking at a reduced set of data for making the fit.) We now have, if r has been chosen large enough, that the covariances between the errors at various channels are zero. Thus,

$$E({}^{(t)}\bar{e}) = 0 \text{ and } E[({}^{(t)}\bar{e})({}^{(t)}\bar{e})'] = \sigma^2({}^{(t)}D) \tag{16}$$

where $({}^{(t)}D)$ is a diagonal matrix. However, we know neither β (15) nor $({}^{(t)}D)$ (16). Hence we must estimate both. To do so, we are forced to an iterative procedure. We estimate β for each of the r sets of data as follows:

(*1*) Estimate β under the assumption that $E[({}^{(t)}\bar{e})({}^{(t)}\bar{e})'] = \sigma^2 D$, where D is a diagonal matrix having elements equal to the square roots of the true mixture counts for the energy level channels of data set t, *i.e.*

$${}^{(t)}\hat{\hat{\beta}} = [({}^{(t)}\bar{X})'({}^{(t)}D_{\bar{y}})^{-1}({}^{(t)}\bar{X})]^{-1}({}^{(t)}\bar{X})'({}^{(t)}D_{\bar{y}})^{-1}({}^{(t)}\bar{Y})$$

where $({}^{(t)}D_{\bar{y}})$ is a diagonal matrix having elements equal to the square roots of the average mixture counts observed at the energy level channels of data set t.

(*2*) Calculate the resulting errors

$$({}^{(t)}c^{(k)})' = [({}^{(t)}Y^{(k)}) - ({}^{(t)}X^{(k)})({}^{(t)}\hat{\hat{\beta}})] \quad (k = 1, 2, \ldots, m)$$

(*3*) Calculate the variance–covariance matrix of these errors.

(*4*) Re-estimate β by

$${}^{(t)}\hat{\hat{\beta}} = [({}^{(t)}\bar{X})'({}^{(t)}S_1)^{-1}({}^{(t)}\bar{X})]^{-1}({}^{(t)}\bar{X})'({}^{(t)}S_1)^{-1}({}^{(t)}\bar{Y})$$

where $({}^{(t)}S_1)$ is a diagonal matrix containing the elements from the diagonal of the matrix calculated in (*3*) above.

(*5*) Repeat steps (*2*) through (*4*) until ${}^{(t)}\hat{\hat{\beta}}$ converges.

Now, suppose we have repeated this iterative procedure for all r sets of data.

We will have r separate estimates of β, *i.e.*, ${}^{(1)}\hat{\hat{\beta}}, {}^{(2)}\hat{\hat{\beta}}, \ldots, {}^{(r)}\hat{\hat{\beta}}$, and can use as our final estimate of β

$$\hat{\hat{\beta}} = \frac{1}{r} \sum_{t=1}^{r} {}^{(t)}\hat{\hat{\beta}} \,. \tag{17}$$

Setting of confidence intervals

In order to set confidence intervals on β, we must determine the variances associated with each element, $\hat{\hat{\beta}}_j$, of the vector $\hat{\hat{\beta}}$. Recall that we have r separate estimates of β_j from the r sets of data. If these estimates were independent, we could compute variances of the estimates in a very straightforward fashion, and then set confidence intervals by using the usual t-distribution approach[2]. However, our estimates are *not* independent. Nevertheless, due to the work of WILKS[9], we can estimate the variance of $\hat{\hat{\beta}}_j$, even though the separate estimates ${}^{(t)}\hat{\hat{\beta}}_j$ are correlated, by

$$v(\hat{\hat{\beta}}_j) = \frac{1}{r^2} \left[r c_{j \cdot 0} + (r-1) c_{j \cdot 1} + \ldots + (r-5) c_{j \cdot 5} \right]$$

where $c_{j \cdot \alpha}$ is the estimate of the lag covariance between estimates of β_j made through use of sets of data which are separated by a lag of α. Then, confidence intervals on β_j can be set through use of the theory developed by BAYLEY AND HAMMERSLEY[10] on the effective number of independent observations in an autocorrelated time series. We set (99%, say) confidence intervals by $\hat{\hat{\beta}}_j \pm t_{r_j^* \cdot .01} [v(\hat{\hat{\beta}}_j)]^{\frac{1}{2}}$, where $t_{r_j^* \cdot .01}$ is the proper tabular t-distribution value for r_j^* degrees of freedom, with r_j^* being the first integer greater than or equal to b_j^* where

$$b_j^* = \frac{1}{\dfrac{1}{r} + \dfrac{2}{r^2 c_{j \cdot 0}} \displaystyle\sum_{\alpha=1}^{5} (r-\alpha) c_{j \cdot \alpha}}$$

Having repeated this procedure for $j = 1, 2, \ldots, p$, we shall have confidence intervals for each element of β. The steps involved in both the estimation and setting of confidence intervals are exemplified in detail in Appendix A.

Test for model goodness of fit

In order to test for model goodness of fit, we must be able to make a statement about the statistical distribution of

$$\psi = [({}^{(t)}\bar{Y}) - ({}^{(t)}\bar{X})\hat{\hat{\beta}}]' ({}^{(t)}S_1)^{-1} [({}^{(t)}\bar{Y}) - ({}^{(t)}\bar{X})\hat{\hat{\beta}}] \tag{18}$$

where $({}^{(t)}S_1)$ is the matrix obtained in the last iteration of the estimation procedure for data set t and $\hat{\hat{\beta}}$ is obtained by eqn. (17). We note that the structure of ψ in eqn. (18) is similar to that of the corresponding value which is usually encountered in ordinary least squares (eqn. (8)) and which has a chi-square distribution. Thus, we assume that ψ is approximately distributed as a chi-square distribution with q–p degrees of freedom. This suggests that we may usefully employ the normalizing log-transformation suggested by BARTLETT AND KENDALL[11]. Use of this transformation leads us to a valid test for model goodness of fit which also employs the work of BAYLEY AND HAMMERSLEY[10] and which involves the use of the t-distribution.

Description of the considerations involved is too lengthy for presentation here. However, the reader interested in details should see SMITH[1].

EXAMPLE

Let us now consider an example of the application of the iterative procedure. The procedure followed in the analysis is very similar to that recommended in the previous section. However, it has been necessary to make slight changes in the analysis in order to make it applicable to the particular data available for study. Because the mass of the mixture of this example is not known, an estimate of this mass by least squares would not prove fruitful as an examination of the effectiveness of the procedures, since we would have no way of checking the accuracy of the estimates. Hence, rather than trying to estimate masses (or proportions), we are interested, in this example, in obtaining merely the coefficients by which the library spectra must be multiplied in order to obtain the mixture spectrum. Conditions of the experiment were made such that a perfect estimation procedure should result in assignment of coefficients of 1.0 to each of the pure elements.

For this particular example, γ-ray emission spectra were repeated 5 times each for a sodium sample, a cobalt sample, and a mixture containing both. In this case, channels 78 through 125 (out of the total of 256 channels) were selected for examination. A complete listing of the data obtained is too lengthy to be included here. We need only realize that 5 repeats of the vectors $(Y^{(k)})$ and $(X_j{}^{(k)})$ $(j = 1, 2)$ were available for analysis, where $(Y^{(k)})$, $(X_1{}^{(k)})$, and $(X_2{}^{(k)})$ are (48×1)-vectors of counts obtained in channels 78 through 125 on the kth repeat of the counting of the mixture, the sodium sample, and the cobalt sample, respectively. Then

$$(\bar{Y}) = \tfrac{1}{5}\sum_{k=1}^{5}(Y^{(k)}) \; ; \quad (\bar{X}_1) = \tfrac{1}{5}\sum_{k=1}^{5}(X_1{}^{(k)}) \; ; \quad (\bar{X}_2) = \tfrac{1}{5}\sum_{k=1}^{5}(X_2{}^{(k)})$$

In order to provide a basis for comparing the recommended analysis procedure with the routine procedure, the routine procedure was applied to $(Y^{(1)})$, $(X_1{}^{(1)})$,

TABLE I

EXAMPLE—SUMMARY OF RESULTS

t (Data Set number)	*Results of iterative procedure*			
	First iteration		*Second iteration*	
	${}^{(t)}\hat{\hat{\beta}}_1$	${}^{(t)}\hat{\hat{\beta}}_2$	${}^{(t)}\hat{\hat{\beta}}_1$	${}^{(t)}\hat{\hat{\beta}}_2$
1	0.874	1.001	0.842	1.025
2	0.854	0.997	0.908	0.998
3	1.017	0.935	1.021	0.939
4	1.058	0.916	1.157	0.854
5	1.053	0.946	1.040	0.953
6	0.973	0.985	0.959	0.982
Average			0.988	0.959

	β_1	β_2
Estimates by routine procedure	1.365	0.781
Estimates by recommended iterative procedure	0.988	0.959
Correct coefficients	1.000	1.000

and $(X_2^{(1)})$. That is we estimate β, where $\beta' = [\beta_1, \beta_2]$, with β_1 and β_2 being the coefficients associated with sodium and cobalt, respectively, by

$$\hat{\beta} = [(X^{(1)})'(D_y)^{-1}(X^{(1)})]^{-1}(X^{(1)})'(D_y)^{-1}(Y^{(1)})$$

where $(X^{(1)}) = [(X_1^{(1)})(X_2^{(1)})]$ and (D_y) is a diagonal matrix having as its diagonal elements the square root of the mixture counts. Results obtained were

$$\hat{\beta}_1 = 1.365 \text{ and } \hat{\beta}_2 = 0.781 \tag{19}$$

(It should be noted that better results might have been obtained had we applied the routinely used procedure to other combinations of the repeats of Y, X_1, and X_2, respectively. However, since, under ordinary circumstances, the only mixture count available would be $Y^{(1)}$, use of this particular repeat seems logical.)

For application of the recommended iterative procedure, the data were divided into 6 sets as follows: Set 1 = all y's and x's corresponding to channels 78, 84, 90, 96, 102, 108, 114, 120; Set 2 = all y's and x's corresponding to channels 79, 85, 91, 97, 103, 109, 115, 121; . . .; Set 6 = all y's and x's corresponding to channels 83, 89, 95, 101, 107, 113, 119, 125. The recommended iterative procedure was applied to the data of each set. Table I presents a summary of the results obtained by both the routine procedure and the recommended iterative procedure. In each of the 6 sets of data, only 2 iterations were necessary for convergence. Hence, we use the results of the second iteration as our final estimates of β_1 and β_2 *i.e.*,

$$\hat{\hat{\beta}}_1 = 0.988 \text{ and } \hat{\hat{\beta}}_2 = 0.959 \tag{20}$$

The 99% confidence intervals established by the recommended procedure are

$$0.911 \leq \beta_1 \leq 1.065 \text{ and } 0.915 \leq \beta_2 \leq 1.003$$

Clearly, the results of the iterative procedure (20) are better than those (19) obtained by application of the routine procedure to $Y^{(1)}$, $X_1^{(1)}$ and $X_2^{(1)}$. Fairly detailed examples of the computations necessary in both the iterative estimation procedure and the procedure for setting confidence intervals are given in Appendix A. The reader interested in even more detail should see SMITH[1].

EXTENSION TO QUADRATIC PROGRAMMING

It should be noted that in some cases negative coefficients have been obtained in the routine application of least squares to the activation analysis problem. Yet we know that this should not be the case, since it is impossible for an element to appear in a negative proportion. Further, although the recommended iterative procedure affords improvement over the routine procedure in several areas, there is nothing inherent in even the improved procedure which will preclude the obtaining of negative coefficients. Hence, it becomes desirable in some cases to apply the technique generally referred to as "restricted" least squares (quadratic programming) to the activation analysis problem. This is merely a problem of minimizing the same quadratic form [eqns. (4) and (8)] as in the case of ordinary least squares, but now we make the restrictions

$$\beta_j \geq 0 \text{ and } \sum_{j=1}^{p} \beta_j \leq 1 \tag{21}$$

since we know that no proportion can be negative and that the sum of the proportions is less than or equal to one. The inequality sign in the second part of eqn. (21) takes account of the fact that the mixture may contain an unknown proportion of some "inert" ingredient not contributing to the mixture spectrum.

We have mentioned earlier that one of the outstanding features of the iterative technique is that it allows construction of confidence intervals and a test for model goodness of fit *even* in the "restricted" least squares case. This is significant indeed, since very little appears in the literature pertaining to construction of confidence intervals for quadratic programming estimators, and that which does appear is concerned with very special cases[1,12]. For the quadratic programming case, our model would remain the same (eqn. (14)). In order to apply the iterative technique, we would first randomly order and divide the data as described earlier. Then we would obtain r sets of quadratic programming estimates of β, *i.e.*, r sets of $\overset{\approx}{\beta}$ where the $\approx$'s represent an iterative quadratic programming estimate, by iteratively minimizing the pertinent quadratic forms subject to proper constraints[13]. We finally would use as an estimate of β, $\overset{\approx}{\beta} = \sum_{t=1}^{r} {}^{(t)}\overset{\approx}{\beta}$. The procedures for constructing confidence intervals and for testing goodness of fit would be the same as in the case of unrestricted least squares, except that everywhere $\hat{\hat{\beta}}$ would be replaced by $\overset{\approx}{\beta}$. A detailed description of the feasible quadratic programming procedure for activation analysis is given by SMITH[1].

FUTURE APPLICATIONS

Recent research at Texas A&M University (where the writer conducted the research leading to the results presented here) in the application of statistical methods to the activation analysis problem has been directed toward investigation of the validity of additivity assumptions inherent in previous work. This approach involves, as an initial step, the estimation of weight proportions of various pure elements present in an unknown mixture. Once these estimates are obtained, a sample mixture is prepared containing proportions equal to these estimates, and a spectrum of γ-ray counts is built for such mixture. Comparison of this spectrum with the unknown mixture spectrum provides information as to the validity of the additivity assumption mentioned above. Obviously, better initial estimates will enable better information concerning additivity. Thus, the improved estimation procedure described here may well provide important contributions to future activation analysis research, particularly in the additivity investigations.

APPENDIX A. EXAMPLE COMPUTATIONS FOR ESTIMATION AND SETTING OF CONFIDENCE INTERVALS

In order to make clearer both the recommended iterative procedure and the method of setting confidence limits, let us examine detailed examples of each. For this example γ-ray emission spectra were repeated 4 times each for a cesium sample, a manganese sample, and a mixture containing both. Visual examination of the data prompted a selection of channels 45 through 84 for detailed analytical examination.

As in the example in the body of the paper, a listing of all the pertinent data would consume far too much space. Hence, let it suffice to say here that 4 repeats of the vectors $(Y^{(k)})$ and $(X_j^{(k)})$ $(j = 1, 2)$ were available for analysis, where $(Y^{(k)})$, $(X_1^{(k)})$, and $(X_2^{(k)})$ are (40×1)-vectors of the counts obtained in channels 45 through 84 on the *k*th repeat of the counting of the mixture, the cesium sample, and the manganese sample, respectively. We thus have

$$(\bar{Y}) = \tfrac{1}{4}\sum_{k=1}^{4}(Y^{(k)}) \; ; \quad (\bar{X}_1) = \tfrac{1}{4}\sum_{k=1}^{4}(X_1^{(k)}) \; ; \quad (\bar{X}_2) = \tfrac{1}{4}\sum_{k=1}^{4}(X_2^{(k)}) \, .$$

For application of the recommended iterative method the data were divided into 8 sets with Set 1 being composed of all *y*'s and *x*'s observed in channels 45, 53, 61, 69, 77. We shall consider the application of the estimation procedure to this set of data only. Table A1 shows the 4 repeats and averages of all pertinent counts for the

TABLE AI

COUNT REPEATS FOR DATA SET I

Mixture count repeats *Channel number*	$(^{(1)}Y^{(1)})$	$(^{(1)}Y^{(2)})$	$(^{(1)}Y^{(3)})$	$(^{(1)}Y^{(4)})$	$(^{(1)}\bar{Y})$
45	594	577	565	561	574
53	1307	1150	1374	1195	1257
61	577	639	523	620	590
69	815	797	827	804	811
77	76	73	69	74	73

Cesium count repeats *Channel number*	$(^{(1)}X_1^{(1)})$	$(^{(1)}X_1^{(2)})$	$(^{(1)}X_1^{(3)})$	$(^{(1)}X_1^{(4)})$	$(^{(1)}\bar{X}_1)$
45	364	366	366	356	363
53	943	949	1034	999	981
61	572	595	511	545	556
69	24	29	21	29	26
77	13	16	14	9	13

Manganese count repeats *Channel number*	$(^{(1)}X_2^{(1)})$	$(^{(1)}X_2^{(2)})$	$(^{(1)}X_2^{(3)})$	$(^{(1)}X_2^{(4)})$	$(^{(1)}\bar{X}_2)$
45	224	234	236	257	238
53	197	169	174	173	178
61	74	77	74	76	75
69	690	724	773	735	731
77	62	47	63	69	60

TABLE AII

AVERAGES EMPLOYED IN AND RESULTS OF LEAST SQUARES FIT

Channel number	$(^{(1)}\bar{X}_1)$	$(^{(1)}\bar{X}_2)$	$(^{(1)}\bar{Y})$	*Weights for first iteration*	*Weights for second iteration*
45	363	238	574	23.96	160
53	981	178	1257	35.45	1580
61	556	75	590	24.29	240
69	26	731	811	28.46	275
77	13	60	73	8.54	17

Results of first iteration: $^{(1)}\hat{\hat{\beta}}_1 = 1.003$ $^{(1)}\hat{\hat{\beta}}_2 = 1.057$

Results of second iteration: $^{(1)}\hat{\hat{\beta}}_1 = 0.948$ $^{(1)}\hat{\hat{\beta}}_2 = 1.059$

channels of data Set I. Table AII shows the pertinent averages used in the least squares fit, along with results of the application of the iterative procedure to data Set 1. It also shows the weights (variances) used on the first iteration (weights obtained by taking the square root of the averages of the mixture counts at the various energy level channels) and those used on the second iteration (weights obtained by estimation). Now, let us consider in detail the iterative estimation procedure used on *data Set 1.*

In order to estimate β initially, we wish to find $^{(1)}\hat{\hat{\beta}}$, where $^{(1)}\hat{\hat{\beta}}$ is the solution to the normal equations

$$(^{(1)}\bar{X})'(^{(1)}D_{\bar{y}})^{-1}(^{(1)}\bar{X})\beta = (^{(1)}\bar{X})'(^{(1)}D_{\bar{y}})^{-1}(^{(1)}\bar{Y}) \tag{1A}$$

where $(^{(1)}\bar{X}) = [(^{(1)}\bar{X}_1)(^{(1)}\bar{X}_2)]$ and $^{(1)}D_{\bar{y}}$ is a diagonal matrix having as its diagonal elements the square root of the *average* mixture counts for channels 45, 53, 61, 69, and 77, respectively, *i.e.*, 23.96, 35.45, 24.29, 28.46, and 8.54. Now, if we let

$$^{(1)}\bar{u}_{i1} = {}^{(1)}\bar{x}_{i1}/{}^{(1)}d_i \text{ and } {}^{(1)}\bar{u}_{i2} = {}^{(1)}\bar{x}_{i2}/{}^{(1)}d_i \tag{2A}$$

where $^{(1)}\bar{x}_{i1}$ = the *i*th element of $^{(1)}\bar{X}_1$; $^{(1)}\bar{x}_{i2}$ = the *i*th element of $^{(1)}\bar{X}_2$; and $^{(1)}d_i$ = the *i*th diagonal element of $^{(1)}D_{\bar{y}}$ ($i = 45, 53, 61, 69, 77$), we can write (1A) as

$$\beta_i \sum_i [^{(1)}\bar{u}_{i1} \cdot {}^{(1)}\bar{x}_{i1}] + \beta_2 \sum_i [^{(1)}\bar{u}_{i1} \cdot {}^{(1)}\bar{x}_{i2}] = \sum_i [^{(1)}\bar{u}_{i1} \cdot {}^{(1)}\bar{y}_i]$$

and (3A)

$$\beta_1 \sum_i [^{(1)}\bar{u}_{i2} \cdot {}^{(1)}\bar{x}_{i1}] + \beta_2 \sum_i [^{(1)}\bar{u}_{i2} \cdot {}^{(1)}\bar{x}_{i2}] = \sum_i [^{(1)}\bar{u}_{i2} \cdot {}^{(1)}\bar{y}_i],$$

where $\sum_i$ denotes a summation over $i = 45, 53, 61, 69, 77$.

From Table AII we obtain the data of Table AIII. Forming the desired sums of products from Table AIII and substituting in (3A), we have the simultaneous equations

$$45{,}413.98\,\beta_1 + 11{,}004.12\,\beta_2 = 57{,}831.36$$

$$11{,}006.58\,\beta_1 + 22{,}689.84\,\beta_2 = 35{,}180.84$$

Solving these equations, we have as initial estimates $^{(1)}\hat{\hat{\beta}}_1 = 1.003$ and $^{(1)}\hat{\hat{\beta}}_2 = 1.057$ (Table AII). We next wish to estimate the weights (variances of errors) for channels 45, 53, 61, 69, and 77 to be used in the second iteration. Consider channel 45 only. We have 4 estimates of the error at channel 45, *i.e.*,

TABLE AIII

INTERMEDIATE ITERATION COMPUTATIONS

Channel number	$(^{(1)}\bar{U}_1)$	$(^{(1)}\bar{X}_1)$	$(^{(1)}\bar{U}_2)$	$(^{(1)}\bar{X}_2)$	$(^{(1)}\bar{Y})$	$(^{(1)}\bar{V}_1)$	$(^{(1)}\bar{V}_2)$
45	15.15	363	9.93	238	574	2.24	1.47
53	27.67	981	5.02	178	1257	0.62	0.11
61	22.89	556	3.09	75	590	2.32	0.31
69	0.91	26	25.69	731	811	0.09	2.66
77	1.52	13	7.03	60	73	0.76	3.53

$$(^{(1)}c_{45}{}^{(1)}) = (^{(1)}y_{45}{}^{(1)}) - (^{(1)}x_{45,1}{}^{(1)})(^{(1)}\hat{\hat{\beta}}_1) - (^{(1)}x_{45,2}{}^{(1)})(^{(1)}\hat{\hat{\beta}}_2)$$

. . .

. . .

. . .

$$(^{(1)}c_{45}{}^{(4)}) = (^{(1)}y_{45}{}^{(4)}) - (^{(1)}x_{45,1}{}^{(4)})(^{(1)}\hat{\hat{\beta}}_1) - (^{(1)}x_{45,2}{}^{(4)})(^{(1)}\hat{\hat{\beta}}_2)$$

where the c's represent errors for channel 45, the y's represent mixture counts at channel 45, the x's represent counts at channel 45 for the proper pure chemical elements, and $^{(1)}\hat{\hat{\beta}}_1$ and $^{(1)}\hat{\hat{\beta}}_2$ are as calculated immediately above. Then, from Tables AI and AII,

$$(^{(1)}c_{45}{}^{(1)}) = 594 - (1.003)(364) - 1.057\,(224) \cong -8$$

$$(^{(1)}c_{45}{}^{(2)}) = 577 - (1.003)(366) - 1.057\,(234) \cong -37$$

$$(^{(1)}c_{45}{}^{(3)}) = 565 - (1.003)(366) - 1.057\,(236) \cong -52$$

$$(^{(1)}c_{45}{}^{(4)}) = 561 - (1.003)(356) - 1.057\,(257) \cong -70$$

Thus, we obtain as an estimate of the variance of the errors at channel 45

$$^{(1)}w_{45} = \frac{\sum_{k=1}^{4}(^{(1)}c_{45}{}^{(k)})^2 - [\sum_{k=1}^{4}(^{(1)}c_{45}{}^{(k)})]^2/4}{3\cdot 4} \tag{4A}$$

or $^{(1)}w_{45} = 162$. In a similar manner, we obtain estimates of the variances of the errors at the other pertinent channels to be

$$^{(1)}w_{53} \cong 1580\,; \quad ^{(1)}w_{61} \cong 240\,; \quad ^{(1)}w_{69} \cong 275\,; \quad ^{(1)}w_{77} \cong 17 \tag{5A}$$

These are shown under the heading "*Weights for second iteration*" in Table AII.

Now, in order to estimate β on the second iteration, we wish to find $^{(1)}\hat{\hat{\beta}}$, where $^{(1)}\hat{\hat{\beta}}$ now is the solution to the *new* set of normal equations

$$(^{(1)}\bar{X})'(^{(1)}W)^{-1}(^{(1)}\bar{X})\beta = (^{(1)}\bar{X})'(^{(1)}W)^{-1}(^{(1)}\bar{Y}) \tag{6A}$$

where $(^{(1)}\bar{X})$ is as given in conjunction with (1A) and $(^{(1)}W)$ is a diagonal matrix having as its diagonal elements the weights (variances) computed in eqns. (4A) and (5A) above. Now, if we let

$$^{(1)}\bar{v}_{i1} = {}^{(1)}\bar{x}_{i1}/{}^{(1)}w_i \quad \text{and} \quad ^{(1)}\bar{v}_{i2} = {}^{(1)}\bar{x}_{i2}/{}^{(1)}w_i$$

where $^{(1)}\bar{x}_{i1}$ and $^{(1)}\bar{x}_{i2}$ are as given in conjunction with eqn. (2A), and $^{(1)}w_i$ is the ith element of $(^{(1)}W)$, we can write eqn. (6A) as

$$\begin{aligned}\beta_1 \sum_i [^{(1)}\bar{v}_{i1}\cdot{}^{(1)}\bar{x}_{i1}] + \beta_2 \sum_i [^{(1)}\bar{v}_{i1}\cdot{}^{(1)}\bar{x}_{i2}] &= \sum_i [^{(1)}\bar{v}_{i1}\cdot{}^{(1)}\bar{y}_i]\\ \beta_1 \sum_i [^{(1)}\bar{v}_{i2}\cdot{}^{(1)}\bar{x}_{i1}] + \beta_2 \sum_i [^{(1)}\bar{v}_{i2}\cdot{}^{(1)}\bar{x}_{i2}] &= \sum_i [^{(1)}\bar{v}_{i2}\cdot{}^{(1)}\bar{y}_i]\end{aligned} \tag{7A}$$

Forming the desired sums of products from Table AIII, substituting in eqn. (7A), and solving the resulting equations, we have as our second iterative estimates $^{(1)}\hat{\hat{\beta}}_1 = 0.948$ and $^{(1)}\hat{\hat{\beta}}_2 = 1.059$ (Table AII). In this case, further iteration will not change these estimates. Hence, we use them as our final estimates of β_1 and β_2 for data Set 1.

Now let us consider the detailed computations involved in the setting of confidence intervals. Suppose we have computed estimates of β_2 from each of 8 sets of data as was done above for data Set 1, and have obtained

$$ {}^{(1)}\hat{\hat{\beta}}_2 = 1.06;\ {}^{(2)}\hat{\hat{\beta}}_2 = 1.09;\ {}^{(3)}\hat{\hat{\beta}}_2 = 1.08;\ {}^{(4)}\hat{\hat{\beta}}_2 = 1.06\ ; $$

$$ {}^{(5)}\hat{\hat{\beta}}_2 = 1.02;\ {}^{(6)}\hat{\hat{\beta}}_2 = 0.95;\ {}^{(7)}\hat{\hat{\beta}}_2 = 1.01;\ {}^{(8)}\hat{\hat{\beta}}_2 = 0.99\ . $$

From these 8 separate estimates of β_2, we have as a final estimate

$$ \hat{\hat{\beta}}_2 = \tfrac{1}{8} \sum_{t=1}^{8} {}^{(t)}\hat{\hat{\beta}}_2 = 1.032 \cong 1.03 $$

We must compute (from WILKS[9])

$$ c_{j\cdot\alpha} = \frac{1}{r-\alpha} \sum_{t=1}^{r-\alpha} [{}^{(t)}\hat{\hat{\beta}}_j - \hat{\hat{\beta}}_j][{}^{(t+\alpha)}\hat{\hat{\beta}}_j - \hat{\hat{\beta}}_j] \quad (\alpha = 0,1,2, \ldots 5) $$

where $c_{j\cdot\alpha}$ represents the covariance between estimates of β_j having lags of α. We compute the pertinent lag covariances in the following manner:

$$ \begin{aligned} c_{2.0} &= \tfrac{1}{8} [(1.06-1.03)^2+\ldots+(0.99-1.03)^2] \\ c_{2.1} &= \tfrac{1}{7} [(1.06-1.03)(1.09-1.03)+\ldots+(1.01-1.03)(0.99-1.03)] \\ c_{2.2} &= \tfrac{1}{6} [(1.06-1.03)(1.08-1.03)+\ldots+(0.95-1.03)(0.99-1.03)] \\ c_{2.3} &= \tfrac{1}{5} [(1.06-1.03)(1.06-1.03)+\ldots+(1.02-1.03)(0.99-1.03)] \\ c_{2.4} &= \tfrac{1}{4} [(1.06-1.03)(1.02-1.03)+\ldots+(1.06-1.03)(0.99-1.03)] \\ c_{2.5} &= \tfrac{1}{3} [(1.06-1.03)(0.95-1.03)+\ldots+(1.08-1.03)(0.99-1.03)] \end{aligned} \tag{8A} $$

From eqns. (8A) we obtain

$$ c_{2.0} = 0.0021;\ c_{2.1} = 0.0013;\ c_{2.2} = 0.0006;\ c_{2.3} = -0.0008; $$
$$ c_{2.4} = -0.0018;\ c_{2.5} = -0.0019\ . $$

Our estimate of the variance of $\hat{\hat{\beta}}_j$ is

$$ \begin{aligned} v(\hat{\hat{\beta}}_j) &= \frac{1}{(r)^2} [rc_{j\cdot 0}+(r-1)c_{j\cdot 1}+\ldots+(r-5)c_{j\cdot 5}] \\ &= \frac{1}{(8)^2} [8(0.0021)+7(0.0013)+\ldots+3(-0.0019)] = 0.000196 \end{aligned} $$

We use as the number of degrees of freedom[10] for setting confidence limits, r_2^* the integer next greater than or equal to

$$ \frac{1}{\dfrac{1}{r} + \dfrac{2}{r^2 c_{2\cdot 0}} \displaystyle\sum_{\alpha=1}^{5} (r-\alpha) c_{2\cdot\alpha}} = \frac{1}{\tfrac{1}{8} + \dfrac{2(-0.0042)}{64(0.0021)}} = 19.1 $$

Thus, we use as our degrees of freedom $r_2^* = 20$. The 99% confidence limits then become $1.032 \pm t_{r_2}{}^*[v(\hat{\hat{\beta}}_2)]^{\frac{1}{2}}$. Thus, we have as our 99% confidence interval

$$ 0.991 \leq \beta_2 \leq 1.073 $$

Confidence limits for β_1 can be established through use of the same procedure.

SUMMARY

Technical methods involved in activation analysis have received widespread publicity during recent years. Even more recently, various statistical techniques have been employed in conjunction with such technical methods in order to provide a better means of estimating the amounts of various pure chemical elements contained in an unknown mixture. In particular, the method of "least squares" has been employed extensively. However, for the most part, usual least squares applications in activation analysis have utilized the ordinary matrix model $Y = X\beta + e$, under the "error" assumptions (*a*) zero means, (*b*) variances proportional to Y and (*c*) zero covariances. In addition to the fact that assumptions (*b*) and (*c*) may lead to erroneous results, previous applications allow only point estimation, with no provision for confidence intervals and tests for model goodness of fit. The present paper is concerned with a feasible iterative estimation procedure which eliminates the necessity for assumptions (*b*) and (*c*), and which allows construction of confidence intervals and a test for model goodness of fit. A numerical example of the application of the technique is included. Further, an indication is given of how the technique can be extended to apply in the case of "restricted" least squares (quadratic programming).

RÉSUMÉ

Divers procédés statistiques sont actuellement employés en relation avec des méthodes techniques, afin de permettre une meilleure estimation des teneurs de divers éléments chimiques dans un mélange inconnu; on utilise en particulier la méthode des "least squares". Un exemple numérique d'application de la technique est donné.

ZUSAMMENFASSUNG

Bei der Neutronenaktivierungsanalyse werden gegenwärtig verschiedene statistische Verfahren verwendet, in Verbindung mit solchen Methoden, die zur besseren Berechnung der Gehalte von verschiedenen Elementen in Mischungen dienen. Es wird besonders die Methode der kleinsten Quadrate benutzt. Die vorliegende Arbeit beschäftigt sich mit iterativen Abschätzungen, die Vorteile bieten und u.a. die Schaffung von Vertrauensbereichen erlauben. Es werden ein numerisches Beispiel für die Anwendung dieser Technik und weitere Möglichkeiten des Verfahrens angegeben.

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POTENTIOMETRIC TITRATIONS WITH ION-EXCHANGING MEMBRANE ELECTRODES

PART I. THEORETICAL ASPECTS OF SIMPLE PRECIPITATION TITRATIONS

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As regards its possible practical applications the membrane electrode can be compared with the glass electrode. On one hand, ratios of ion activities can be measured, but reliable results are only to be achieved for simple solutions. With complex solutions the insufficient specificity of the membrane for the ions to be measured causes trouble. However, it is possible to use a membrane electrode as indicating electrode with potentiometric titrations as will be discussed in this article. For this application the specificity of the membrane for some kind of ion is not so essential.

The membranes that can be used in electrodes can be divided according to the following properties:

(*1*) *Composition*: precipitate, synthetic or natural ion-exchanging material.

(*2*) *Homogeneous/heterogeneous*: without or with indifferent binder.

(*3*) *Porous/permselective*: permeable for anions and cations, or only for one of these classes of ions.

Several authors have described attempts to indicate end-points in potentiometric titrations with the aid of membrane electrodes, several types of membranes being used. SINHA[1] titrated an acid, making use of a heterogeneous, permselective cation-exchanging membrane. Chloride or sulphate were also titrated with solutions of silver(I) or barium(II) respectively with the aid of a heterogeneous, permselective anion-exchanging membrane. PARSONS[2] used heterogeneous permselective ion-exchanging electrodes for the titration of barium(II) with sulphate solution. FISCHER AND BABCOCK[3] performed the same titrations with the aid of heterogeneous membranes consisting of paraffin as binder and barium sulphate as precipitate. BERSIER *et al.*[4] used a film of alumina for the precipitation titrations of several silver and barium salts. In some experiments a constant current was sent through the membrane during the titration.

GEYER AND NIKLAS[5] performed acidimetric titrations with homogeneous permselective ion-exchanging membranes of differing compositions. With a membrane prepared from anthranilic acid, resorcinol and formaldehyde good results were obtained. Apart from the normal potentiometric method the titrations were also carried out while passing a constant current through 2 membrane electrodes. In a recent publication GEYER *et al.*[6] have extended their investigations concerning acidimetric titrations and mentioned some attempts at precipitation and oxidation–reduction titrations. Methods of titrating silicofluoride with potassium ions, and potassium with tetraphenylborate ion have been described by the same authors[7,8].

Basu[9] performed precipitation titrations of several silver salts, utilizing permselective, heterogeneous ion-exchanging membrane electrodes.

Materova and Yurchenko[10] also used this type of electrode for acidimetric titrations and for the precipitation of several silver halides and barium sulphate. Nakagaki, Koga and Noguchi[11] performed similar precipitation titrations; in addition to the customary ion-exchanging membranes a collodion membrane was used, that was prepared in a specific manner to obtain permselective properties. These authors also derived theoretically a number of titration curves; after some simplifying assumptions had been introduced, the membrane potentials were calculated making use of Henderson's formula for the diffusion potential. The ions present in the solution to be titrated and in the reagent were distinguished according to their permeability through the membrane. Three classes of permeability were introduced: good, moderate and not permeable.

Generally it can be said that better results were obtained for acidimetric titrations than for the precipitation titrations. Very few data are available on the accuracy and precision of the titrations. Especially with the precipitation titrations the evaluation of the end-point of the titration is often a source of considerable error. In the present paper, a more general method is used to calculate potentiometric titration curves for precipitation titrations.

In contrast to the results of Nakagaki *et al.* several important parameters, such as the diffusion coefficients of the ions present in the solution to be titrated and in the reagent and the capacity of the membrane, have been specified and introduced into the calculations. The membrane is supposed to consist of permselective ion-exchanging material.

THEORY

To derive a titration curve it is necessary to calculate the membrane potential for the case that the solution on one side of the membrane (the reference solution) is of constant composition during the titration, while the solution at the other side of the membrane changes quantitatively as well as qualitatively on addition of the reagent. Figure 1 shows a block diagram of the titration system.

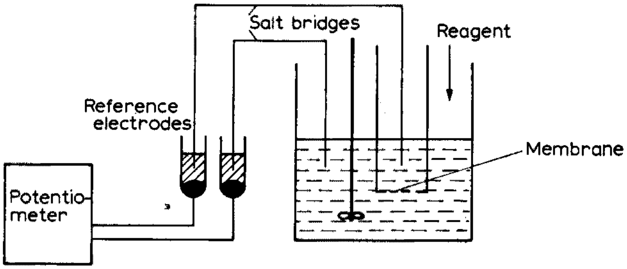

Fig. 1. Block diagram of the titration system.

The theory concerning membrane potentials of ion-exchanging membranes has been developed by Teorell[12] and Meyer and Sievers[13], making use of the so-called "fixed-charge" model. The ion-exchanging material is supposed to consist of a flexible random network (the matrix) and irregularly branched pores, that connect the 2 sides of the membrane (Fig. 2).

With the matrix are connected fixed charges, negative in cation- and positive in anion-exchanging material. The pores are filled with solution. The average diameter of the pores is small with respect to the expansion of the Debye–Hückel sphere of the ions in the solution. As a result the solution in the pores is practically homogeneous. With the generally used permselective membranes the concentration of the fixed charges in the membrane (the capacity) is large with respect to the concentration of the solutions outside the membrane. The membrane as a whole is electrically neutral and it follows that the concentration of the ions with the same charge sign as the fixed charges (the co-ions) in the pore solution is much smaller than the con-

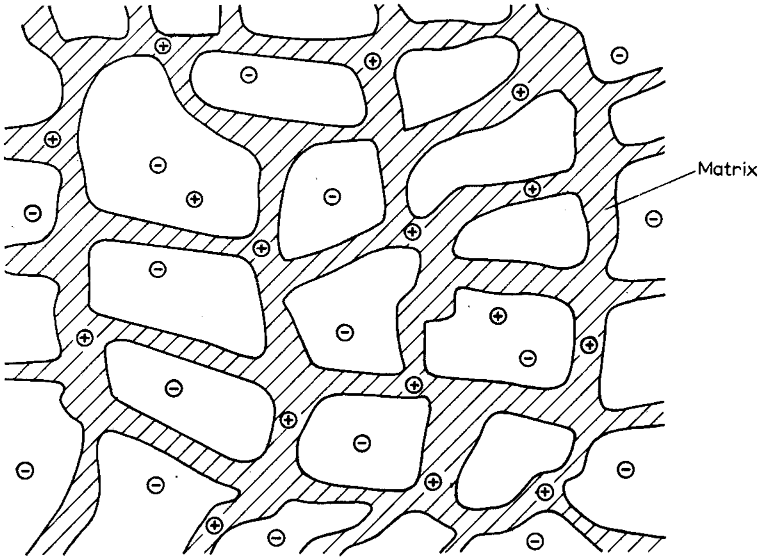

Fig. 2. Structure of an anion-exchanging resin. Matrix with fixed positive charges; in the pore solution cations as co-ions and anions as counter-ions.

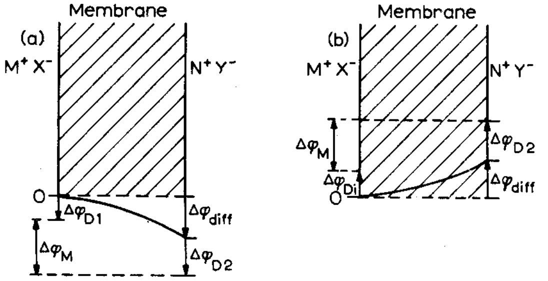

Fig. 3. Schematic presentation of the 3 potential jumps of which the membrane potential consists. The solution of M^+X^- is supposed to be of greater concentration than the solution of N^+Y^-, while the ions M^+ and X^- have greater diffusion coefficients than the ions N^+ and Y^-. $\Delta\varphi_{D1}$ and $\Delta\varphi_{D2}$ = Donnan potentials; $\Delta\varphi_{\text{diff}}$ = diffusion potential; $\Delta\varphi_M$ = membrane potential. (a) anion-exchanging and (b) cation-exchanging membrane.

centration of the ions of opposite charge sign (the counter-ions). The resulting effect is a much greater permeability of the membrane for the counter-ions than for the co-ions. The membrane is permselective for the counter-ions, provided that there is no special interaction of the membrane material with the ions.

According to the theory of TEORELL and MEYER AND SIEVERS, the membrane potential is supposed to consist of 3 parts, 2 potential jumps at the boundaries membrane/solution and a diffusion potential in the membrane itself (see Fig. 3). The phase boundary potentials (often called Donnan potentials) are considered as equilibrium potentials. The Donnan potentials originate in the diffusion of a small fraction of the counter-ions out of the pore solution into the solution outside the membrane. There results a depletion of counter-ions at the membrane surface, which disturbs locally the electroneutrality and a difference in electric potential between the solutions inside and outside the membrane is generated. By the action of the Donnan potential further diffusion of counter-ions to the solution outside the membrane is prevented, as well as the uptake of co-ions by the membrane.

The Donnan potentials can be calculated with the aid of the formula:

$$\sum_k z_k c_k E_D^{-z_k} = -wX \tag{1}$$

where z_k = valence of ions with charge k; c_k = concentration of these ions in the solution outside the membrane; E_D = Donnan potential; $w = +1$ for anion-exchanging and -1 for cation-exchanging material; X = capacity of the membrane.

In contrast to the Donnan potentials, the diffusion potential in the inside of the membrane is not an equilibrium potential. As a rule the diffusion potential is generated by the different velocities with which the ions present at the surfaces of the membrane will diffuse through the membrane (multi-ionic diffusion potential). Of course, with a sufficiently high value of the capacity of the membrane only the diffusion of the counter-ions needs to be considered. For the calculation of the diffusion potential it is necessary to solve the flux equations of the different ions. After introducing the following assumptions:

(*1*) no convection of solution through the membrane,

(*2*) constant values for the diffusion coefficients, the activity coefficients and the capacity throughout the membrane,

(*3*) the rate-determining step is the diffusion through the membrane,

the most general flux equation for an ion through a membrane is reduced to the well-known Nernst–Planck equation:

$$J_i = -D_i\left(\operatorname{grad} C_i + z_i C_i \cdot \frac{F}{RT} \operatorname{grad} \varphi\right) \tag{2}$$

where J_i = flux of ion i; D_i = diffusion coefficient of ion i; grad C_i = gradient of the concentration of ion i inside the membrane; z_i = valence of ion i; grad φ = gradient of the potential φ inside the membrane; F, R and T have the usual meaning.

The solution of the simplified flux equations is still a complicated and laborious matter. SCHLÖGL[14] has given a general scheme for such calculations, but neglecting the activity coefficients. For the practical application of the method it is necessary to classify the ionic species present in valence groups with charge z_k. An ion of species i, belonging to valence group k, is also specified by the subscript j within this group.

For instance, with the 3 electrolytes $CaCl_2$, KCl and Na_2SO_4, the valence groups are: $z_1 = +2\,(Ca^{2+})$ $z_2 = +1\,(K^+$ and $Na^+)$ $z_3 = -1\,(Cl^-)$ $z_4 = -2\,(SO_4^{2-})$

For the given example the group index k is 1, 2, 3 or 4. The individual ionic species within the groups can be identified by the notation jk ($Ca^{2+} = 11$, $K^+ = 12$, $Na^+ = 22$ and so on).

Summarizing, the following calculations must be made. First the Donnan potentials are calculated by means of eqn. (1). Next the concentrations of the ions at the surfaces of the membrane are calculated, making use of the formulae:

$$C_{1.jk} = c_{1.jk} \cdot E_{D1}^{-z_k} \quad \text{and} \quad C_{2.jk} = c_{2.jk} \cdot E_{D2}^{-z_k} \tag{3a, b}$$

where c_{jk} = concentration of the ionic species jk in the solution outside the membrane; C_{jk} = concentration of this ion at the surface of the membrane; the subscripts 1 and 2 are used to indicate the two sides of the membrane. The concentrations C_{jk} are used as the boundary conditions for the integration of the flux equations.

For the integration are also needed the group concentrations C_k and the total ion concentration C, defined by:

$$C_k = \sum_j C_{jk} \quad \text{and} \quad C = \sum_k C_k \tag{4a, b}$$

(the subscripts 1 or 2 are eventually added for the two sides of the membrane).

The following step is the calculation of the fluxes of the individual ions present as a function of the intramembrane potential E_{im}. In this respect it must be noted that for the calculations the electrical potential differences $\Delta\varphi$ of Fig. 3 must be normalized according to

$$\ln E = \frac{F\Delta\varphi}{RT} \tag{5}$$

This holds for the intramembrane potential E_{im}, as well as for the Donnan potentials E_{D1} and E_{D2}, defined by eqn. (1). Moreover, the normalization of the electric potential is carried out in such a way that the potential at the inside of the membrane at side 1 is zero. The flux equations for the individual ionic species are found by integration across the membrane:

$$J_{jk} = -\frac{D_{jk}}{d} \cdot \frac{C_{2.jk} \cdot E_{im}^{z_k} - C_{1.jk}}{C_{2.k} \cdot E_{im}^{z_k} - C_{1.k}} \cdot L_k (1/z_k - q_1) \ldots (1/z_k - q_{n-1}) \cdot (C_2 - C_1 - wX \cdot \ln E_{im}) \tag{6}$$

where d = thickness of the membrane and L_k is a function, related to the valence of the group, the value of which is given by:

$$1/L_k = \prod_{\substack{i=1\ldots n \\ i \neq k}} (1/z_k - 1/z_i) \tag{7}$$

The parameters $q_1, q_2 \ldots q_{n-1}$ are obtained from the relation:

$$\ln E_{im} = q \cdot \ln \frac{\sum_k z_k C_{1.k}/(q - 1/z_k)}{\sum_k z_k C_{2.k}/(q - 1/z_k)} \tag{8}$$

which can also be written as:

$$\ln E_{tm} = q \cdot \ln \frac{(q-Q_{1\cdot 1}) \ldots (q-Q_{1\cdot n-1})}{(q-Q_{2\cdot 1}) \ldots (q-Q_{2\cdot n-1})} \tag{9}$$

The characteristic roots Q can be found by solving the equations:

$$\sum_k z_k C_{1\cdot k}/(q-1/z_k) = 0 \quad \text{and} \quad \sum_k z_k C_{2\cdot k}/(q-1/z_k) = 0 \tag{10}$$

The most convenient method is to tabulate $\ln E_{tm}$ as a function of q. For the case of n groups one value of $\ln E_{tm}$ corresponds to $n-1$ values of q. The corresponding values of $\ln E_{tm}$ and q are used for solving eqn. (6). With the aid of the data obtained in this manner, the current–voltage characteristic of the membrane in the specified solutions can be calculated. The diffusion potential can be found from the current–voltage characteristic of the membrane, namely as the intramembrane potential, corresponding to the limiting case of zero electric current. Eventually the membrane potential can be found by coupling the diffusion potential to the Donnan potentials for the given case.

Finally it must be remarked that several theories concerning membrane phenomena have been developed besides the theory of TEORELL and MEYER AND SIEVERS. Generally speaking these treatments are based on the principles of thermodynamics of irreversible processes or on the theory of absolute reaction rates. Although these theories have proved their value and can be considered as being more rigorous and realistic than the treatment of TEORELL and MEYER AND SIEVERS in several respects, the latter has been used for our calculations because the model underlying the theory is simple and straightforward, and because the accuracy of the calculated membrane potentials was thought to be quite adequate for the derivation of potentiometric titration curves.

For a summary of the theory of the membrane potentials the monographs of HELFFERICH[15], SCHLÖGL[16] and TUWINER[17] and a recent review of LAKSHMINARAYANAIAH[18] should be consulted; the articles of LÄUGER AND KUHN are also of interest[19,20].

CALCULATIONS

At present the work has been confined to the calculation of the potentiometric titration curves of the following precipitation reactions:

$$N^+Y^- + A^+B^- \rightarrow AY\downarrow + N^+B^-$$
$$N^+Y^- + A^+B^- \rightarrow NB\downarrow + A^+Y^-$$

In both cases a solution of M^+X^- was used as the reference solution.

It is supposed that the reference solution is not contaminated by the solution at the titration side of the membrane. As a result the Donnan potential E_{D1} at the side of the reference solution (subscript 1) remains constant during the titration. Of course this is not the case for the diffusion potential E_{diff} and the Donnan potential E_{D2} at the titration side of the membrane (subscript 2), because the composition of the titrated solution changes continuously on addition of the reagent solution (namely precipitation, dilution of the volume and addition of reagent species).

As the calculations are very time-consuming, especially the calculation of the diffusion potentials, it seemed advantageous to make use of a computer. The programming was made in Algol 60, following the scheme of SCHLÖGL as explained in the preceding section.

In the designed programme the reagent solution is added to the solution to be titrated in equal increments. The number of steps in which the reagent solution is added before the reaction is completed, can be chosen. After the equivalence point the membrane potential is calculated automatically for the same number of increments. In this manner a clear picture is obtained of the course of the titration curve before and after the equivalence point. The following data are introduced in the calculations:

(*1*) the concentration of the reference solution M^+X^-,
(*2*) the volume of the solution to be titrated,
(*3*) the initial concentration of N^+Y^- in the solution to be titrated,
(*4*) the concentration of the titrant A^+B^-,
(*5*) the capacity of the membrane,
(*6*) the diffusion coefficients of the ions present in the solutions,
(*7*) the thickness of the membrane,
(*8*) the needed values of the factor L_k.

For each addition of reagent solution the following computations are carried out successively.

(*a*) The concentrations $c_{2 \cdot jk}$ of all ionic species present in the solution at the titration side of the membrane.

(*b*) the Donnan potentials E_{D1} and E_{D2} by means of eqn. (1).

(*c*) The concentrations of the ionic species at the surfaces of the membrane $C_{1 \cdot jk}$ and $C_{2 \cdot jk}$ by means of eqn. (3).

(*d*) The corresponding group concentrations ($C_{1 \cdot k}$ and $C_{2 \cdot k}$) and the total ion concentrations (C_1 and C_2) with the aid of eqn. (4).

(*e*) The characteristic roots $Q_{1 \cdot 1}$ and $Q_{2 \cdot 1}$ for respectively the reference and the titration side of the membrane by means of eqn. (10).

(*f*) Next an interval is selected outside the closed intervals ($Q_{1 \cdot 1}$, $Q_{2 \cdot 1}$) and ($Q_{2 \cdot 1}$, $Q_{1 \cdot 1}$). For 3 distinct values of q in this interval (namely the values at the 2 end-points and at the center), the corresponding values of $\ln E_{im}$ and E_{im} are computed, using eqn. (9). For these corresponding values of q, $\ln E_{im}$ and E_{im} the flux of each ionic species through the membrane is calculated, making use of eqn. (6). Then it is verified whether the total flux changes its sign in the interval used. When this is not the case, a new interval is selected and the whole procedure as previously described is repeated until an interval is found in which the change of sign sought for occurs (the diffusion potential to be determined is a special case of the intramembrane potential, namely the case of zero electric current and also zero total flux through the membrane; an interval in which the total flux changes its sign must also contain the value of E_{im} for the case of zero total flux).

(*g*) When this interval is found a more exact value for E_{diff} is obtained by means of bisection and interpolation, following the same procedure as described in the preceding section. In this way the error in the calculated value of E_{diff} as related to the true value becomes progressively smaller; the procedure is continued until the obtained value of E_{diff} changes only very little.

(*h*) Lastly, the obtained values of E_{D1}, E_{D2} and E_{diff} are combined to form the

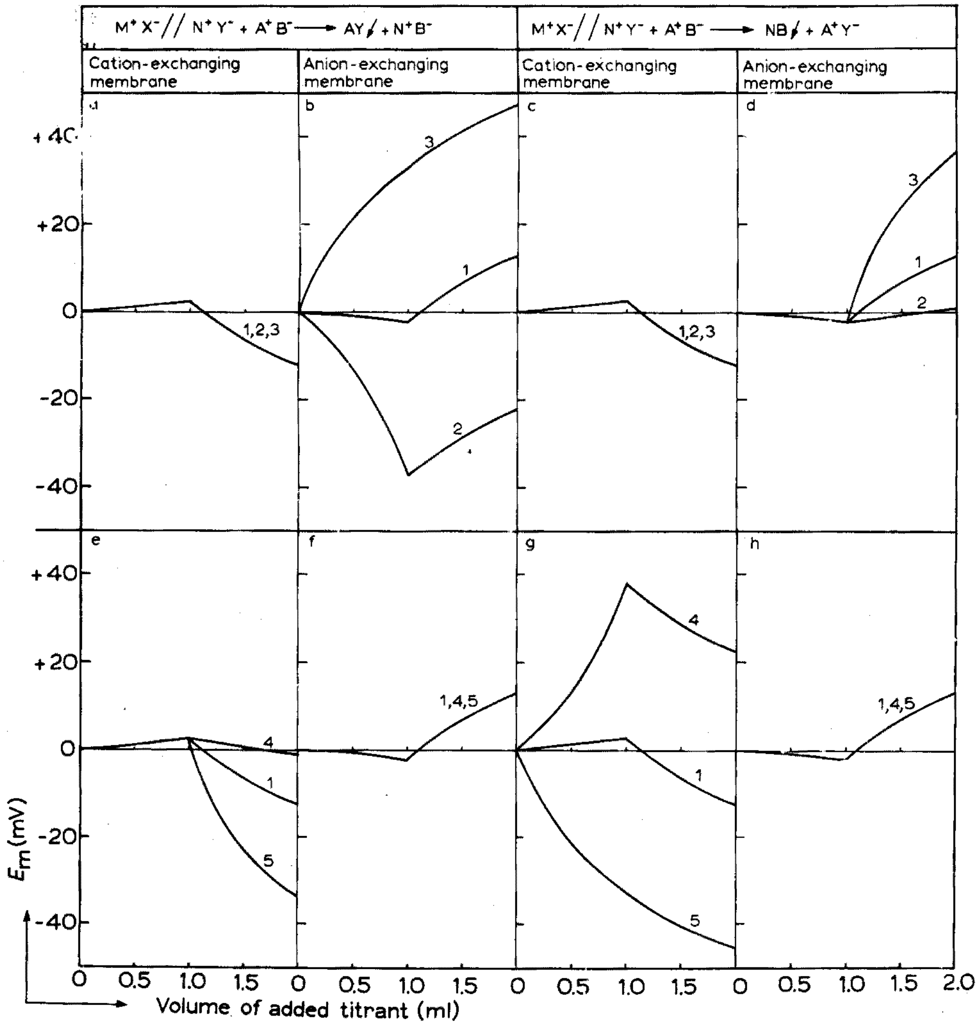

Fig. 4. Potentiometric titration curves for the titration of 10 ml of a 0.1 M solution of N^+Y^- with 1 M solution of A^+B^-; 0.1 M solution of M^+X^- as reference solution; the reagent is added in volumes of 0.1 ml. Capacity of the membrane 1 meq/cm³. The membrane potentials are calculated as the difference in potential of the solution to be titrated with respect to the potential of the reference solution. Values of the diffusion coefficients (in units of $1 \cdot 10^{-6}$ cm²/sec):

	M^+	N^+	A^+	X^-	Y^-	B^-	ratio D_{Y^-}/D_{B^-}	ratio D_{N^+}/D_{A^+}
curve 1	4	4	4	6	6	6	1	1
curve 2	4	4	4	6	6	1.5	4	1
curve 3	4	4	4	1.5	1.5	6	0.25	1
curve 4	4	4	1	6	6	6	1	4
curve 5	1	1	4	6	6	6	1	0.25

a–d: variation of the diffusion coefficients of the anions.

e–h: variation of the diffusion coefficients of the cations.

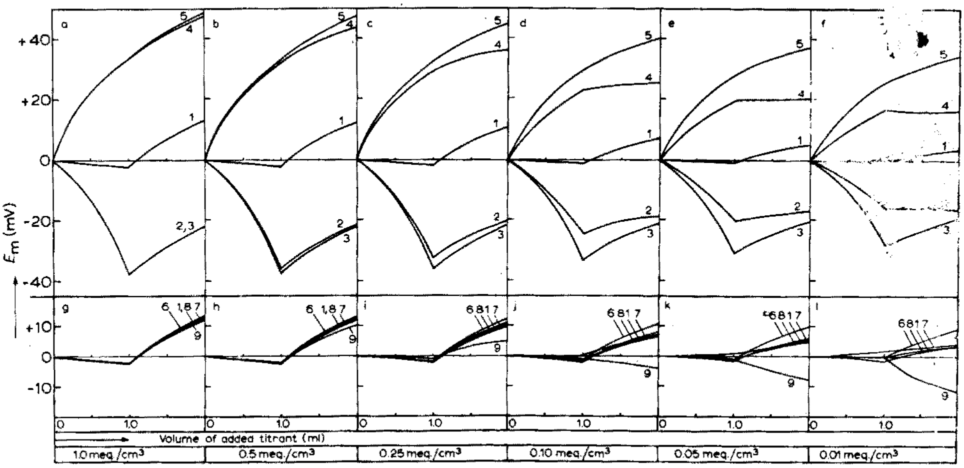

Fig. 5. Potentiometric titration curves: influence of the capacity of the membrane, calculated for an anion-exchanging membrane (case Fig. 4b) and for different ratios of the diffusion coefficients of the ions. Data similar to Fig. 4.
Values of the diffusion coefficients (in units of $1 \cdot 10^{-6}$ cm^2/sec):

a–f: Influence of the counter-ions

	M^+	N^+	A^+	X^-	Y^-	B^-
curve 1	4	4	4	6	6	6
curve 2	4	4	4	6	6	1.5
curve 3	4	4	4	24	24	6
curve 4	4	4	4	1.5	1.5	6
curve 5	4	4	4	6	6	24
g–l: Influence of the co-ions						
curve 1	4	4	4	6	6	6
curve 6	4	4	1	6	6	6
curve 7	16	16	4	6	6	6
curve 8	1	1	4	6	6	6
curve 9	4	4	16	6	6	6

membrane potential.

Copies of the Algol 60 programme are available from the authors on request.

The titration curves that were calculated are illustrated in Figs. 4–7. In Fig. 4 the titration curves are given for the possible cases, varying the values of the diffusion coefficients. In Fig. 5 the influence of the capacity of the membrane on the form of the titration curves is shown for a single case. In Fig. 6 the concentrations of the solutions to be titrated and of the reagent are varied for two fixed capacities of the membrane and for several ratios of diffusion coefficients. Finally, in Fig. 7 the influence of the type of the reference solution is shown.

DISCUSSION

Referring to Fig. 4 it is evident that the values of the diffusion coefficients of the counter-ions can exert a large influence on the shape of the titration curve. On the contrary the values of the diffusion coefficients of the co-ions have only a very limited effect, at least when the capacity of the membrane is large (Fig. 4a,c,f,h); this is true

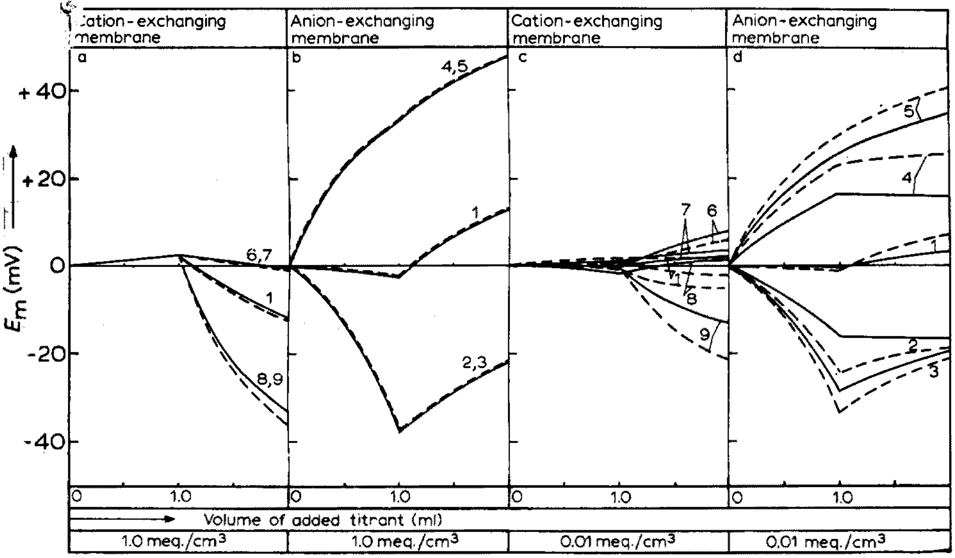

Fig. 6. Potentiometric titration curves: influence of the concentration of the solution to be titrated and of the reagent, calculated for an anion-exchanging membrane (b and d, case Fig. 4b) and for a cation-exchanging membrane (a and c, case Fig. 4e). The numbers of the titration curves refer to the same combinations of diffusion coefficients as given in Fig. 5.
——— 0.1 M soln. of N^+Y^- titrated with 1 M solution of A^+B^-.
- - - - - - - - 0.01 M soln. of N^+Y^- titrated with 0.1 M solution of A^+B^-.

when the capacity is greater than 5 times the concentrations of the surrounding solutions.

When the differences between the diffusion coefficients of the ions are small, the membrane potential changes little during the titration. In that case it does not matter much whether one uses an anion- or a cation-exchanging membrane (Fig. 4a,f or c,h). However, when the diffusion potential contributes notably to the membrane potential the choice of the type of ion-exchanging material becomes decisive for the successful application of the method. The most abrupt changes in the titration curves in the end-point are obtained when the relative changes in the fluxes of the ions in this point are greatest. Generally membranes of high capacity are used so that only the fluxes of the counter-ions are of interest. With definite values of the capacity and the concentrations, the decisive parameter is the ratio between the diffusion coefficient of the ion to be precipitated and the ion of the same charge sign added with the reagent.

A sharp end-point is obtained with the precipitation of a counter-ion, when the diffusion coefficient of this ion is larger than the diffusion coefficient of the counter-ion to be added with the reagent (Fig. 4b,g). The opposite holds for the precipitation of a co-ion (Fig. 4d,e). This rule becomes clear when the changes of the concentrations of the different ions during the titration are examined (Fig. 8); in this respect it must be remembered that the flux of an ion is principally defined by the value of the diffusion coefficient and the concentration gradient.

In Fig. 5 the influence of the capacity of the membrane on the shape of the titration curve can be seen. When the capacity becomes smaller, the Donnan poten-

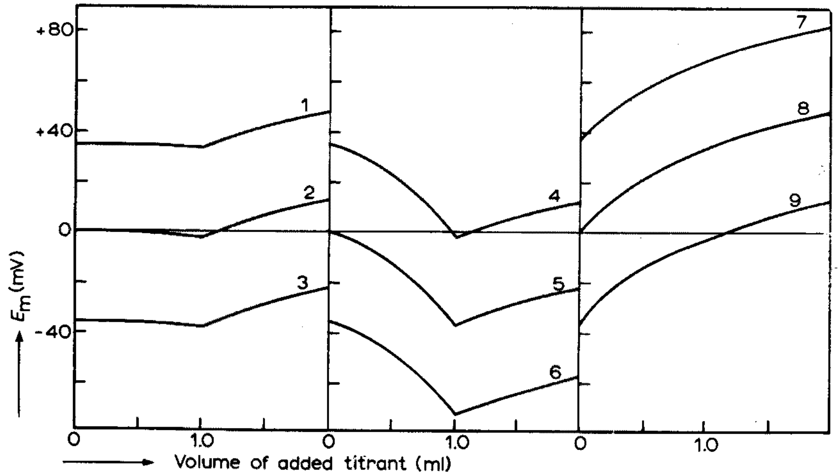

Fig. 7. Potentiometric titration curves: influence of the diffusion coefficient of the counter-ion of the reference solution M^+X^-, calculated for an anion-exchanging membrane (case Fig. 4b). Capacity of the membrane 1 meq/cm^3, further data similar to Fig. 4.
Values of the diffusion coefficients (in units of $1 \cdot 10^{-6}$ cm^2/sec):

	M^+	N^+	A^+	X^-	Y^-	B^-
curve 1	4	4	4	1.5	6	6
curve 2	4	4	4	6	6	6
curve 3	4	4	4	24	6	6
curve 4	4	4	4	1.5	6	1.5
curve 5	4	4	4	6	6	1.5
curve 6	4	4	4	24	6	1.5
curve 7	4	4	4	1.5	6	24
curve 8	4	4	4	6	6	24
curve 9	4	4	4	24	6	24

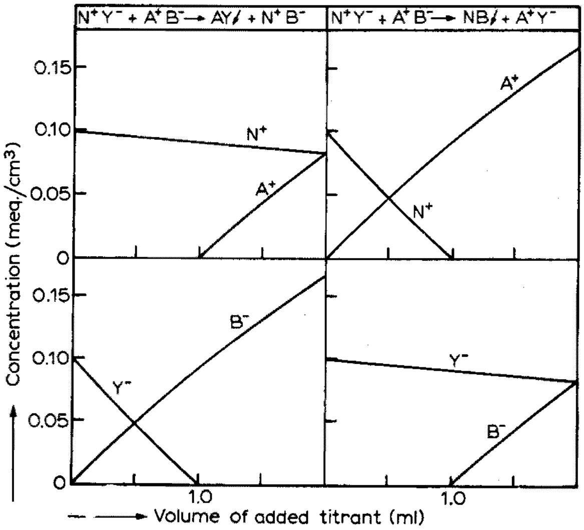

Fig. 8. Changes of the concentrations of the ions in the solution during the titration, calculated for the titration of 10 ml of 0.1 *M* solution of N^+Y^-, with 1 *M* solution of A^+B^- as titrant.

tials diminish and also the permselectivity of the membrane. In this respect 2 limiting cases can be distinguished: with high values of the membrane capacity the changes of the diffusion potential are only determined by the values of the diffusion coefficients of the counter-ions (Fig. 5a,g); on the contrary with low values of the membrane capacity with respect to the concentrations of the surrounding solutions, the diffusion potential is determined by the diffusion coefficients of all ions present in the solutions. Moreover in the last-mentioned case the Donnan potentials are small and the diffusion potential constitutes nearly the whole membrane potential (Fig. 5j,k,l; compare with curves a of Fig. 5, in which the diffusion potentials are negligibly small and as a result the membrane potentials in these curves are almost entirely determined by the Donnan potentials).

The following conclusions can be drawn from Fig. 6. With membranes of large capacity the form of the titration curves and the values of the membrane potentials are independent of the concentrations of the solutions to be titrated, provided that the concentrations of the reagent solutions are altered in the same ratio (Fig. 6a,b). The same behaviour is observed for the absolute values of the diffusion coefficients of the ions, provided that the ratio between the diffusion coefficient of the ion to be precipitated and the diffusion coefficient of the replacing ion added with the reagent is not altered (Fig. 6a: compare curves 6 with 7 and 8 with 9; Fig. 6b: compare curves 2 with 3 and 4 with 5). For membranes with a low capacity neither the first nor the second conclusion can be drawn. On the contrary, there is a definite dependence on the concentrations of the solutions to be titrated (Fig. 6c,d), as well as on the absolute values of the diffusion coefficients (Fig. 6c: compare curves 6 with 7 and 8 with 9; Fig. 6d: compare curves 2 with 3 and 4 with 5). The theoretical explanation must be sought in the fact that with low capacities the membranes are no longer permselective.

Referring to Fig. 7 it can be concluded that the value of the diffusion coefficient of the counter-ions of the reference solution is not important as regards the shape of the titration curve generally; the whole titration curve is moved to another potential level. This rule holds only for high capacities of the membrane. As regards the influence of the value of the diffusion coefficient of the co-ion present in the reference solution, it can be mentioned that no differences in the membrane potential greater than 1 mV were calculated, when the diffusion coefficient was varied over a range of $1–16 \cdot 10^{-6}$ cm^2/sec, further data being the same as mentioned in Fig. 7.

Generally speaking the titration curves calculated by us are in good agreement with the calculations of NAKAGAKI *et al.*[11], at least as regards the shape; absolute values of the membrane potential were not given by these authors. This agreement was only to be expected because the application of Henderson's formula does not give large errors when only $+1$ and -1 charged ions are present.

FUTURE INVESTIGATIONS

In testing the theory, precipitation titrations of several silver salts gave results that are in good agreement with the theory. The theory also seems to hold for acidimetric titrations of strong acids with strong bases, as would be expected for ion-exchanging membranes with strong acidic and basic fixed groups. These studies will be communicated shortly.

The calculation of the titration curves will be extended to cases in which ions of higher valencies may also be present, as well as to acidimetric, complex formation and oxidation–reduction titrations. Further calculations will be made for potentiometric titrations with one membrane- and one reference-electrode with a constant electric current and for the cases of 2 membrane electrodes with zero current or with a constant electric current. Eventually, the theory will be checked for other types of membrane electrodes, *e.g.* membranes consisting of binder material and some kind of precipitate.

The authors gratefully acknowledge the valuable assistance of Drs. W. T. DE VRIES of this Laboratory, who carried out the programming of the calculations; thanks are also due to the Mathematical Centre at Amsterdam for making available the computer.

SUMMARY

Titration curves were derived for potentiometric titrations with zero electric current, utilizing a membrane electrode as indicating electrode, the membrane consisting of permselective, ion-exchanging material. As a first example, calculations were made for simple precipitation titrations with only +1 or −1 charged ions present in the solution to be titrated and in the reagent. For the calculations of the membrane potentials the theory of TEORELL and MEYER AND SIEVERS was used. The influence of several parameters, such as the diffusion coefficients of the ions, the capacity of the membrane and the concentration of the solutions, was examined.

RÉSUMÉ

Des courbes de titrage pour des titrages potentiométriques à intensité de courant nulle, utilisant une électrode de membrane pour l'indication, ont été calculées. La membrane permsélective se composait de matériel échangeurs d'ions. En premier lieu nous avons calculé des courbes de titrage pour quelques titrages de précipitation simples; nous avons supposé qu'il n'y a que des ions de charge +1 ou −1 présents dans les solutions. Pour les calculations nous avons employé la théorie de TEORELL et MEYER ET SIEVERS. L'influence des quelques paramètres, tels que les coefficients de diffusion des ions, la capacité de la membrane et la concentration des solutions, a été étudiée.

ZUSAMMENFASSUNG

Es wurden Titrationskurven berechnet für die potentiometrische Titration mit Stromstärke Null, wobei eine Membranelektrode als Indikatorelektrode verwendet wurde. Die Membrane wurden aus permselektivem, ionenaustauschendem Material hergestellt. An erster Stelle wurden Titrationskurven für einfache Fällungstitrationen berechnet, wobei nur +1 und −1 wertige Ionen anwesend sind. Für die Berechnung der Membranpotentialen wurden die Theorien von TEORELL und MEYER UND SIEVERS benutzt. Der Einfluss verschiedener Parameter, z.B. die Kapazität der Membrane, die Diffusionskoeffizienten der Ionen und die Konzentration der Lösungen wurde untersucht.

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PREPARATIVE, INFRARED AND THERMOGRAVIMETRIC STUDIES OF THREE SCANDIUM 8-HYDROXYQUINOLINATES

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8-Acetoxyquinoline can be readily hydrolysed to produce 8-hydroxyquinoline and thus precipitate metal ions from homogeneous solution[1-5]. In the present work a study of scandium was undertaken, resulting in the preparation of 3 scandium 8-hydroxyquinolinates. Two of the compounds were prepared from homogeneous solution and the third by a solid-phase reaction.

In the first scandium is precipitated at pH 8.8 as a bright-yellow compound of composition $(ScQ_3)_2.HQ$, where $Q = C_9H_6NO$. A second scandium compound was precipitated at pH 6.5 as a lemon-yellow compound of composition $ScQ_3.HQ$. A third scandium 8-hydroxyquinolinate was obtained by a solid-phase reaction between the lemon-yellow compound obtained at pH 6.5 and 8-hydroxyquinoline.

As a continuation of the earlier parts of the series on metal 8-hydroxyquinolinates[6], the infrared spectra of the 3 scandium chelates were examined in the range 4000–400 cm^{-1}.

The thermogravimetric analyses of the chelates have also been examined.

EXPERIMENTAL

Reagents

Scandium. 125 mg of spectroscopically pure Sc_2O_3 (Johnson, Matthey & Co. Ltd.) was dissolved in 25 ml of 72% perchloric acid with gentle heating until all the cloudiness had disappeared. The solution was evaporated to incipient dryness and the residue dissolved in 200 ml of distilled water. The solution was standardised by precipitation of scandium with ammonia solution, followed by ignition to Sc_2O_3. The solution contained 4.076 mg of Sc^{3+} in 10 ml solution.

8-Acetoxyquinoline. A solution of the reagent (supplied by Burdick and Jackson Laboratories, Muskegan, Michigan, U.S.A.) was prepared in acetone, as required.

8-Hydroxyquinoline. 200 mg of the reagent (Laboratory Grade with no further purification) was dissolved in 2 ml of glacial acetic acid and diluted to 100 ml with distilled water.

Preliminary investigations

(a) Precipitation of scandium 8-hydroxyquinolinates from homogeneous solution.

A suitable temperature range for the reaction was found to be 65–70°. Two concentrations of 8-acetoxyquinoline were used. When twice the stoichiometric amount of 8-acetoxyquinoline was used (assuming initially the precipitate to be $ScQ_3.HQ$ as formed in the conventional procedure) to precipitate 4.08 mg of scandium(III), no precipitate was formed below pH 7.0, but a finely divided precipitate was formed quantitatively at pH 8.8.

On the other hand, when 10 times the stoichiometric amount of 8-acetoxyquinoline was used (again assuming a final precipitate of formula $ScQ_3.HQ$), quantitative precipitation of a lemon-yellow compound occurred at pH 6.5.

The precipitates obtained by the 2 procedures were compared with that obtained by conventional means[7] at pH 7.5 and were found to possess much better physical characteristics. In both cases precipitation was quantitative after heating for 3 h at 65–70°.

(b) Preparation of scandium 8-hydroxyquinolinate by solid-phase reaction. It was found that the lemon-yellow scandium 8-hydroxyquinolinate, prepared by the conventional method[7] or as indicated in this paper from homogeneous solution and to which the formula $ScQ_3.HQ$ has been given, reacts with 8-hydroxyquinoline in the solid phase to produce a new compound, an orange scandium 8-hydroxyquinolinate of composition $(ScQ_3)_2.3HQ$. The optimum temperature was found to be 100–110°. Varying quantities of 8-hydroxyquinoline were used corresponding to various ratios. Reaction first took place when the equivalent of 0.5 molecule of 8-hydroxyquinoline was used.

The degree of grinding, as expected, was found to be important. When constituents were well ground in an agate mortar, reaction took place in 2 or 3 min. The reaction was carried out in a porcelain or quartz crucible.

According to VOSKRESENSKII[8], in solid-phase reactions reagents, particularly organic reagents, are best used in the form of a mixture with pure silica gel. In the present work, the reagent content in the silica gel was varied from 1% upwards and the appropriate weights equivalent to 0.5 molecule of 8-hydroxyquinoline and other ratios were used, but in no case did a reaction take place even after several hours. The most effective method of purification of the compound was that based on the volatility of 8-hydroxyquinoline; by heating the orange compound at 110° for 2–5 h, excess 8-hydroxyquinoline was driven off. Final confirmation of the removal of 8-hydroxyquinoline was made from infrared spectra.

Alternatively, an evacuation technique was used to remove excess 8-hydroxyquinoline. A short piece of pyrex glass tubing, closed at one end, was connected at the open end to a vacuum pump; the closed end, containing the impure sample, was placed in a water bath maintained at 45–50°. After 30 min 8-hydroxyquinoline impurity had volatilised and the sample was pure.

Procedures

(i) Precipitation at pH 8.8

Dissolve 100 mg of pure 8-acetoxyquinoline in 45 ml of 1:1 acetic acid. Add to this a solution containing 2–4 mg of scandium, and dilute to 100 ml with water. Adjust the pH to 8.8 with concentrated ammonia solution and heat at 65–70° for 3 h. Cool, filter, and wash the precipitate with a minimum (50 ml) of cold distilled water. Dry the precipitate for 2 h at 110°.

(ii) Precipitation at pH 6.5

Dissolve 500 mg of pure 8-acetoxyquinoline in 20 ml of 1:1 acetic acid. Add to this a solution containing 2–5 mg of scandium, and dilute to 100 ml with water. Adjust to pH 6.5 using concentrated ammonia solution and heat at 65–70° for 3 h. Cool, filter, wash and dry as above.

(iii) The solid-phase reaction

Mix 100 mg of the scandium 8-hydroxyquinolinate, prepared at pH 6.5 as indicated above, with 12 mg of 8-hydroxyquinoline reagent and grind to an intimate mixture in an agate mortar. Place the mixture in a quartz or porcelain crucible and heat in an oven at 110°. An orange coloured scandium 8-hydroxyquinolinate forms within 2–3 min, but it is considered desirable to leave it in the oven for 2 h at 110° to remove unreacted 8-hydroxyquinoline.

RESULTS AND DISCUSSION

The results obtained in the examination of the completeness of the precipitation are shown in Tables I and II. These data indicate that scandium is precipitated at pH 8.8 as $(ScQ_3)_2.HQ$, and at pH 6.5 as $ScQ_3.HQ$. The composition of the 2 com-

TABLE I

PRECIPITATION OF SCANDIUM AT pH 6.5

Scandium taken (mg)	*Weight of oxinate expected on basis of $ScQ_3.HQ$ (mg)*	*Weight of oxinate expected on basis of $(ScQ_3)_2.HQ$*	*Oxinate found[a] (mg)*
2.038	28.2	24.9	28.2
2.038	28.2	24.9	28.3
2.625	36.3	32.1	36.3
2.625	36.3	32.1	36.3
5.250	72.6	64.2	72.4
5.250	72.6	64.2	72.6

[a] No residual scandium was found in the filtrate when the method of BECK[9] was used.

TABLE II

PRECIPITATION OF SCANDIUM AT pH 8.8

Scandium taken (mg)	*Weight of oxinate expected on basis of $ScQ_3.HQ$ (mg)*	*Weight of oxinate expected on basis of $(ScQ_3)_2.HQ$ (mg)*	*Oxinate found[a] (mg)*
2.038	28.2	24.9	24.9
2.038	28.2	24.9	24.9
2.625	36.3	32.1	32.1
2.625	36.3	32.1	32.0
5.250	72.6	64.2	64.0
5.250	72.6	64.2	64.2

[a] No residual scandium was found in the filtrate when the method of BECK[9] was used.

pounds was confirmed by elemental analysis:

Precipitate at pH 6.5
Theoretical: C, 69.45%; H, 4.05%; Ash, 11.08%.
Found: C, 69.05%; H, 4.10%; Ash, 11.00%.

Precipitate at pH 8.8
Theoretical: C, 68.79%; H, 3.94%; Ash, 12.56%.
Found: C, 68.16%; H, 3.86%; Ash, 12.64%.

Further, the compound obtained at pH 6.5 was found to be identical with that obtained by the conventional method of precipitation[7]. This identity was established by infrared, spectrophotometric, diffuse reflectance and thermogravimetric studies.

In the solid-phase reaction, the compound obtained was orange in colour, *i.e.*, distinctly different from the other 2 compounds, obtained directly from solution. The preliminary investigations indicated a composition $(ScQ_3)_2.3HQ$ and this was confirmed by elemental analysis:

Theoretical: C, 69.97%; H, 4.10%; Ash, 9.92%.
Found: C, 69.51%; H, 4.21%; Ash, 10.10%.

Diffuse reflectance spectra and infrared spectra of all 3 complexes showed that the orange compound was different in structure from the other 2 compounds.

The orange chelate is soluble in chloroform, acetone, alcohol, but insoluble in water. However, in the former solvents, there was evidence that it breaks down to give the lemon-yellow oxinate $ScQ_3.HQ$ and free 8-hydroxyquinoline. For example, on allowing an alcoholic solution of the compound to evaporate slowly in air to dryness, it was found that the residue consisted of the lemon-yellow oxinate and 8-hydroxyquinoline. These observations were confirmed by an infrared study of the complexes.

It is interesting to consider the lack of reaction in the solid phase when silica is present in the mixture. Clearly, the silica molecules prevent interaction of the scandium oxinate $ScQ_3.HQ$ and 8-hydroxyquinoline. This may provide a reason why the orange compound is not formed in homogeneous solution: water and ammonia molecules may prevent interaction.

It is interesting to note that, in the precipitation of uranium from homogeneous solution, BORDNER *et al.*[5] obtained 2 uranium 8-hydroxyquinolinates, a dark-red compound of formula $UO_2Q_2.HQ$ and an orange compound $(UO_2Q_2)_2.HQ$. MAGEE AND GORDON[10] suggested that the uranyl group, even after reacting with 2 molecules of 8-hydroxyquinoline is co-ordinatively unsaturated and capable of adding further molecules of solvation. In such circumstances, the rate of precipitation and the number of molecules of reagent available could well determine the particular chelate formed. Evidence in support of these contentions would appear to be available in the present work on scandium, where there is a similarity in the technique of producing the compounds and in the compounds themselves. However, as far as is known, a solid-phase uranium 8-hydroxyquinolinate has not been prepared.

Infrared measurements

The 3 compounds obtained as described above were examined by infrared spectroscopy. Both KBr disc and nujol-mull techniques were used to obtain the infrared spectra. A Perkin-Elmer die was used to make the discs in conjunction with a hydraulic press delivering a load of 10 tons. Spectra were recorded on a Perkin-Elmer, model 137 spectrophotometer in the range 4000–400 cm^{-1}. The spectra obtained for the 3 scandium chelates are shown in Figs. 1–3.

The precipitate prepared by conventional means shows the same absorption peaks as the precipitate prepared by PFHS at pH 6.5.

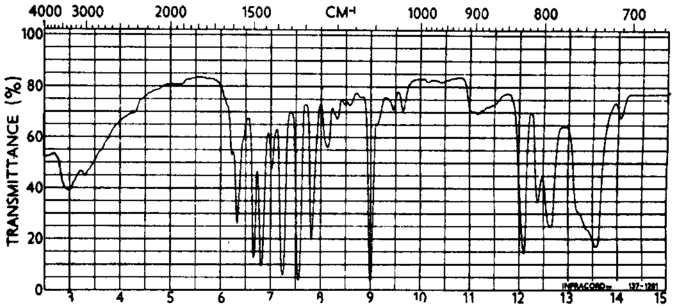

Fig. 1. Infrared spectrum of scandium 8-hydroxyquinolinate prepared by PFHS at pH 6.5.

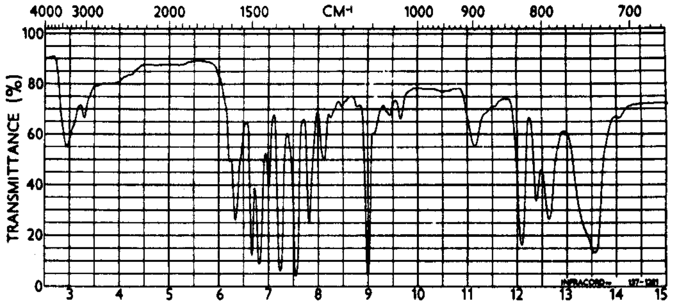

Fig. 2. Infrared spectrum of scandium 8-hydroxyquinolinate prepared by PFHS at pH 8.8.

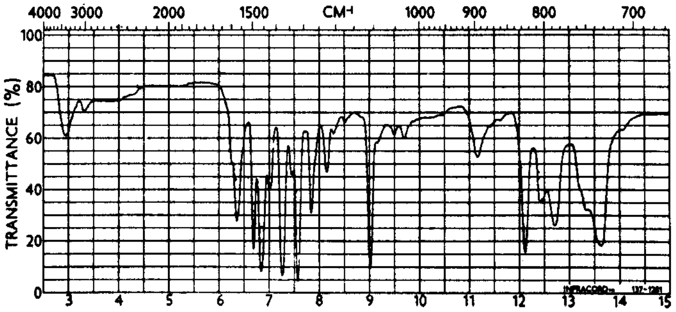

Fig. 3. Infrared spectrum of scandium 8-hydroxyquinolinate prepared by solid-phase reaction.

Between the 2 compounds obtained from homogeneous solution, differences are very slight.

(*i*) The peak at 907 cm^{-1} in the spectrum of the pH 6.5 sample has shifted to 896 cm^{-1} in the spectrum of the pH 8.8 sample, and has increased in intensity. This peak is also the main difference between the 3 scandium chelates and 8-hydroxyquinoline, and it has been suggested in the earlier parts of the series on the use of infrared spectra in the study of metal 8-hydroxyquinolinates that this peak is possibly due to a metal–oxygen stretching frequency[6].

(*ii*) The intensity of the peak at 614 cm^{-1} of the pH 8.8 sample is much greater than that in the pH 6.5 sample. The infrared spectra thus indicate very close similarity in the structure of the 2 compounds.

Between the 2 compounds prepared from homogeneous solution and that obtained by solid-phase reaction the following differences in the spectra were observed:

(*i*) A new peak is resolved at 1345 cm^{-1} in the spectrum of the chelate obtained by solid-phase reaction.

(*ii*) A greater number of differences occurs in the 820–730 cm^{-1} region. Peaks at 827 cm^{-1}, 808 cm^{-1}, 785 cm^{-1} and 738 cm^{-1} in the spectra of the chelates prepared from homogeneous solution are shifted to 826 cm^{-1}, 807 cm^{-1}, 788 cm^{-1} and 735 cm^{-1} in the spectrum of the solid-phase compound. Further, the peak at 735 cm^{-1} in the orange chelate shows a minor peak at 752 cm^{-1}, absent in the spectra of the other 2 compounds.

(*iii*) Two peaks at 1060 cm^{-1} and 1035 cm^{-1} in the spectra of the chelates from homogeneous solution, are shifted in the orange compound to 1055 cm^{-1} and 1032 cm^{-1}.

(*iv*) The peak at 614 cm^{-1} in the spectra of the precipitated oxinates is shifted to 608 cm^{-1} in the spectrum of the orange chelate, and has an intensity comparable to that found in the pH 8.8 sample. A minor peak is also resolved at 580 cm^{-1} in the spectrum of the solid-phase compound.

(*v*) A peak occurs at 516 cm^{-1} in all 3 spectra; however, in the spectrum of the orange chelate a minor peak is resolved at 507 cm^{-1}.

(*vi*) The peak occurring at 494 cm^{-1} in the spectra of the precipitated oxinates is shifted to 492 cm^{-1} in the spectrum of the orange compound prepared by solid-phase reaction.

In the region 900–700 cm^{-1} the peaks are due to ring vibrations and C–H deformations[11] and differences in this region between the spectrum of the solid-phase compound and those of the precipitated chelates are small.

The most characteristic differences are those which occur in the far infrared around 500 cm^{-1}. It is supposed that the 2 major peaks at 516 cm^{-1} and 494 cm^{-1} in the spectra of the compounds precipitated from homogeneous solution are due to metal–nitrogen stretching[12].

The changes would appear to be due to the binding of the extra half molecule of 8-hydroxyquinoline. However, the differences while characteristic are not very great and the extra half molecule of HQ is probably loosely bound.

Thermogravimetric studies

A study of scandium 8-hydroxyquinolinate prepared by conventional precipitation was carried out by WENDLANDT[13], who found that the compound was thermally stable up to 125°. No constant weight plateau was found corresponding to the unsolvated or "normal" chelate. However, a mixture of solvated chelate $ScQ_3.HQ$ and "normal" chelate existed up to approximately 400°. Conversion to the oxide, Sc_2O_3, was complete at about 600°. No further weight loss occurred above this temperature.

In an attempt to find analytical data which would support the infrared studies reported above, thermogravimetric studies were carried out on the 2 scandium(III) 8-hydroxyquinolinates precipitated from homogeneous solution, the solid-phase scandium 8-hydroxyquinolinate, the conventionally prepared chelate, $ScQ_3.HQ$[7], and 8-hydroxyquinoline itself. For these studies, 20-mg samples were transferred to freshly ignited platinum crucibles and the samples subjected to a heating rate of 300°/h in the thermobalance constructed as described by DUVAL[14].

RESULTS AND DISCUSSION

Comparison of the thermogravimetric curves of scandium(III) 8-hydroxyquinolinates prepared by PFHS at pH 6.5, pH 8.8, and by conventional precipitation

The pyrolysis curves obtained are shown in Fig. 4.

Precipitates prepared by conventional precipitation and by PFHS at pH 6.5 behaved similarly, and were thermally stable up to about 125°. However, no constant weight level corresponding to ScQ_3 occurred in either case. The chelate exists until the remaining organic material disappears between 450° and 550° to form the oxide Sc_2O_3 which is stable above 600°.

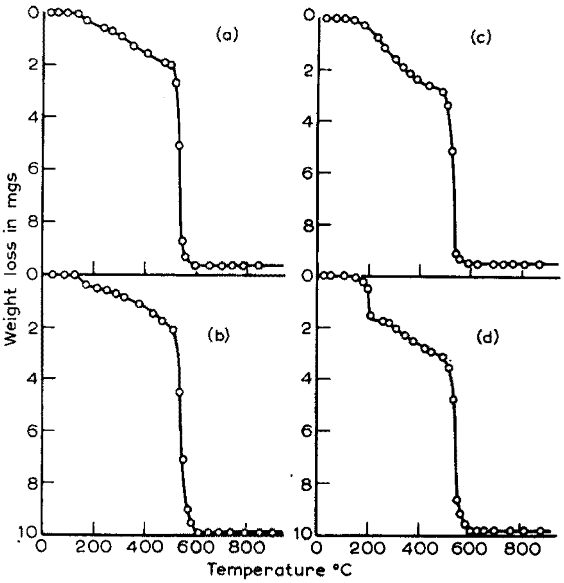

Fig. 4. Thermogravimetric curves for scandium(III) 8-hydroxyquinolinates. (a) $ScQ_3.HQ$ prepared by conventional precipitation; (b) $ScQ_3.HQ$ prepared by PFHS at pH 6.5; (c) $(ScQ_3)_2.HQ$ prepared by PFHS at pH 8.8; (d) $(ScQ_3)_2.3HQ$ prepared by solid-phase reaction (heating rate 300°/h).

With pure 8-hydroxyquinoline the first weight loss occurred at 85°. Thus, the conventional precipitate and that prepared from homogeneous solution at pH 6.5 can be dried and excess 8-hydroxyquinoline removed in the region 85–125°.

The behaviour of the scandium chelate precipitated at pH 8.8 is quite similar to that precipitated at pH 6.5. It can be dried and excess 8-hydroxyquinoline removed between 85° and 125°.

The compound prepared by solid-phase reaction

The pyrolysis curve for the solid-phase reaction chelate shows considerable differences compared with those of the other chelates. $(ScQ_3)_2.3HQ$ is thermally stable up to 125°, but above 125°, it is less stable than the compounds prepared by precipitation from homogeneous solution. Between 200° and 205° a loss of weight corresponding to a half molecule of HQ is recorded, followed by a constant weight level corresponding closely to $ScQ_3.HQ$. From this point on, the thermogravimetric behaviour is identical to that obtained for the other 2 compounds.

Conclusions

Precipitation from homogeneous solution using 8-acetoxyquinoline can be utilized for the determination of scandium. Scandium is precipitated at pH 8.8 as $(ScQ_3)_2.HQ$ or at pH 6.5 as $ScQ_3.HQ$, and the precipitates have much better physical characteristics than that obtained by conventional means. Thermogravimetric analysis confirms that scandium can be determined either as the 8-hydroxyquinolinate or after ignition to the oxide.

In the present work it was hoped that the infrared studies might indicate sufficient differences between the 3 scandium chelates to allow a definite conclusion to be drawn about the structures of the compounds. However, as the above results show, the spectral differences are small, so that the only conclusion is that the chelates are structurally similar.

Thermal data show that the compound prepared by solid-phase reaction is different from the chelates prepared in solution. The extra half molecule of HQ is removed at a much lower temperature than the other ligands, which indicates that it is fairly loosely bound.

One of the authors (T.J.C.) wishes to thank the Ministry of Education (N.I.) for a Postgraduate Studentship which allowed the present work to be carried out.

SUMMARY

The preparation of 3 scandium 8-hydroxyquinolinates is reported. Two were prepared by precipitation from homogeneous solution using 8-hydroxyquinoline generated by hydrolysis of 8-acetoxyquinoline, and the third by a solid-phase reaction. The first precipitate was obtained at pH 6.5 as a lemon-yellow compound with the composition $ScQ_3.HQ$ ($Q = C_9H_6NO$). The second chelate was obtained at pH 8.8 as a bright-yellow compound of composition $(ScQ_3)_2.HQ$. The third scandium 8-hydroxyquinolinate was obtained by a solid-phase reaction between the lemon-yellow compound $ScQ_3.HQ$ and 8-hydroxyquinoline. The orange compound has the composition $(ScQ_3)_2.3HQ$. Infrared spectra and pyrolysis curves indicated that the 3 chelates have very similar structures.

RESUME

On a préparé 3 hydroxy-8-quinoléates de scandium; deux sont obtenus par précipitation en utilisant l'hydroxy-8-quinoléine formée par hydrolyse de l'acétoxy-8-quinoléine et le troisième par réaction en phase solide. Le premier, précipité au pH 6.5, est jaune citron, de formule $ScQ_3.HQ$ ($Q = C_9H_6NO$); le second chélate, obtenu au pH 8.8, est jaune brillant de composition $(ScQ_3)_2.HQ$; le troisième, obtenu par réaction entre $ScQ_3.HQ$ et hydroxy-8-quinoléine est orange et correspond à $(ScQ_3)_2.3HQ$. Les spectres infrarouges et les courbes de pyrolyse indiquent que les 3 chélates ont des structures très similaires.

ZUSAMMENFASSUNG

Es wird über die Herstellung von 3 Scandium-8-Hydroxychinolaten berichtet. Zwei wurden durch Fällen aus homogener Lösung mit 8-Hydroxychinolin, das dritte durch Reaktion in fester Phase hergestellt. Das erste wurde beim pH-Wert 6.5 als eine zitronengelbe Verbindung mit der Zusammensetzung $ScQ_3.HQ$ ($Q = C_9H_6NO$), das zweite beim pH-Wert 8.8 als strahlend gelbe Verbindung der Zusammensetzung $(ScQ_3)_2.HQ$ und das dritte durch Festphasenreaktion zwischen $ScQ_3.HQ$ und 8-Hydroxychinolin erhalten. Die letztere orange Verbindung hat die Zusammensetzung $(ScQ_3)_2.3HQ$. Infrarotspektren und Pyrolysekurven ergaben, dass die 3 Chelate sehr ähnliche Strukturen besitzen.

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THE ACCURATE DETERMINATION OF THALLIUM BY DIRECT TITRATION WITH EDTA USING METHYLTHYMOL BLUE AS INDICATOR

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(Received March 11th, 1966)

A fairly large number of indicators for the direct compleximetric titration of thallium(III) have been described in the literature[1-6]. With the exception of 4-(2-methylanabasineazo)-resorcinol[6], which is not available commercially, the indicators are not satisfactory for accurate work. Various existing back-titration procedures[7-12] are even less satisfactory. The best of the commercially available indicators seems to be xylenol orange, which is used in weakly acidic medium (pH 3–5) in the presence of an ammonium acetate buffer[1,2].

Halides and especially bromide[2] interfere strongly when thallium(III) is titrated with EDTA in acidic media. This excludes the use of the bromic oxidation procedure of thallium which is the most elegant and reliable one. Compleximetric titration of thallium in alkaline media therefore seemed to be quite attractive provided that it could be carried out in the presence of substantial amounts of bromide and other anions and could be combined with a selective procedure for the separation from many other elements which are also titrated with EDTA in alkaline solutions.

Since thallium(III) tends to hydrolyse even at fairly low pH values, the titration in alkaline media requires the presence of a suitable complexing agent which complexes thallium(III) strongly enough to prevent its precipitation by hydrolysis but less strongly than the chosen indicator. Xylenol orange cannot be used above pH 6, because of its own color in the alkaline region, but methylthymol blue[13], which in many respects is very similar, can be applied successfully. Tentative experiments revealed that tartaric acid as the complexing agent and methylthymol blue as the indicator meet the requirements for the compleximetric titration of thallium(III) in alkaline media very satisfactorily. The details of this procedure therefore were thoroughly investigated.

EXPERIMENTAL

Reagents and apparatus

Analytical reagent-grade chemicals were used whenever possible. Methylthymol blue and xylenol orange indicators were obtained from E. Merck A. G., Darmstadt, Germany. The indicators were used as solid 1% mixtures with finely ground potassium nitrate. Thallium(III) solutions were prepared from A.R. grade thallous nitrate by oxidation with nitric–hydrochloric acid mixtures. Most of the acid was removed by evaporation, so that the final standard solution contained only about 0.05 N free acid. After it had been established that bromide did not interfere, the Tl(III) standard solutions for the quantitative work with the methylthymol blue indicator were prepared by bromine oxidation in a small volume of dilute nitric acid. For stabilization, enough hydrobromic acid was added to give a final concentration of 0.01 *N*.

A Beckman DU model spectrophotometer was used for the preparation of optical density against wavelength plots and a Metrohm E336 recording potentiograph coupled to a Metrohm E1009 colorimeter, both obtained from Metrohm Ltd., Herisau, Switzerland, were employed for the preparation of spectrophotometric titration curves.

Color changes of methylthymol blue during the complexímetric titration of Tl(III) in alkaline tartrate media

Since it was observed that depending on conditions methylthymol blue produced various colors with solutions containing thallium(III), the formation of these colors was investigated. About 75 ml of a solution containing 0.2455 millimol of thallium(III) and 0.5 g of tartaric acid was neutralized with ammonium hydroxide to the desired pH value and after addition of the indicator titrated with standard 0.01 *M* EDTA. The results are summed up in Table 1.

Comparison of the xylenol orange and methylthymol blue end-points

An initial optical density of 0.700 was chosen tentatively. From experimental optical density against wavelength curves it was decided to carry out the spectrophotometric titrations at 470 mμ for xylenol orange and at 515 mμ for methylthymol

TABLE I

COLOUR CHANGES OF METHYLTHYMOL BLUE DURING TITRATION

pH value	*Initial colour*	*Before end-point*	*After end-point*	*Remarks*
5	Blue-green	Blue-green	Yellow	Bad end-point, low titration
6	Blue-green	Red	Yellow	Not very sharp
7	Brilliant blue-green	Red	Yellow	Very sharp
8	Blue-red	Red	Blue-green	Very sharp
9	Purple	Red	Blue	Very sharp
10	Purple	Red	Blue	Very sharp
11	Rose red	Rose red	Grey	Not very sharp

TABLE II

COMPARISON OF TITRATION CURVES FOR XYLENOL ORANGE AND METHYLTHYMOL BLUE INDICATORS

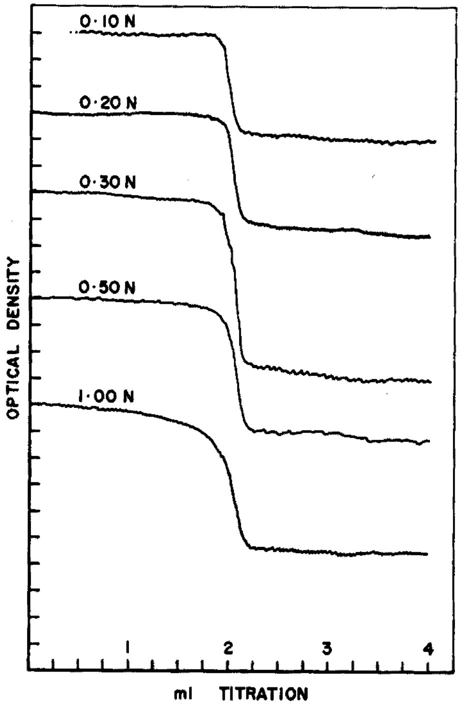
Values for tan α			*EDTA molarities for equal values of tan α*[a]			
Molarity EDTA	*Xylenol orange*	*Methylthymol blue*	*Tan α*	*Molarity EDTA*		*Molarity ratio*
				Xylenol orange	*Methylthymol blue*	
0.01	2.65	7.69	1.5	0.00385	0.00102	3.78
0.003	1.30	3.22	2.0	0.00618	0.00148	4.18
0.001	0.62	1.47	2.5	0.00902	0.00201	4.49

[a] These values were read from plots of molarity EDTA against tan α.

blue. The pH values were adjusted to 4.0 and 9.0, respectively, keeping the amount of buffer to a minimum, and the total solution volume before titration was 70 ml. Titration curves were obtained using 0.01, 0.003, and 0.001 *M* EDTA; particularly with the lower EDTA concentrations, much sharper end-points were obtained when methylthymol blue was used as indicator. Table II presents experimental values for tan α taken from the spectrophotometric titration curves, where α is the angle between a horizontal through the end-point and the steepest part of the titration curve. When those concentrations of EDTA are compared which give similar experimental values of tan α for the 2 indicators, it is found that the methylthymol blue indicator at pH 9.0 is about 4 times as sensitive as xylenol orange at pH 4.0 (Table II).

The influence of tartrate and acetate

Spectrophotometric titrations with 0.01 *M* EDTA using 70-ml volumes containing various amounts of tartrate, a pH of 9.0 and methylthymol blue as indicator were carried out and the titration curves are presented in Fig. 1. Because it was observed that the end-point in the titration of thallium(III) using xylenol orange as indicator is very strongly dependent on the concentration of the ammonium acetate buffer present, spectrophotometric titration curves with 0.01 *M* EDTA also were prepared using the same volume, various amounts of ammonium acetate, a pH of 4.0, and xylenol orange as indicator. The curves are presented in Fig. 2. Figure 1 shows



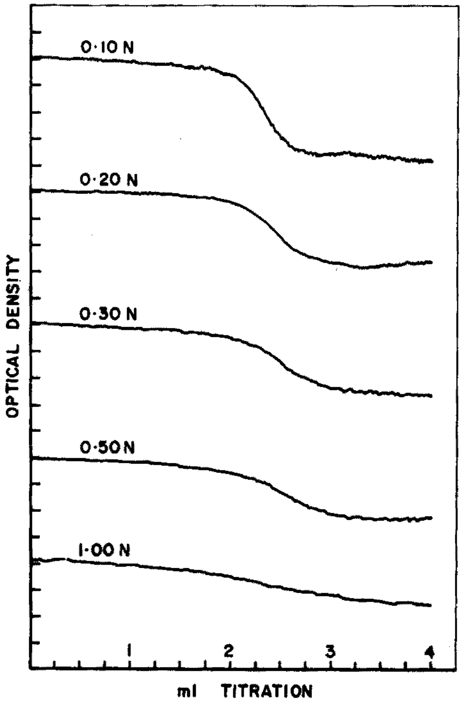


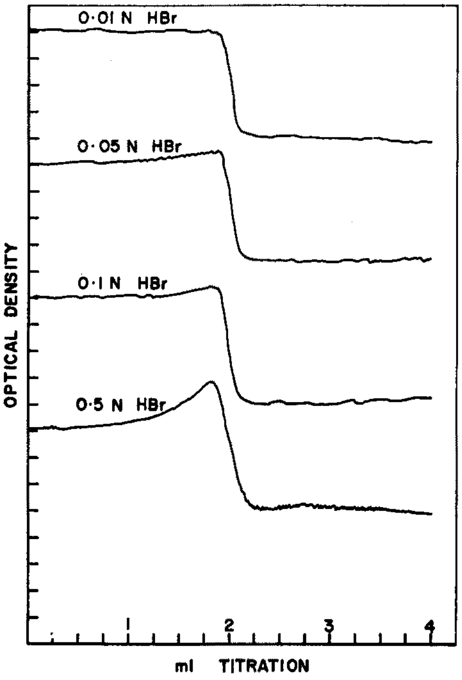
Fig. 1. The influence of the concentration of tartrate on the spectrophotometric titration of Tl(III) with EDTA. Methylthymol blue indicator.

Fig. 2. The influence of the concentration of acetate on the spectrophotometric titration of Tl(III) with EDTA. Xylenol orange indicator.

that the titration with methylthymol blue as indicator can be carried out even in 1.0 N tartrate medium; but for optimum results the tartrate concentration should be between 0.1 and 0.3 N. At tartrate concentrations lower than 0.05 N, precipitation of $Tl(OH)_3$ by hydrolysis takes place. The titration with xylenol orange as indicator on the other hand is very strongly dependent on the ammonium acetate concentration. The end-point is completely obscured in 1.0 N and quite bad in 0.3 N solutions. Even in 0.10 N solutions, it is distinctly less sharp than without the addition of extra ammonium acetate.

The influence of bromide

Spectrophotometric titration curves using 70-ml volumes containing various amounts of bromide were prepared with 0.01 M EDTA as titrant and the 2 indicators at their specified pH values. The curves are presented in Figs. 3 and 4. The curves very distinctly demonstrate that the presence of 0.1 N HBr has no appreciable effect on the methylthymol blue end-point at pH 9, and even in 0.5 N HBr the end-point is quite sharp (Fig. 3). However, here another color (brilliant blue-green) is obtained at the beginning of the titration, which turns to red before the end-point is reached and then to blue. The xylenol orange end-point at pH 4 is seriously obscured by the presence of bromide and becomes indistinct even in 0.01 N HBr (Fig. 4).



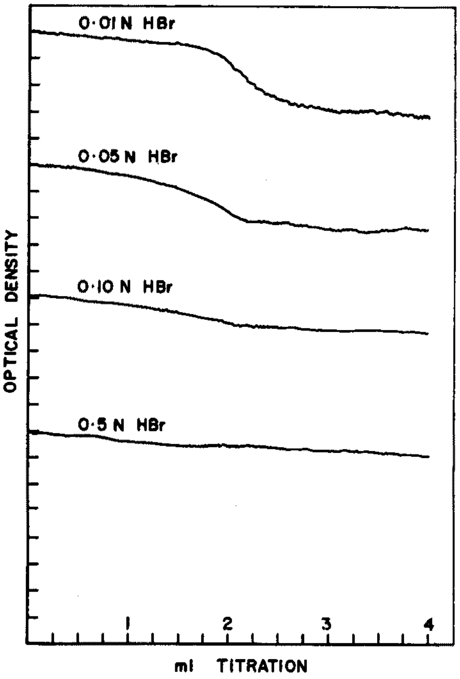


Fig. 3. The influence of the bromide concentration on the spectrophotometric titration of Tl(III) with EDTA. Methylthymol blue indicator.

Fig. 4. The influence of the bromide concentration on the spectrophotometric titration of Tl(III) with EDTA. Xylenol orange indicator.

Quantitative titrations

A solution of thallium(III) was prepared by bromine oxidation of thallous nitrate. For stabilization, enough HBr was added to give a final concentration of 0.05 *N*. The solution was standardized gravimetrically by precipitating thallium as Tl_2CrO_4 from a solution containing 2% of ammonium hydroxide and 2% of potassium chromate[14] after the bromide had been removed by evaporation with nitric acid and Tl(III) had been reduced to Tl(I) with sulphur dioxide. A solubility correction[14] of 0.95 mg of Tl_2CrO_4 per 100 ml of solution was applied to the results and the thallium concentration was determined as 5.015 ±0.003 mg Tl per ml at 25° by quadruplicate analysis. A 0.02 *M* EDTA solution was prepared and standardized in quadruplicate against a calcium solution, prepared from A.R. grade calcium carbonate, using methylthymol blue as indicator. These 2 solutions were titrated against each other using various volumes and dilutions, a pH of 9, and methylthymol blue as indicator. The results for some visual and for one spectrophotometric titration at a wavelength of 515 mμ are presented in Table III. Results obtained in the presence of some common anions are included.

TABLE III

QUANTITATIVE TITRATIONS OF Tl(III) WITH EDTA AND METHYLTHYMOL BLUE AS INDICATOR (pH 9.0)[a]

mg Tl(III) taken	*Anion added*	*Molarity of titrant*	*mg Tl(III) found*
100.30	Nil	0.01	100.33±0.06
50.15	Nil	0.01	50.18±0.05
25.08	Nil	0.01	25.11±0.06
10.03	Nil	0.002	10.04±0.02
5.02	Nil	0.002	5.02±0.02
1.003[b]	Nil	0.001	1.005±0.002
50.15	5 g NH_4NO_3	0.01	50.16±0.03
50.15	5 g $(NH_4)_2SO_4$	0.01	50.17±0.03
50.15	5 g KBr	0.01	50.25±0.06
50.15	2.5 g KBr	0.01	50.13±0.04
50.15	5 g NH_4Cl	0.01	49.96±0.04
50.15	2.5 g NH_4Cl	0.01	50.12±0.06
50.15	5 g NH_4-tartrate	0.01	50.18±0.05
50.15	5 g NH_4-acetate	0.01	50.14±0.05

[a] The results are means of triplicate determinations with calculated standard deviations.

[b] Means of 6 results using spectrophotometric titration.

DISCUSSION

The described method provides a means for the accurate direct compleximetric determination of thallium. The end-point is about 4 times sharper than when xylenol orange is used as indicator (Table II). While the xylenol orange end-point is obscured by the presence of fairly low concentrations of other salts including the generally used ammonium acetate buffer (Fig. 2) and seriously masked by halides (Fig. 4), the methylthymol blue end-point in the alkaline region is very much less affected (Figs. 1 and 3). Accurate visual titrations with 0.01 *M* EDTA can be carried out when 5 g of ammonium nitrate, sulphate, tartrate, or acetate are present in a final volume of about 75 ml; 5 g of potassium bromide cause slightly higher and 5 g of ammonium chloride slightly lower results. However, the errors are only about $+0.2$ and -0.4%, relative for 50-mg amounts. Accurate results are obtained when 2.5 g of the same salts are present. Because fairly large amounts of bromide do not interfere, bromine can be employed for the oxidation of Tl(I) to Tl(III). When smaller total volumes (about 5–10 ml) and a 10-ml buret are used, visual titrations with 0.002 *M* EDTA still give sharp end-points and accurate results. The amounts of indicator for the visual titrations, especially those with very dilute EDTA solutions, should not be excessive, otherwise a less distinct end-point will be obtained. Titrations with 0.001 *M* EDTA in 75-ml total volume can be carried out spectrophotometrically at a wavelength of 515 mμ. Thus, 1 mg of thallium can be determined with an accuracy of ±2 μg.

Accurate titrations can be carried out in the pH range 7–10. At lower or higher pH values, the end-points are less sharp. A large number of other elements are also titrated under the described experimental conditions. Two alternative procedures are suggested for their separation. The first one is solvent extraction of thallium(III) bromide from 0.5 *N* or 1.0 *M* hydrochloric or hydrobromic acid into methyl isobutyl ketone after preliminary oxidation of thallium(I) with bromine. The second one is anion-exchange chromatography of the bromide complexes. All metallic elements with the exception of Cd(II), Bi(III), Tl(III), Pd(II), Au(III), Pt(IV), and Ir(IV) can be eluted from a column of AG1-X8 anion-exchange resin in the bromide form by using 0.30 *N* nitric acid and 0.025 *N* hydrobromic acid as eluant[15]; Cd(II) and Pd(II) can be eluted with 1.0 *N* ammonia. Then Tl(III) is eluted with a solution containing 0.5 *M* nitric acid and 0.1 *M* thiourea. The only elements to accompany Tl(III) partially are Bi(III), Au(III), Pt(IV), and Ir(IV). When present, Bi(III) can be separated from thallium by cation-exchange chromatography after thallium has been reduced to Tl(I) with sulphur dioxide. This also precipitates any gold as the metal which can be separated by filtration. The solution from which free halides have been removed by evaporation with nitric acid is made 0.5 *N* in nitric acid and passed through a column of AG50-X8 cation-exchange resin in the hydrogen form. Bi(III) can be eluted with 0.3 *N* hydrobromic acid while Tl(I) (but not Tl(III)) is retained by the column; Tl(I) can then be eluted with 2 *N* nitric acid. Alternatively, Tl(III) probably could be determined in the presence of bismuth by an equivalent of the procedure suggested by BUSEV *et al.*[5,6]. This entails a compleximetric titration of Bi(III) plus Tl(III) followed by a reduction of Tl(III) to Tl(I) using sulphur dioxide or sulphite solution and titration of the released EDTA with a suitable metal cation. Cadmium(II) or calcium(II) would be very suitable for such a back-titration in alkaline tartrate media using methylthymol blue as indicator.

SUMMARY

After oxidation with bromine, thallium can be determined accurately by titration with EDTA in alkaline tartrate media of pH 7–10 using methylthymol blue as indicator. The end-point in this titration is considerably sharper than that obtained with xylenol orange as indicator in weakly acidic solution, and is considerably less influenced by the presence of bromide, tartrate and acetate. Up to 2.5 g of ammonium or potassium bromide or chloride and up to 5 g of tartrates, acetates, nitrates or sulphates can be tolerated. About 1 mg of thallium in 75 ml can be determined with an error of about 2 μg by spectrophotometric titration. A selective solvent extraction and an anion-exchange procedure are suggested for the separation of Tl(III) from most other titratable elements.

RÉSUMÉ

Le thallium peut être dosé avec précision par titrage au moyen d'EDTA, après oxydation au brome. On procède en milieu tartrate alcalin (pH 7–10), en présence de bleu de méthylthymol comme indicateur. Le virage est plus net que celui obtenu avec le xylénol orange en solution faiblement acide; le titrage est beaucoup moins influencé par la présence des bromures, des tartrates et des acétates. On peut doser ainsi 1 mg de thallium dans 75 ml avec une erreur d'environ 2 μg, par titrage spectrophotométrique. On propose une extraction sélective dans un solvant et un procédé par échange d'anions pour la séparation du thallium(III) d'avec de nombreux autres éléments.

ZUSAMMENFASSUNG

Thallium kann nach Oxydation mit Brom durch Titration mit AeDTE in alkalischem Tartratmedium vom pH 7–10 bestimmt werden unter Verwendung von Methylthymolblau als Indikator. Bei dieser Titration ist der Endpunkt beträchtlich schärfer als der mit Xylenolorange in schwach saurer Lösung, und wird wesentlich weniger durch die Gegenwart von Bromid, Tartrat und Acetat beeinflusst. In 75 ml Lösung können bis zu 2.5 g Ammonium- oder Kaliumbromid oder -chlorid und 5 g Tartrat, Acetat, Nitrat oder Sulfat anwesend sein. Etwa 1 mg Thallium kann durch spektralphotometrische Titration mit einem Fehler von etwa 2 μg bestimmt werden. Ein selektives Extraktions- und Austauscherverfahren wird für die Abtrennung des Thallium(III) von den meisten anderen titrierbaren Elementen vorgeschlagen.

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SPECTROPHOTOMETRIC DETERMINATION OF SULPHONYL HALIDES WITH ALKALINE PYRIDINE REAGENT

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Sulphonyl halides have been hitherto mostly determined by one of 2 methods: hydrolysis to the corresponding acids, followed by their titration with a correction for the free acid(s) originally present[1,2]; or titrimetric reduction with sulphide, to a visual (yellow) or instrumental (polarovoltric) end-point[3]. Although these methods are evidently of reasonably general application, they remain macro or semimicro methods. A micro or submicro method is desirable for these compounds which are important intermediates in syntheses of many sulphonamides and anionic surface-active materials.

During investigation of the sulphide reduction method, an intense red colour was observed in aqueous pyridine solution. This was similar to the colour described first by GEBAUER-FÜLNEGG AND RIESENFELD[4] and studied later by SAKAMOTO[5]. They used sulphonyl chloride/pyridine/alkali hydroxide mixtures and considered that pyridine ring fission occurred. In the present case, the alkali was formed by hydrolysis of the sulphide.

The absorption spectra of solutions containing a sulphonyl halide, pyridine and bases were therefore examined in more detail. On adding, for example, *p*-toluenesulphonyl chloride to pyridine/aqueous alkali mixtures, a pale yellow solution with absorption maximum at *ca.* 435 nm was initially obtained. This maximum, which appears not to have been previously reported, gave place to a maximum at 395 nm, connected with the first maximum via an isosbestic point at *ca.* 415 nm. The change was very rapid and could be demonstrated only indirectly, namely by plotting curves of light absorption against time for several wavelengths between 390 and 450 nm. This demonstration was practicable only at less high pH values (*ca.* 9) and at room or lower temperature; under these conditions the change was not too fast. In the presence of larger amounts of sulphonyl chloride or on heating, the yellow solution became red, with a maximum at 550 nm. On treatment with acid, the red colour changed to yellow with an absorption maximum between 420 and 440 nm, depending on the solvent. The transition occurred fairly sharply at pH 11. The yellow solution showed a strong yellow-green fluorescence. Strong acidification with acids like 50% sulphuric or 70% perchloric acid, bringing the pH to *ca.* 0, yielded a red solution again, this time with an absorption maximum at *ca.* 525 nm. After longer standing, all these solutions became colourless and the maximum was displaced to 365 nm. Further variations were possible by replacing the alkali with an amine or with an aqueous solution of cyanide and 1-phenyl-3-methyl-2-pyrazolin-5-one[5] or barbituric acid. Other sulphonyl halides gave similar results with absorption maxima within a few nm of the above values.

In the present work, the maxima at 550 and 395 nm were studied in more detail. The development of a red colour with absorption maximum between 520 and 550 nm has been known for some time as the FUJIWARA reaction[6] and is the basis of colorimetric determinations of some halogen compounds, *e.g.* chloroform, bromoform, carbon tetrachloride and trichloroethylene. A maximum at 391 nm was used by ASMUS, KRAETSCH AND PAPENFUSS[7] in their determination of pyridine using a chloramine T/cyanide/barbituric acid reagent. There appears, however, to have been no adaptation of the reaction and these absorption maxima to the determination of sulphonyl halides. The maxima are not too pointed but fairly flat over a range of about 5 nm; this is a potential advantage because negligible error is then introduced by a slight error in wavelength setting. Accordingly we have attempted to work out such methods, based on these 2 maxima.

EXPERIMENTAL

Chemicals

Sulphonyl halides. Those used were: methane- and butanesulphonyl chlorides, benzenesulphonyl chloride, likewise the *p*-chloro, *p*-bromo, *p*-iodo and *m*-nitro derivatives; *o*-, *p*- and ω-toluenesulphonyl chlorides, β-naphthalenesulphonyl chloride, and naphthalene-1,5-disulphonyl chloride.

These were bought materials or prepared as described by HUNTRESS AND CARTEN[8]. The aromatic sulphonyl chlorides were freed from sulphonic acid by precipitation with water from concentrated acetone solution. The precipitates were dried and crystallised several times from petroleum ether/benzene, 1:1. The two aliphatic chlorides were pure, bought materials.

Solvents. These were purified in the usual way without elaborate precautions. Special purification methods[9,10] for pyridine were tested. The commercial materials (Merck "reinst" and Gesellschaft für Teerverwertung, Duisburg "rein") gave a colour with a *m*-dinitrobenzene/aqueous sodium hydroxide reagent (JANOVSKY reaction due to traces of pyridones?). This was eliminated by a combination of the 2 quoted purification methods (precipitation as complex with mercury(II) chloride, crystallisation of the complex from water, decomposition with alkali, distillation of the pyridine thus obtained, reflux with selenium dioxide, distillation again, drying over potassium hydroxide and finally distillation). This treatment was however subsequently not used because it clearly had no influence on the spectrophotometric data in the present work. The pyridine and pyridine-containing reagents were kept in darkened vessels since relatively rapid decomposition into ammonium glutacondialdehyde enolate can occur under the influence of light in the presence of oxygen and moisture[11].

Solutions. Sodium hydroxide (Merck), 0.1 *N* and *N* aqueous solutions.

Buffers (Merck "Titrisol" solutions), pH 8 (borate/hydrochloric acid); pH 9 (borate/potassium chloride/sodium hydroxide); pH 10 (borate/potassium chloride/sodium hydroxide); pH 11 (phosphate/sodium hydroxide); and pH 12 (glycine/sodium hydroxide).

Apparatus

Unicam SP. 600 spectrophotometer with 1-cm cuvettes.

Procedure

The light absorptions at the maxima of 550 and 395 nm of various mixtures of sulphonyl halides, pyridine, aqueous sodium hydroxide or an alkaline buffer and of organic solvents were measured. The influence of several parameters was examined, namely of alkali concentration (pH); pyridine concentration; sulphonyl halide concentration; solvent composition; temperature; time; and order of mixing.

RESULTS

Determination based on the maximum at 550 nm

A study of the different parameters was undertaken with *p*-toluenesulphonyl chloride. Semiquantitative experiments showed that for mixtures of 1 ml of pyridine with *ca.* 0.2–1 ml of *N* sodium hydroxide solution, the light absorption was fairly constant, with a flattish maximum corresponding to about 0.25 ml of alkali. Outside these proportions, the absorption fell off rapidly. For the examination of the influence of other parameters, the 1:1 volume proportion was chosen for subsequent work.

Later work with the buffer solutions in place of the alkali hydroxide showed that with falling pH the absorption first decreased and then increased to another maximum at pH *ca.* 10. This was not studied further, mainly because the subsequently developed method (below) was considered to be superior.

A solvent was needed for the sulphonyl chloride sample and, if possible, to render homogeneous the pyridine/aqueous alkali mixture. Most of the more polar homogenising solvents such as lower alcohols, acetone, tetrahydrofuran, dioxan, dimethylformamide, dimethyl sulphoxide and excess pyridine drastically reduced the light absorption. Many halides were excluded (positive FUJIWARA reaction). Aromatic hydrocarbons were found to permit the largest light absorptions. After colour development, a 1:1 mixture of acetone and methanol was added to give a homogeneous solution on which the light absorption measurements could be made.

The data given in Table I show that, as expected, a rise in temperature increased the light absorption and accelerated the attainment of the maximum value. Conditions of heating for 4 min at 70° were finally selected, giving a compromise between greater sensitivity and greater susceptibility to error. This demanded the use of tightly stoppered vessels to prevent losses.

TABLE I

LIGHT ABSORBANCE AT 550 nm

(0.5 ml pyridine + 0.5 ml *N* sodium hydroxide/water + 20 μg *p*-toluenesulphonyl chloride in 0.5 ml benzene + 1 ml acetone + 1 ml methanol)

Temperature (°)	*Time of reaction (min)*					
	2	*4*	*6*	*8*	*10*	*12*
50	0.17	0.27	0.29	0.285	0.27	0.245
60	0.27	0.41	0.41	0.40	0.375	0.345
70	0.42	0.56	0.55	0.525	0.50	0.475

The order and nature of mixing were found to be important. Thus addition of alkali to a mixture of pyridine and the sulphonyl chloride gave no or only a weak colour. Further, it was found that the largest absorption values were obtained when the aliquot of sulphonyl chloride solution was pipetted into the pyridine/aqueous alkali without shaking.

Final procedure. A mixture of 0.5 ml of pyridine and 0.5 ml of aqueous *N* sodium hydroxide was brought to 70° by standing for 2 min in a thermostat at that temperature; 0.5 ml of a benzene solution of *p*-toluenesulphonyl chloride was then carefully added without shaking or mixing, and the tube was restoppered and left for a further 4 min in the thermostat. The tube was then removed from the thermostat and 2 ml of a 1:1 (volume) mixture of acetone and methanol was added to yield a homogeneous solution. This was transferred to a cuvette and the light absorption at 550 nm was measured 8 min from the moment of placing the pyridine/alkali solution in the thermostat.

Under these conditions a straight standardisation curve was obtained between 12 and 50 μg of *p*-toluenesulphonyl chloride. The mean absorbances for these 2 amounts were 0.167 and 0.990, respectively, corresponding to a molar absorptivity of *ca.* 11,400, based on the sulphonyl chloride. The error, based on Gauss analysis of 10 determinations, did not exceed 1% and in the 30–45 μg range, was as low as 0.3%.

As stated above, the method was developed for only *p*-toluenesulphonyl chloride. Some orientation experiments showed that it is almost certainly applicable to many other sulphonyl halides. These showed maxima deviating only slightly from 550 nm (see Table III) and with different molar absorptivities. Further work on the method was suspended in favour of the second method, described below. Possible interferences by other compounds were thus not investigated but it may be mentioned that the corresponding free acids (hydrochloric and *p*-toluenesulphonic acid) did not interfere unless of course present in such amounts as to influence the pH appreciably. This would be an advantage in purity determinations where these acids are the usual impurities.

Determination based on the maximum at 395 nm

Increase in the proportion of pyridine to sulphonyl halide progressively augmented the light absorption of mixtures in acetone/aqueous sodium hydroxide. It reached an asymptotic value at a ratio of about 20,000:1, which corresponds to about 1 ml of pyridine per 40 μg of sulphonyl halide. This amount of pyridine was used in the subsequent work.

Fairly flat curves of absorbance against time were obtained for solutions containing the buffers (pH 8 up to 12) and sodium hydroxide. Rounded maxima were attained after times which decreased with increase in the pH value. Little sensitivity was thus lost by using a short reaction time; moreover, negligible errors would then be introduced by a slight inaccuracy in measuring this time. In contrast to the belief of many authors, it was found that the greatest absorbance occurred not in more strongly alkaline solutions containing sodium hydroxide, but with the pH 10 buffer (Table II). (It may be mentioned that in the determination by ASMUS *et al.* mentioned above, using chloramine T/cyanide/barbituric acid, maximum light absorption was obtained at pH 9 with a borate buffer.)

Increase in temperature reduced the light absorption markedly when sodium hydroxide solutions were used. At lower pH values with the buffers, flatter curves of absorbance against temperature were obtained, with even a slight increase to asymptotic values at 50–60°. This increase was however too small to justify the use of higher temperatures. The flat curves rendered thermostatting superfluous at these lower pH values.

In the preliminary work, acetone was used as a convenient solvent for the sulphonyl halides. Systematic studies of other solvents showed that with benzene alone could larger light absorption values be achieved, but then only at higher temperature (60°), using *N* solutions of alkali hydroxide and with the formation of 2 layers.

TABLE II

LIGHT ABSORBANCE AT 395 nm

(20°; 3 min reaction time; 0.5 ml buffer pH 10 + 1 ml acetone + 0.5 ml pyridine + 38 μg *p*-toluenesulphonyl chloride in 1 ml acetone)

pH of buffer					
8	*9*	*10*	*11*	0.1 *N NaOH*	*N NaOH*
0.34	0.84	> 2.0	0.88	0.57	0.56

TABLE III

LIGHT ABSORBANCES AT 395 nm

(*ca.* 20°; 3 min reaction time; 0.3 ml buffer pH 10 + 0.4 ml water + 1 ml pyridine + 1.8 ml acetone + 6 or 16 μg sulphonyl chloride)

Sulphonyl chloride	*Position of maximum (nm)*	*Absorbance (16 μg)*	*Absorbance (6 μg)*	*Absorptivity (Molar)*
p-Toluene-	395	0.93	0.32	40,600
p-Chlorobenzene-	391	0.57	0.19	28,000
p-Bromobenzene-	395	0.33	0.105	20,000
p-Iodobenzene-	394	0.38	0.12	27,500
m-Nitrobenzene-	395			
β-Naphthalene-	397	0.62	0.22	31,700
Naphthalene-1,5-di-	396	0.44	0.15	33,000
Methane-	386			
Butane	387	0.05		1,370
ω-Toluene		Negligible light absorption		

The gain in sensitivity was considered not to compensate for the increased susceptibility to error and practical inconvenience of working at a higher, thermostatically controlled temperature. Acetone at room temperature and with the pH 10 buffer was therefore used and the buffer/solvent mixture finally chosen was prepared from 30 ml of buffer (pH 10), 40 ml of distilled water, 100 ml of pyridine and 80 ml of acetone.

Final procedure. To 2.5 ml of the buffer/solvent mixture was added 1 ml of an acetone solution of the sulphonyl halide. After shaking, this was left for 3 min and the absorbance then measured at the wavelength given in Table III.

The results were highly reproducible. Thus in 15 determinations with 5 μg of *p*-toluenesulphonyl chloride, all the absorbances lay between 0.274 and 0.276, except a single value of 0.278; for 10 μg, the extremes were 0.575 and 0.579. A good straight line was obtained between about 2 and 17 μg.

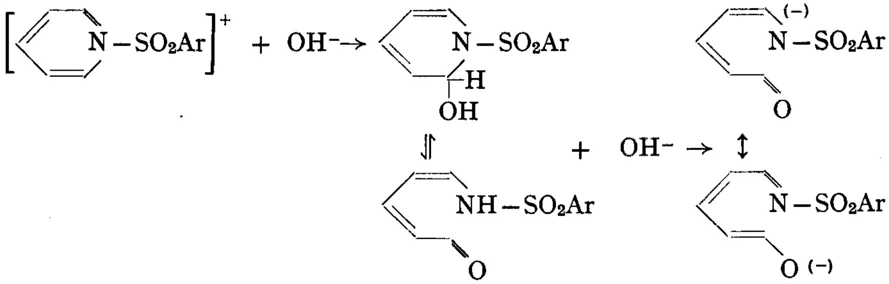
Several aromatic and aliphatic sulphonyl chlorides were investigated and straight lines were obtained for the former between about 4 and 30 µg. The 3 aliphatic compounds tried gave weak absorption values and flat curves. An idea of the various sensitivities can be obtained from Table III in which the absorbances for 6-µg and 16-µg samples and the molar absorptivities calculated for the original sulphonyl halide are given.

It was expected that interference would be caused by other compounds known to lead to pyridine ring fission in alkaline solution. In fact, under the less strongly alkaline conditions used, this did not occur. Neither chlorine, chloramine T, chloroform and other halides, nor benzoyl chloride interfered. Of the compounds studied, only ethyl *p*-toluenesulphonate gave a positive reaction and of course polynitro compounds interfered through their own absorption maxima near 400 nm. Neither hydrochloric nor the corresponding sulphonic acids interfered unless present in amounts which influenced the pH of the mixture.

DISCUSSION

The pyridine ring fission in alkaline solution with active halides has been the subject of considerable study. It seems generally accepted that the first step is the formation of a pyridinium compound, which, with a sulphonyl chloride would be:

We have prepared the compound where Ar equals *p*-toluene and found it to be identical with the compound of GEBAUER-FÜLNEGG AND RIESENFELD[4]. However, it gives no, or only a very weak, colour with alkali, which can probably be attributed to its rapid hydrolysis (as mentioned above, the sulphonyl chloride has to be added to the pyridine/alkali mixture). The salt cannot therefore be a definite intermediate, but simultaneous reaction with alkali, opening the ring, must occur. This may be formulated:

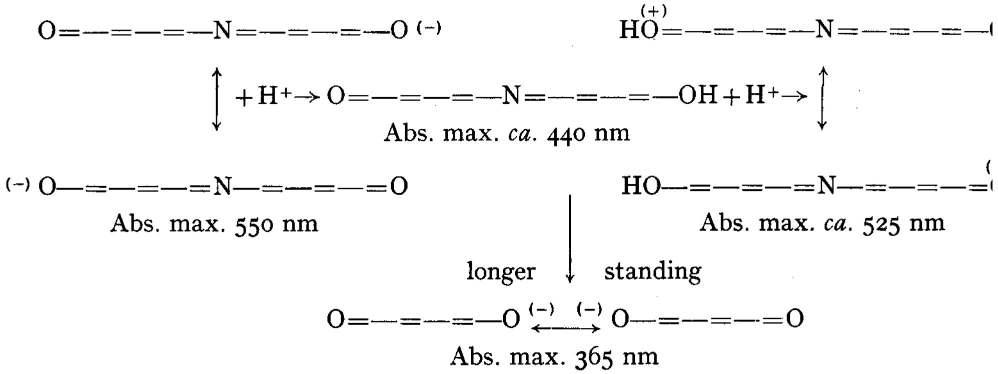


The nature of the species absorbing at *ca.* 435 nm is unclear but the last anion may be that absorbing at 395 nm. The influence of the different Ar groups may account for the small variations in the position of the maxima. Replacement of —N—SO$_2$Ar by —O gives glutacondialdehyde enolate, which is known to absorb at 365 nm. The 30-nm displacement is plausible and supports the above structure. Unfortunately, attempts to isolate the material absorbing at 395 nm failed, since it decomposes during the usual separation and purification procedures.

The species with an absorption maximum at 550 nm can very probably be formulated as:

$$\mathrm{O{=}{-}{=}{-}{=}{-}N{=}{-}{=}{-}{=}{-}O^{(-)} \leftrightarrow {}^{(-)}O{-}{=}{-}{=}{-}{=}N{-}{=}{-}{=}{-}{=}O}$$

SCHWARZENBACH AND WEBER[12] allotted this structure to the coloured product, absorbing at 550 nm, obtained by alkali treatment of a pyridine/bromine cyanide/diethylammonium perchlorate mixture. Further evidence of identity is that the pK values were found to be essentially the same and that the same changes in absorption maxima were observed on acidification and on longer standing; these changes were formulated by SCHWARZENBACH AND WEBER as follows:



Since the present work was concerned with the development of the quantitative methods, no systematic experimental study of the successive reaction products and of the mechanism was made.

SUMMARY

Two micromethods are described for the determination of sulphonyl halides, which depend on measurement of light absorption at *ca.* 395 and at 550 nm, respectively. These are the absorption maxima of products formed by reaction with pyridine in alkaline solution.

RÉSUMÉ

On décrit 2 microméthodes pour le dosage de sulfohalogénures, basées sur une mesure d'absorption à 395 et 550 nm respectivement; ce sont les maxima d'absorption des produits de réaction de la pyridine en solution alcaline.

ZUSAMMENFASSUNG

Es wurden zwei Mikromethoden zur Bestimmung von Sulfohalogeniden entwickelt, die auf Messungen der Lichtabsorption bei *ca.* 395 und bei 550 nm beruhen. Dies sind Absorptionsmaxima von Reaktionsprodukten, die durch Behandlung mit Pyridin in alkalischer Lösung entstehen.

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LE DOSAGE SPECTROPHOTOMETRIQUE DU COBALT DANS LE FER DE TRES HAUTE PURETE

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La spectrophotométrie du β-nitroso-α-naphtolate de cobalt dissous dans le chloroforme constitue une méthode de dosage classique de faibles quantités de cobalt[1,2]. Elle a été mise en oeuvre notamment dans le cas du fer et des aciers, mais les différentes longueurs d'onde proposées ne permettent pas de doser avec une bonne précision les teneurs inférieures à $5 \cdot 10^{-6}$ g même en opérant sur des prises d'essai très importantes et en utilisant des cuves de plusieurs centimètres d'épaisseur[3].

Nous avons donc été amenés à reprendre l'étude de cette méthode afin d'en améliorer si possible la sensibilité et de pouvoir ainsi déterminer la teneur en cobalt du fer de très haute pureté élaboré par fusion de zone, teneur qui est estimée inférieure à $5 \cdot 10^{-6}$ g. Nous avons étudié successivement la spectrophotométrie du β-nitroso-α-naphtolate de cobalt et l'interférence du fer dans le dosage du cobalt.

ÉTUDE SPECTROPHOTOMÉTRIQUE DU β-NITROSO-α-NAPHTOLATE DE COBALT

Le spectre d'absorption du β-nitroso-α-naphtolate de cobalt est bien connu dans l'intervalle de longueurs d'onde compris entre 350 et 700 nm[3]. Il présente 2 maximums d'absorption à 365 et 530 nm et c'est en général à l'une ou à l'autre de ces longueurs d'onde que s'effectue la détermination spectrophotométrique du cobalt.

L'utilisation d'une lampe à hydrogène comme source lumineuse nous a permis d'opérer à des longueurs d'onde inférieures à 350 nm, limite d'utilisation des lampes au tungstène couramment employées. Nous avons ainsi pu déterminer l'allure du spectre dans le domaine compris entre 200 et 700 nm en utilisant successivement une lampe à hydrogène et une lampe au tungstène comme sources lumineuses. La Fig. 1 représente le spectre obtenu avec une solution chloroformique de β-nitroso-α-naphtolate de cobalt à 0.8 μg de cobalt par millilitre contenue dans une cuve de 1 cm d'épaisseur (courbe A). Ce spectre présente à 308 nm un troisième maximum d'absorption dont l'existence n'avait pas été signalée jusqu'à présent.

Nous avons vérifié la validité de la loi de Beer pour cette longueur d'onde (Fig. 2) en adoptant les conditions opératoires indiquées plus loin et nous avons constaté que malgré une légère augmentation de l'absorption du blanc des réactifs (courbe B), le coefficient d'extinction molaire correspondant est notablement plus élevé qu'à 365 et 530 nm (Tableau I).

La spectrophotométrie du β-nitroso-α-naphtolate de cobalt à 308 nm permet donc d'effectuer la détermination de traces de cobalt avec une précision et une sensibilité notablement accrues. Dans les conditions opératoires utilisées 1 μg de

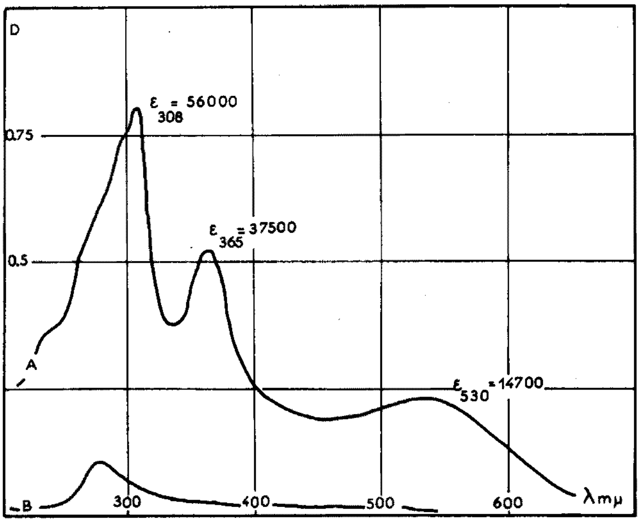

Fig. 1. Spectre d'absorption de β-nitroso-α-naphtolate de cobalt (solution chloroformique): courbe A. Courbe B: blanc des réactifs.

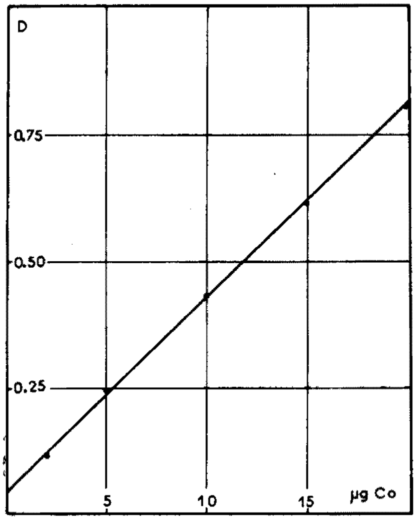

Fig. 2. Vérification de la loi de Beer.

TABLEAU I

VARIATION DU COEFFICIENT D'EXTINCTION MOLAIRE

λ (nm)	*Coefficient d'extinction molaire (ε)*
308	56,000
365	37,500
530	14,700

cobalt entraine une variation de densité optique de 0.038 et nous avons pu ainsi doser 20 μg de cobalt à 2.5% près et 2 μg à 10% près. C'est donc finalement cette méthode que nous avons mise en oeuvre pour doser le cobalt dans le fer de très haute pureté.

SÉPARATION DU FER

On sait que les ions fer(II) et fer(III) forment avec le β-nitroso-α-naphtol un complexe que l'on peut extraire par le chloroforme. Le dosage du cobalt par la méthode envisagée exige donc que le fer éventuellement présent soit ou complexé préalablement ou extrait.

Dans une étude préliminaire, nous avons tenté de complexer le fer(III) par le citrate trisodique, mais nous avons constaté que même en présence d'eau oxygénée une certaine quantité de fer était réduite par l'excès de β-nitroso-α-naphtol obligatoirement présent. La séparation du fer s'impose donc.

Parmi les techniques d'extraction utilisables[3,4] nous avons opté pour celle décrite par CLAASEN ET BASTINGS[5]. Elle consiste à séparer le fer(III) en milieu chlorhydrique 9 *N* par un mélange à parties égales de méthylisobutylcétone et d'acétate d'amyle. Le coefficient de partage est égal à 8,000 et des essais préliminaires nous ont montré que 2 extractions successives suffisent pour séparer 2 g de fer avec un rendement de 99.99%.

Nous avons enfin étudié le comportement du cobalt lors de cette extraction. D'après CLAASEN ET BASTINGS, pour 1 g de cobalt initialement présent 1 mg seulement est retenu dans la phase organique après extraction. Pour confirmer ce résultat, nous avons procédé à 2 types d'essais. Nous avons traité tout d'abord 100 ml d'acide chlorhydrique 9 *N* contenant, 5, 10, 15 et 20 *μg* de cobalt par les quantités de solvant nécessaires pour séparer 2 g de fer et nous avons enfin extrait le fer d'une solution contenant 2 g de fer et 5 *μg* de cobalt. Dans un cas comme dans l'autre nous avons dosé le cobalt restant dans la phase aqueuse.

TABLEAU II

COMPORTEMENT DU COBALT LORS DE L'EXTRACTION

Co ajouté (μg)	*Co trouvé (μg)*	*Ecarts*
5.0[a]	4.9	−0.1
10.0[a]	10.1	+0.1
15.0[a]	15.2	+0.2
20.0[a]	19.8	−0.2
5.0[b]	4.8	−0.2
5.0[b]	4.8	−0.2
5.0[b]	4.5	−0.5
5.0[b]	4.8	−0.2
5.0[b]	5.2	+0.2

[a] Ajouté dans 100 ml de HCl 9 *N*

[b] Ajouté à 2 g de fer.

TABLEAU III

RÉSULTATS OBTENUS POUR L'ACIER NBS NO. 55E

Prise d'essai	*% Co*
1	0.0062
	0.0072
2	0.0062
	0.0062
	Valeur moyenne: 0.0065%

Les différents résultats obtenus (Tableau II) sont satisfaisants. La méthode d'extraction du fer par le mélange méthylisobutylcétone et acétate d'amyle convient donc parfaitement pour séparer des traces de cobalt d'une très grande quantité de fer.

MODE OPÉRATOIRE

Réactifs

Solution de cobalt. 1 μg/ml en milieu nitrique 0.1 *N*.

Solution de β-nitroso-α-naphtol. On dissout 1 g de β-nitroso-α-naphtol dans 100 ml d'acide acétique pur. On ajoute 1 g de charbon actif. On agite et on filtre.

Solution purifiée de citrate trisodique de sodium. A 400 g de citrate trisodique dissous dans 800 ml d'eau distillée, on ajoute 100 g de nitrate de sodium. On amène à pH neutre par addition de soude *N*. On transvase en ampoule à décanter de 2 l et on ajoute 10 ml d'eau oxygénée à 110 volumes. Après agitation on ajoute 200 mg de β-nitroso-α-naphtol dissous dans 10 ml d'acide acétique. On agite pendant quelques minutes puis on laisse reposer 24 h. On procède ensuite à des extractions successives par 25 ml de chloroforme pur jusqu'à obtention d'une phase chloroformique incolore.

Blanc d'acides. Au 100 ml d'eau distillée, on ajoute 20 ml d'acide perchlorique 10 *N* et 15 ml d'acide nitrique 14 *N*. On amène à 200 ml par addition d'eau distillée.

Mise en solution de l'échantillon

On attaque 2 g d'échantillon par 50 ml d'acide chlorhydrique 9 *N* et 5 ml d'eau oxygénée à 110 volumes. Après dissolution on ajoute de l'acide nitrique 14 *N* goutte à goutte jusqu'à cessation de l'effervescence, puis un excès de 5 ml. On évapore à siccité. On reprend par HCl 9 *N* et on évapore à nouveau à siccité. On reprend finalement par 75 ml de HCl 9 *N* en chauffant au bain marie jusqu'à dissolution complète. On laisse refroidir.

Extraction du fer

On transvase la solution d'attaque dans une ampoule à décanter de 500 ml. On rince le bécher dans lequel l'attaque a eu lieu avec 25 ml d'acide chlorhydrique 9 *N*. On ajoute ensuite par fractions successives et en agitant 100 ml du mélange méthylisobutylcétone–acétate d'amyle (50:50). On agite vigoureusement pendant 30 sec. Après décantation on recueille la phase aqueuse dans une ampoule à décanter de 500 ml et on refait une deuxième extraction dans les mêmes conditions. On transvase la phase aqueuse dans un bécher de 500 ml.

On réunit les 2 phases organiques obtenues et on procède à la récupération du cobalt éventuellement entrainé. On ajoute pour cela 50 ml d'acide chlorhydrique 9 *N*. On agite pendant 30 sec, on laisse reposer et on recueille la phase aqueuse. On recommence cette opération 3 fois de suite. On réunit les trois phases aqueuses ainsi obtenues et on ajoute 20 ml du mélange méthylisobutylcétone–acétate d'amyle. On agite et après décantation on recueille la phase aqueuse et on la joint à celle obtenue lors de la première série d'extractions. On lave encore une fois la phase organique par 20 ml de HCl 9 *N* et on réunit finalement toutes les phases aqueuses.

Pour éliminer les solvants organiques éventuellement dissous on évapore la solution jusqu'à ce que le volume soit réduit à 5 ml environ. On ajoute dans l'ordre 5 ml d'acide nitrique et 5 ml d'acide perchlorique. On chauffe jusqu'à ce que la solution se soit clarifiée et que la majeure partie de l'acide perchlorique soit éliminée. On reprend par 20 ml d'acide nitrique *N*.

Détermination du cobalt

Tracé de la courbe d'étalonnage. Dans 6 béchers de 250 ml contenant chacun 20 ml du mélange blanc d'acides, on ajoute 0, 2, 5, 10, 15 et 20 ml de la solution contenant 1 µg de cobalt par ml puis respectivement 20, 18, 15, 10, 5 et 0 ml d'eau distillée. On amène à pH 3–4 à l'aide de la solution tampon de citrate trisodique purifié. On transvase en ampoule à décanter de 250 ml. On rince les béchers avec 2 fois 10 ml d'eau distillée et on ajoute dans chaque ampoule 10 ml d'eau oxygénée à 20 volumes.

On agite et on ajoute immédiatement 5 ml de la solution de β-nitroso-α-naphtol. On agite à nouveau pendant 3 min et on laisse reposer 12 h.

On procède ensuite à 2 extractions successives à l'aide de 15 puis 5 ml de chloroforme. On recueille les 2 phases organiques dans une ampoule à décanter de 100 ml contenant 20 ml de HCl 2 *N*. Ce lavage acide est destiné à éliminer les traces de nickel éventuellement présentes. On recueille à nouveau la phase organique dans une ampoule à décanter de 100 ml et on la lave plusieurs fois de suite avec 20 ml de soude 2 *N* pour éliminer l'excès de β-nitroso-α-naphtol. Trois à quatre lavages suffisent en général pour obtenir une phase aqueuse incolore. On recueille finalement la phase organique dans des ballons jaugés de 25 ml et on ajuste ce volume avec du chloroforme.

On a ainsi réalisé une gamme étalon de 0 à 20 μg/ml de cobalt.

On homogénéise et on filtre sur papier sans graisse. On procède finalement à la détermination spectrophotométrique en mesurant les densités optiques par rapport au chloroforme à 308 nm avec des cuves de 1 cm d'épaisseur.

Dosage du cobalt. Pour la détermination du cobalt dans le fer ou dans les aciers faiblement alliés, on opère exactement comme lors de l'établissement de la courbe d'étalonnage en tenant compte du blanc des réactifs.

RÉSULTATS

Afin de vérifier la validité de la méthode proposée, nous avons tout d'abord dosé le cobalt dans un acier NBS no. 55E, dont la teneur en cobalt déterminée par ailleurs est de 0.0066% ±0.0014. Le Tableau III rend compte des résultats obtenus. Les valeurs trouvées concordant bien avec les valeurs annoncées par le certificat d'étalonnage, nous avons enfin utilisé la méthode proposée pour doser les microquantités de cobalt contenues dans le fer purifié par fusion de zone, en ajoutant des quantités connues de cobalt.

Les résultats obtenus figurent au Tableau IV.

TABLEAU IV

Prise d'essai	*Co ajouté (μg)*	*Co trouvé (μg)*	*Co dans l'échantillon (%)*
1	0	5.9	0.00029
2	5.0	10.3	0.00026
3	5.0	10.7	0.00028
4	10.0	14.9	0.00024
5	10.0	14.8	0.00024
		Valeur moyenne:	0.00026%

RÉSUMÉ

L'étude spectrophotométrique du complexe formé par le β-nitroso-α-naphtol et le cobalt entre 200 et 350 nm a permis de mettre en évidence l'existence à 308 nm d'un maximum d'absorption très sensible. L'utilisation de cette longueur d'onde permet de doser des quantités de cobalt de $1 \cdot 10^{-6}$ à $10 \cdot 10^{-6}$ g avec une bonne

précision. La méthode proposée convient parfaitement bien pour la détermination du cobalt dans le fer de très haute pureté.

SUMMARY

A spectrophotometric study of the cobalt–β-nitroso-α-naphthol complex between 200 and 350 nm showed the existence of a very sensitive absorption maximum at 308 nm. Utilization of this wavelength allows cobalt in the range 10^{-6}–10^{-5} g to be determined with good precision. The proposed method is very suitable for the determination of cobalt in high-purity iron.

ZUSAMMENFASSUNG

Der Kobalt–β-Nitroso-α-naphthol-Komplex besitzt bei 308 nm ein sehr empfindliches Absorptionsmaximum. Die Verwendung dieser Wellenlänge erlaubt die spektralphotometrische Bestimmung des Kobalts im Bereich von 10^{-6}–10^{-5} g. Die vorgeschlagene Methode ist für die Bestimmung von Kobalt in hochreinem Eisen sehr geeignet.

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THE SEPARATION OF FISSION PRODUCTS BY ELECTROPHORETIC FOCUSSING OF IONS

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The quantitative determination of fission products in nuclear fuels is important for the control of the uranium "burn-up" and also during the reprocessing of fuel elements. For the control of the burn-up it is often desirable to determine several fission products, whereas during the reprocessing, the decontamination factor from the long-lived fission products is required. In principle, 2 different approaches can be used: non-destructive γ-spectrometric determination of the fission products from the complex γ-spectrum or chemical separation of the individual species. Both procedures have a number of inherent shortcomings. Owing to the poor resolution of sodium iodide–thallium scintillators the accuracy of the non-destructive procedure is often unsatisfactory and pure β-emitters cannot be determined, whereas the chemical separations are time-consuming, because of the complex nature of the fission product mixture. Different authors have investigated fast separation procedures by chromatographic or electrophoretic techniques[1-6]. In comparison with electrofocussing of ions (E.F.I.) they are however time-consuming and do not succeed in separating completely all the long-lived fission products from each other. SCHUMACHER[7] attempted to separate a number of fission products, namely lanthanum, strontium and barium, by E.F.I. The same technique was used by SHINAGAWA AND KISO[8], but they did not achieve a quantitative separation of all the fission products. As E.F.I. is a fast quantitative separation technique, it seemed worthwhile to apply it to a separation of all the most important long-lived fission products, *i.e.* $^{90}Sr + ^{90}Y$, ^{91}Y, $^{95}Zr + ^{95}Nb$, $^{103+106}Ru$, ^{137}Cs and $^{141}Ce + ^{144}Ce$, as these nuclides make up the main activity after a cooling period of 3 months or more. In this paper zirconium–niobium and ruthenium are not considered, as their behaviour is complex and will be dealt with subsequently.

Principles of E.F.I.

SCHUMACHER has described in detail the principles of E.F.I. separations[9,10]. The technique is mainly based on paper electrophoresis of cations in a gradient of a complexing agent. This is achieved by using a ligand in the cathode compartment and a complex destroyer, *e.g.* an acid, in the anode compartment. After spotting the solution in the center of a paper strip, the anodic and cathodic solutions are allowed to diffuse towards the applied zone and an electric voltage of several hundred volts is applied. After a few minutes sharp focusses are obtained, whose locations depend upon the shape of the complex gradient and the stability constants of the complexes. As the

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current is of the order of 10 mA, cooling is required. This is achieved by immersing the paper strip in carbon tetrachloride, stirred by means of a magnetic stirrer. A diagram of the apparatus is given in Fig. 1.

Choice of experimental conditions

In the long-lived fission products mixture, 2 rare earths occur, namely Y and Ce. As SCHUMACHER[11] has already described a separation of rare earths, using nitrilotriacetic acid (NTA) as cathodic electrolyte, this ligand seemed an obvious choice. To this ligand, used as a 0.08 *M* solution of the diammonium salt, 0.06 *M* sodium acetate was added to achieve a sharper separation of strontium from cesium. Hydrochloric acid (0.5 *M*) was chosen as the anodic electrolyte. It would of course be more practical to use nitric acid, as fuel elements are usually dissolved in this acid. Nitric acid however causes difficulties in the focussing of cerium, probably owing to oxidation of cerium(III) to cerium(IV) and gives rise to double focusses of this element. Thus after removal of the nitric acid, the residue is dissolved in hydrochloric acid, taken to dryness again and redissolved in 0.08 *M* NTA adjusted to pH 7 with ammonia solution. A lower pH appears to give higher cross-contaminations of the fission products especially in the separation of cerium from yttrium. It also appeared that, in the presence of uranium, carrier-free fission products are not focussed very sharply and stay in the applied zone together with the broad uranium focus. This interference can be avoided by an adequate addition of carriers, namely 10 μg per element in 25 μl of applied solution. The carrier solution is added before the removal of the nitric acid.

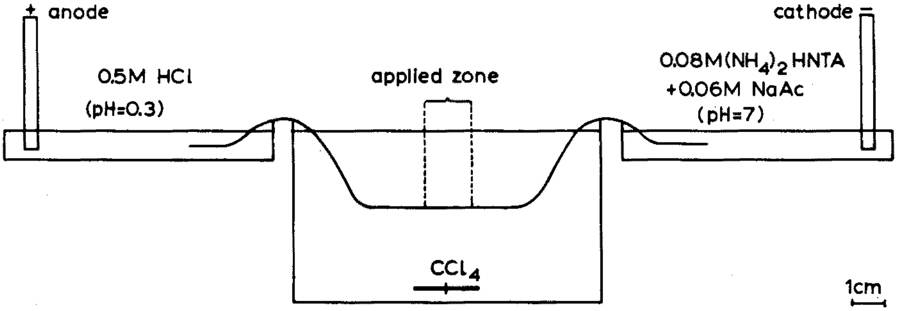

Fig. 1. Apparatus for E.F.I.

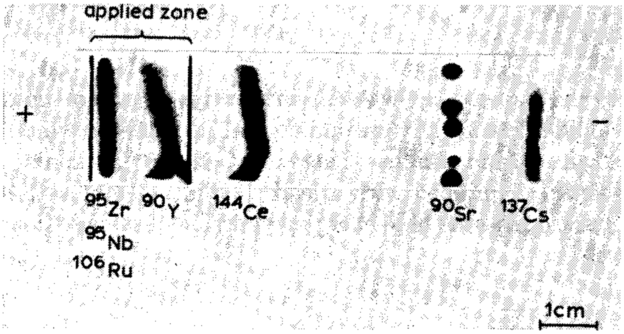

Fig. 2. Autoradiogram of separated ions.

If 500 V is applied during 6–10 min a quantitative separation is obtained. A typical autoradiogram of a Y–Ce–Sr–Cs separation is given in Fig. 2. It should be noted that under these conditions Zr–Nb–Ru give rise to a single focus at the left, *i.e.* more anodic than Y, the cross-contamination being negligible as appears from Fig. 3.

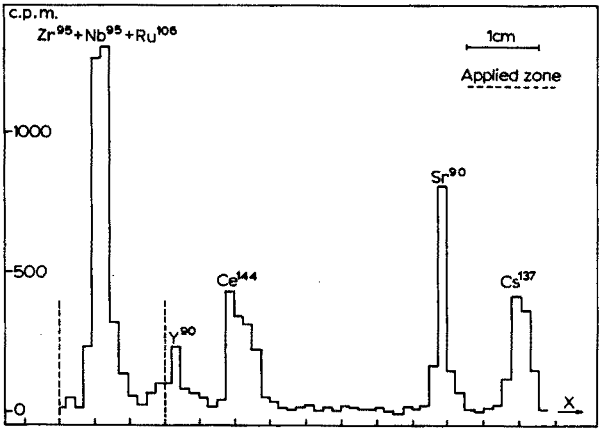

Fig. 3. Cross-contamination of focusses.

Measurements

To identify the focusses, the paper strip was cut into strips of 1 mm and counted in a well-type sodium iodide detector. Strontium-90 and yttrium-90, which are pure β-emitters were counted with an end-window (2 mg/cm^2) G.M.-tube. Scanning the paper strips under a G.M.-counter equipped with a lead slit did not give satisfactory results as broadening occurs, due to the high energy γ-emission of some fission products.

EXPERIMENTAL

Procedure for E.F.I.

Add to *ca.* 1 μc of a nitric acid solution of a fuel element, containing no more than 200 mg of uranium, 1 mg each of the following carriers: Zr, Nb, Ru, Y, Ce, Sr and Cs. Zirconium and niobium are added as aqueous solutions of the NTA complexes, the others as the chlorides. Add 10 ml of 12 *M* hydrochloric acid and take to dryness on a hot plate. Dissolve the residue in 10 ml of 12 *M* hydrochloric acid, take again to dryness and treat the residue with 20 ml of a 0.08 *M* solution of the diammonium salt of NTA. Adjust to pH 7 with ammonia solution. Boil for 1 h under reflux and dilute to 25 ml. Spot 25 μl on a paper strip, Whatman no. 1, 22 × 2 cm. Place the ends of the strip in the cathode and anode compartments and immerse the central part in the carbon tetrachloride cell. Allow the anode and cathode solutions to diffuse to the applied zone. Apply the 500-V potential to the platinum electrodes during 6–10 min. Stir the carbon tetrachloride solution by means of the magnetic stirrer to provide more efficient cooling. Remove the paper strip and dry under a warm air blower. The detection of the focusses is done by autoradiography or by counting.

Autoradiography

Place the paper strip on Gevaert Scientia film Structure X and expose for 4 to 12 h. Develop in Gevaert 251 for 4 min.

Counting

Cut the paper strip into pieces of 1–3 mm width. Place the pieces into counting vials for counting the γ-emitters or mount on planchets for G.M.-counting in the case of pure β-emitters. Purity checks of the focusses were done by γ-spectrometry with a 400-channel analyser.

DISCUSSION

As can be seen from Figs. 2 and 3, clearly defined focusses are obtained of the fission products Cs, Sr, Ce, Y and the mixture Zr–Nb–Ru. The uranium can be located visually as a rather broad zone of up to 1 cm situated between the focusses of Y and Zr+Nb+Ru. As also appears from Figs. 2 and 3, the distances between the focusses are respectively Zr+Nb+Ru–Y: 1 cm; Y–Ce: 1–1.5 cm; Ce–Sr: 3.5 cm; Sr–Cs: 1.5 cm. The purity of the different focusses was checked by γ-spectrometry, referring to the pure nuclides. The results are given in Table I.

TABLE I

CROSS-CONTAMINATION OF THE FOCUSSES

Focus	*Nuclide*	*% Found*	*Standard deviation*
Zr + Nb + Ru	^{144}Ce	4.2	2.2
	^{106}Ru	99.2	2.5
	^{95}Zr + ^{95}Nb	98.4	1.4
Y[a]	^{144}Ce	4.7	1.8
	^{106}Ru	1.3	1.8
	^{95}Zr + ^{95}Nb	0.0	0.6
Ce	^{144}Ce	91.1	2.3
	^{106}Ru	−0.5	1.8
	^{95}Zr + ^{95}Nb	1.5	0.7

[a] Cross-contaminations measured after decay of ^{90}Y.

It appears from Table I that the cross-contaminations are practically within the computed standard deviations, except for cerium where a slight cross-contamination occurs in the Zr+Nb+Ru and yttrium focusses.

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SUMMARY

Electrophoretic focussing of ions was applied to the separation of the long-lived fission products Zr, Nb, Ru, Y, Ce, Sr and Cs. With hydrochloric acid and nitrilotriacetic acid as the anodic and cathodic electrolytes respectively, a quantitative separation could be obtained, but Zr+Nb+Ru was left as one focus. Detection of the nuclides was by autoradiography or by γ- and β-counting.

RÉSUMÉ

Une méthode de focalisation électrophorétique d'ions est proposée pour la séparation de produits de fission de longues périodes: Zr, Nb, Ru, Y, Ce, Sr et Cs. On peut obtenir une séparation quantitative avec l'acide chlorhydrique et l'acide nitrilotriacétique comme électrolytes respectivement anodique et cathodique (à l'exception de Zr+Nb+Ru). La détection des nuclides se fait par autoradiographie ou par comptage γ et β.

ZUSAMMENFASSUNG

Es wurde die elektrophoretische Fokussierung von Ionen bei der Trennung folgender langlebiger Spaltprodukte angewandt: Zr, Nb, Ru, Y, Ce, Sr und Cs. Mit Salzsäure und Nitrilotriessigsäure als anodischer bzw. kathodischer Elektrolyt gelang es, eine quantitative Trennung zu erhalten, jedoch blieben Zr+Nb+Ru als ein Fokus zurück. Der Nachweis der Nuklide geschah durch Autoradiographie oder durch γ- und β-Zählung.

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THE METHOD OF CONCENTRATION-DEPENDENT DISTRIBUTION IN THE QUANTITATIVE USE OF RADIOISOTOPES

PART III. THE DETERMINATION OF SUBMICROGRAM AMOUNTS OF CAESIUM BY EXTRACTION WITH CALCIUM DIPICRYLAMINATE INTO NITROBENZENE

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The essential features and theory of the method of concentration-dependent distribution in the use of radioisotopes, as well as its utilization for a sorption system, have been presented in the preceding papers[1,2].

In the present paper this method is applied to the extraction of caesium dipicrylaminate[3-5] into nitrobenzene. The system mentioned is suitable for the application of this method for several reasons. First, the concentration of the reagent required to reach the appropriate distribution ratio of caesium is so high (10^{-7} to 10^{-4} *M*) that the method of isolating equal amounts[1,6] (the "substoichiometric principle" in isotopic dilution method—henceforth designated as method I) cannot be used for the determination of microgram amounts. However, this reagent concentration is low enough to allow a concentration-dependent distribution method (method II) to be applied Secondly, with this extraction system, a pH region (pH 9–13) exists where the distribution ratio of caesium is independent of pH, which is very important[1] for reproducibility. Moreover, a suitable carrier-free radioisotope (^{137}Cs) is available, so that the specific activity will not be a factor limiting the sensitivity of the determination. It is also worth noting that no sensitive determination of caesium by method I has as yet been proposed[7].

The present work was designed to establish which dipicrylaminate and hydroxide give the highest values of the distribution ratio q_{Cs} at pH *ca.* 10; to establish calibration curves for the estimation of caesium; to compare the sensitivity and reproducibility of methods I and II and of the radiometric titration method; and to develop a method for the determination of caesium in the presence of large amounts of sodium, potassium, calcium and barium after a preliminary separation of caesium by the polyiodide extraction method.

EXPERIMENTAL

Chemicals

All chemicals used were of analytical-reagent grade purity. The stock solutions of inactive caesium were prepared from caesium chloride (product of "Lachema"). Calcium and sodium dipicrylaminates were prepared by heating an excess of dipicrylamine (product of "Chemapol") with the solution of calcium or sodium hydroxide for 4 h; the unreacted dipicrylamine was filtered off and the respective salts were crystallized out.

Methods

Counting was performed as previously described[3]. The pH was measured by a pH meter.

Equal volumes (2 ml each) of the aqueous phase and nitrobenzene were usually used for the extractions. The aqueous phase contained inactive and radioactive caesium and usually calcium hydroxide also; the required amounts of calcium or sodium dipicrylaminate were previously dissolved in nitrobenzene. The mixture was shaken for 30 min. Each point of the radiometric titration curve was obtained from one extraction experiment so that it was possible to keep the volume ratio of both phases exactly at the value of 1:1; the aqueous phase was always 0.01 *M* in calcium hydroxide for these experiments.

Procedure. Add diluted hydriodic acid to the solution containing 5–100 p.p.m. of caesium in sodium, calcium, lithium, barium or strontium, to give a final concentration of 1 *M* in cation and 0.07 *M* in HI, and then label with ^{137}Cs. Shake 2 ml of this solution with 1 ml of 0.07 *M* iodide in nitrobenzene. Discard the aqueous phase (with a loss of caesium of about 4%). Add 2 ml of 1 *M* hydrochloric acid, shake, and discard the aqueous phase containing the rest of the unwanted cation (8% loss of Cs). Scrub the organic phase with 6 ml of distilled water (3% loss of Cs). Dilute the organic phase with 3 ml of diethyl ether and re-extract caesium into 2 ml of distilled water. Discard the organic phase (0.1% loss of Cs), add a sufficient amount of calcium hydroxide to an aliquot (1.8 ml) of the aqueous phase to give a final concentration of 0.01 *M* of calcium ion. Agitate 3 ml of this solution with 3 ml of a $5 \cdot 10^{-6}$ *M* $Ca(DPA)_2$ solution in nitrobenzene, which has previously been equilibrated with 0.01 *M* calcium hydroxide. Take equal aliquots for the activity counting and evaluate q_{Cs}. Plot these values as a function of the initial concentration of caesium in the original sample. If an excess of potassium is present, adjust the solutions containing 0.5–10% of caesium in potassium to $1 \cdot 10^{-3}$ *M* in potassium and proceed as described above.

RESULTS

It has already been reported[3,4] that above pH 9 and at low concentrations of dipicrylaminate, the value of the equilibrium constant K_{Me}^{Cs} of the reaction

$$Cs_{(a)}^{+} + Me_{(org)}^{+} \rightleftharpoons Cs_{(org)}^{+} + Me_{(a)} \text{ (where } Me^{+} = Li^{+}, Na^{+}, K^{+}, Rb^{+}\text{)}$$

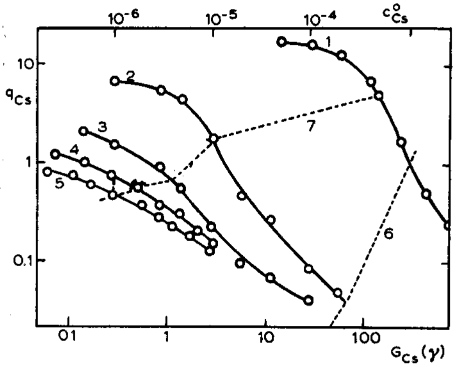
controls the partition ratio of caesium between the aqueous phase and the solution of dipicrylaminate in nitrobenzene.

The values of K_{Me}^{Cs} diminish from lithium to rubidium ($K_{Li}^{Cs} \doteq 1 \cdot 10^4$; $K_{Rb}^{Cs} \doteq 6$). Therefore, the use of lithium hydroxide and lithium dipicrylaminate seemed to be most promising. Hydroxides of magnesium, calcium, strontium and barium were also examined in the present work and calcium proved most suitable. For example, the following values of q_{Cs} were obtained: 3.8, 13, 25, 20 and 14 for Na, Li, Ca, Sr and Ba respectively, in a system with $1 \cdot 10^{-4}$ *M* dipicrylaminate ion, $1.53 \cdot 10^{-3}$ *M* Na^+, $3 \cdot 10^{-2}$ *N* Me^+ or Me^{2+} at pH 10.

The calcium compounds were therefore mainly used in later work. However, the extraction mechanism in the presence of calcium ions has not been quantitatively investigated, so that no value of the sensitivity can be estimated theoretically. Our experimental results on the extraction of traces of caesium (v_a:v_o = 1:1; pH = 10; $[Ca^{2+}] = 0.01$ *M*) fit the following empirical relationship:

$$\log q_{Cs} = 0.70 \log c_{DPA} + 4.65$$

where c_{DPA} is the initial molar concentration of dipicrylaminate in the organic phase. Consequently, about $4 \cdot 10^{-6}$ *M* (Ca/2)·DPA is needed for $q_{Cs} = 1$. Concentrations of the reagent from $1 \cdot 10^{-6}$ *M* upwards were therefore used to investigate the extraction of caesium as a function of its initial concentration while keeping the initial concentration of the reagent, the pH, temperature, etc. constant. The calibration curves are shown in Fig. 1, where the limits for the substoichiometric region ($G_{DPA} = G_{Cs}$) and method I (a constant equilibrium concentration of caesium in the organic phase) are also indicated. It can be seen, that the sensitivity of method II is by about 2 orders of magnitude higher than for method I and that the estimation is in principle possible even in the superstoichiometric region.



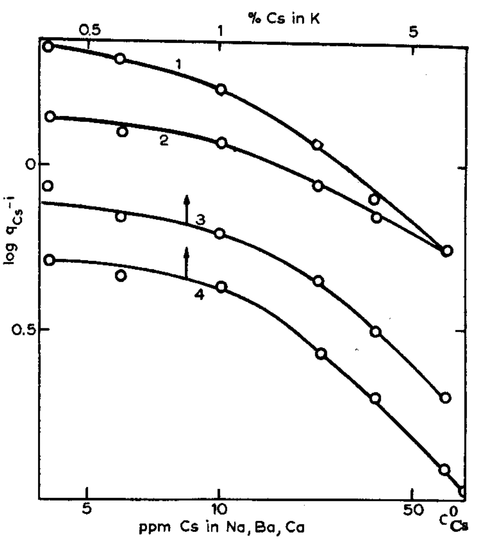


Fig. 1. The calibration curves for the determination of caesium. G_{Cs}, the initial amount of caesium in 2 ml of aqueous phase; c^0_{Cs}, the initial concn. of caesium in the organic phase in moles per litre; pH = 10. (*1*) $5 \cdot 10^{-4}$ *M* NaDPA; 0.01 *M* NaOH (the initial concentrations); (*2*) $1 \cdot 10^{-5}$ *M* Ca/2 DPA; $1 \cdot 10^{-2}$ *M* $Ca(OH)_2$; (*3*) $4 \cdot 10^{-6}$ *M* Ca/2 DPA; $1 \cdot 10^{-2}$ *N* $Ca(OH)_2$; (*4*) $1 \cdot 10^{-6}$ *M* Ca/2 DPA; $5 \cdot 10^{-3}$ *N* $Ca(OH)_2$; (*5*) as sub 4, 6°; (*6*) the applicability limits for the method I; (*7*) the limits for the superstoichiometry.

Fig. 2. The calibration curves for the determination of caesium after separation. i, the shift of individual curves along the y axis for the sake of greater clarity. (*1*) Ca, i = 0; (*2*) K, i = 0; (*3*) Ba, i = 0.5; (*4*) Na, i = 0.7. (In reality, curves 1, 3 and 4 are nearly identical.)

The shapes of the calibration curves, including the inflexions for higher concentration, are in qualitative agreement with the theory[1], though the actual extraction mechanism is probably not in full accordance with the assumptions used in the calculation. Moreover, for the extraction at 6° the curves are shifted towards higher q_{Cs} values in accordance with the published results[5].

Radiometric titration curves were prepared for 2 concentrations of caesium chloride ($1 \cdot 10^{-3}$ *M* and $5 \cdot 10^{-3}$ *M*) at pH 10 in presence of $5 \cdot 10^{-3}$ *N* calcium hydroxide. The determination of the equivalence point was rather difficult even at a concentration of $1 \cdot 10^{-3}$ *M* Cs, so that the sensitivity was about 3 orders of magnitude lower for the radiometric titration than for method II.

The dependence of the reproducibility of the distribution ratio upon the concentration of caesium was investigated. It became apparent that the reproducibility was mainly influenced not by the distance of the point from the "stoichiometry curve", but rather by the value of q_{Cs} (which decreased with decreasing q_{Cs} in the range $1 > q_{Cs} > 10^{-2}$). For this reason the utilization of the calibration curve corresponding to an initial concentration of reagent which equals 20–60% of the expected concentration of caesium can be recommended.

The standard deviation of the mean of 3 estimations of caesium concentration varied within 3–10% depending on the q_{Cs} value in question. The accuracy of the determination could be increased by using larger phase volumes when sufficient sample was available.

The selectivity of the method is given in principle by the value of the equilibrium constants such as K_{Me}^{Cs}. The change in the value of q_{Cs} caused by a foreign cation increases as the initial concentration ratio of caesium to dipicrylaminate decreases (Fig. 2, curve 2). When this ratio has a value of 2, the value of q_{Cs} is reduced by 20% if the molar ratio of the cation to caesium is 150, 2 and 0.5 for sodium, potassium and rubidium, respectively.

It is clear from these results that a preliminary separation is necessary if larger amounts of other cations are present. For this purpose, preliminary extraction of caesium with polyiodide[8–10] was chosen because of its simplicity, reproducibility and convenience. Back-extraction of caesium into water was found to be feasible provided that nitrobenzene was diluted with a less polar solvent so that polyiodides would be retained in the organic phase; diethyl ether and amyl alcohol were very suitable diluents, giving a residual aqueous phase of pH 3.4 (q_{Cs} *ca.* 10^{-2}).

The calibration curves obtained after the preliminary separation are shown in Fig. 2. The reproducibility of these curves was practically the same as for pure caesium, which indicates that the losses of caesium, and possibly the amounts of the foreign cation remaining (mainly potassium) are readily reproducible.

As the extraction of caesium polyiodides is fairly selective, this method can be used for the determination of caesium in the presence of many cations. Ammonium ions would probably interfere like potassium, and only rubidium and thallium ions would interfere to a greater extent[3,10].

The time required for an analysis depends on the time required to establish each of the distribution equilibria mentioned. This is affected mainly by the mode of mixing and can be reduced to 1–5 min for one equilibration.

The method proposed (without the separation of polyiodides) was applied to the estimation of carrier concentration (100 μg in one separation) in a preparation of ^{134}Cs. The results were in good agreement with the data supplied by the manufacturers and with the results of an independent estimation by means of sorption on paper discs impregnated with Prussian blue[2].

The latter method[2] offers the advantage of greater sensitivity and selectivity than the method described herein, but the dipicrylaminate extraction method is considered superior if a small number of samples containing approximately $1 \cdot 10^{-4}\,M$ Cs^+ in the absence of rubidium is to be analysed, because the preparation of impregnated paper discs is time-consuming.

SUMMARY

The dependence of the partition ratio of caesium between a nitrobenzene solution of calcium dipicrylaminate on the total amount of caesium in the system can be used as an analytical calibration curve. An appropriate method of isolating caesium for this determination was worked out using the polyiodide extraction of caesium. The selectivity, sensitivity and accuracy of the method were evaluated.

RÉSUMÉ

La relation du coefficient de partage du césium entre une solution de dipicrylaminate de calcium dans le nitrobenzène et la teneur en césium du système peut être utilisé comme courbe d'étalonnage analytique. Une méthode appropriée de séparation du césium pour ce dosage est mise au point, utilisant l'extraction à l'aide de polyiodure. On a évalué la sélectivité, la sensibilité et l'exactitude de ce procédé.

ZUSAMMENFASSUNG

Die Abhängigkeit des Verteilungsverhältnisses von Cäsium zwischen Nitrobenzol mit Calciumdipicrylaminat und wässriger Lösung von der Gesamtkonzentration des Cäsiums kann als analytische Eichkurve verwendet werden. Es wurde eine angemessene Methode zur Isolierung des Cäsiums unter Verwendung der Polyjodid-Extraktion für diese Bestimmung ausgearbeitet. Die Selektivität, Empfindlichkeit und Genauigkeit der Methode wurde abgeschätzt.

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THE DETERMINATION OF MOLYBDENUM IN NATURAL WATERS, SILICATES AND BIOLOGICAL MATERIALS

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In the last few years interest in the marine geochemistry and biogeochemistry of many trace elements has increased. Our knowledge of the marine chemistry of molybdenum is very fragmentary and much of the available information is unreliable owing to the use of inaccurate analytical procedures. A reinvestigation of the problem is being carried out in these laboratories and this paper describes the development of analytical methods for the determination of the element in sea water, sediments and biological materials.

The results of earlier determinations of molybdenum in sea water are summarized in Table I. It is probable that most of the variations in the more recent figures are caused by analytical error. Since the concentration of molybdenum in sea water is too low for direct determination, it is necessary to concentrate the element before determination. For this purpose solvent extraction, coprecipitation and cocrystallization have been used, the determinations being completed either spectrographically or spectrophotometrically.

TABLE I

DETERMINATIONS OF MOLYBDENUM IN SEA WATER

Origin of water	*Concentration found (μg/l)*	*Method of concentration*	*Method of determination*	*Reference*
North Atlantic	0.5–1	Coprecipitated with ferric hydroxide	Spectrographic	1
Atlantic	2	Coprecipitated	Spectrographic	2
Gullmarfjord	0.4	Coprecipitated with mercuric sulphide	Spectrographic	3
English Channel	12–16	Coprecipitated with	Spectrographic	4
West Atlantic	6–14	tannin + oxine + thionalide + Fe^{3+} + Al^{3+}		5
Pacific	9–13	Coprecipitated with ferric hydroxide	Photometric with thiocyanate; or with dithiol	6,7 8
Pacific, Atlantic and Indian Ocean	9.6–12.5	Coprecipitated with manganese dioxide	Photometric with thiocyanate	9,10 11
Pacific	12.2	Cocrystallized with α-benzoinoxime	Photometric with thiocyanate	12
Atlantic	3.9	Extracted as diethyl dithiocarbamate	Spectrographic	13

The concentrations of molybdenum present in most rocks are close to the normal limits of spectrographic detection if preliminary concentration is not employed. A number of photometric methods have been described for the determination of the element in silicate rocks; in most of these, the sample is opened up by an alkaline fusion. After digestion with water and filtration, the molybdenum is determined photometrically. If the determination is carried out by extraction of the molybdenum–thiocyanate complex[14,15], no separation of molybdenum from other elements is normally employed; however, the precision of the method is only poor (*ca.* ±10% at a molybdenum level of *ca.* 3 μg/g). When the dithiol extraction procedure is used for the photometric determination of molybdenum in the alkaline digest, it is usually necessary to remove silica by evaporation with acid. Although procedures have been described for direct photometry[16,17] it is probably advisable to separate molybdenum, for example by extraction as the α-benzoinoxime complex[18–20], since a number of elements interfere in the photometric procedure[21,22].

Interest in the biochemical role of molybdenum has quickened since it was realized that it plays an important role in the bacterial fixation of nitrogen. Direct spectrographic methods are barely sensitive enough for the determination of molybdenum in the ashes of marine plants, but they have been employed after preliminary concentration[4]. FUKAI AND MEINKE[23] have employed neutron activation techniques for the determination of molybdenum in marine organisms. A number of photometric procedures have been described for the determination of the element in the ashes of plants; in most of these, the element is concentrated and separated from other elements by solvent extraction, *e.g.* of the complexes with α-benzoinoxime[24–26] or cupferron[27,28]. After destruction of the organic matter molybdenum is determined photometrically by either the thiocyanate or dithiol methods.

This paper describes the use of manganese dioxide for the concentration of traces of molybdenum by coprecipitation from natural waters, silicate rocks and marine organisms. Since the coprecipitation is selective, molybdenum can usually be determined photometrically by means of dithiol directly on a sulphurous acid solution of the manganese dioxide precipitate; this obviates the tedious destruction of organic matter which is necessary if an organic extraction technique is used.

Concentration of molybdenum

Since an initial concentration and separation of molybdenum from commoner ions is necessary, coprecipitation with metal hydroxides was investigated. MORACHEVSKII AND SHIPUNOVA[29] have demonstrated that iron(III) hydroxide is more effective for this purpose than the hydroxides of aluminium or titanium. ISHIBASHI[30] has observed that the percentage coprecipitation depends markedly on pH and is maximal in the range 3.5–4. These observations were confirmed in the present work in which it was found that *ca.* 95% of the molybdenum present in sea water could be coprecipitated at pH 4 with iron(III) hydroxide (20 mg Fe/l). At pH values above and below 4, the percentage coprecipitation decreased markedly; reaching 80% and 70% at pH 3.0 and 5.2 respectively.

TANAKA[31] has claimed that hydrous manganese dioxide, produced by the reaction between manganese(II) and permanganate ions, is superior to iron(III) hydroxide for the coprecipitation of molybdenum, and both SUGAWARA *et al.*[9,10] and BACHMANN AND GOLDMAN[11] have employed it in the determination of molybdenum in sea water. This method was tested, and it was found that molybdenum could be coprecipitated from 1 l of sea water with greater than 99% efficiency with manganese dioxide produced by boiling the buffered sea water (pH 3.7) after addition of 20 ml of 0.1% manganese(II) sulphate solution and 2 ml of 1% potassium permanganate solution. However, highly adsorptive manganese dioxide can be more readily precipitated by the reaction at room temperature between the permanganate ion and ethanol. It was therefore decided to investigate the use of this process for the concentration of molybdenum.

Experiments were carried out to find the optimum pH conditions for the coprecipitation. Aliquots (1 l) of sea water, stripped of molybdenum by coprecipitation, were enriched with 10 μg of molybdate-molybdenum, adjusted to a range of pH values with hydrochloric acid or ammonia and treated with 2 ml of ethanol and 2 ml of 3% potassium permanganate solution. On the following morning, the manganese dioxide precipitate which had formed was filtered off and dissolved in 15 ml of sulphur dioxide solution, and molybdenum was determined using dithiol as described below. These tests showed (Table II) that coprecipitation was complete in the pH range 1.3-5.5; in all further work a pH of *ca.* 2 was employed. Experiments showed that at this pH value it was necessary to use not less than 2 ml of 3% potassium permanganate solution (equivalent to *ca.* 20 mg of manganese) per litre of sea water to ensure complete coprecipitation of molybdenum; this amount would, however, carry molybdenum quantitatively from sea water at concentrations up to at least 100 μg/l.

TABLE II

PERCENTAGE COPRECIPITATION OF MOLYBDENUM WITH MANGANESE DIOXIDE AS A FUNCTION OF pH

pH	0.8	1.3	2.2	3.7	4.4	5.5	6.3	7.6	8.8
Mo coprecipitated (%)	75	100	100	100	100	100	95	67	35

Separation of molybdenum

Since manganese dioxide is a much more selective coprecipitant than iron(III) hydroxide, it will not generally be necessary to purify the concentrate if molybdenum is to be determined spectrophotometrically with dithiol. If, however, analyses are to be made on rocks containing considerable amounts of other elements carried by manganese dioxide, *e.g.* antimony and bismuth, it is advisable to carry out a separation. This can be most readily achieved by adsorbing the molybdenum on a cation exchanger and eluting it, together with any vanadium present, by means of hydrogen peroxide[32-34].

It was found that a column 0.8 cm in diameter and 8 cm long packed with ZeoKarb 225 (8% cross-linked, 52–100 mesh) was able to take up the manganese and adsorbed ions from a solution of the manganese dioxide precipitate in sulphur dioxide water. Molybdenum could be eluted completely by means of 100 ml of 0.3% hydrogen peroxide solution. Increasing the strength of the hydrogen peroxide did not lead to any worthwhile increase in the rate of elution. Vanadium, which is also coprecipitated with manganese dioxide is also eluted with 100 ml of 0.3% hydrogen peroxide, but 1 mg amounts of Co^{2+}, Zn^{2+}, Al^{2+}, Ti^{4+}, U^{6+}, Co^{3+}, Bi^{3+}, Cu^{2+}, Pb^{2+}, Sn^{2+}, 5 mg of Fe^{3+}, and 0.1 g of Mn^{2+} were not eluted. Before molybdenum can be determined in the eluate, hydrogen peroxide must be destroyed by evaporating to small volume in a platinum dish.

Photometric determination of molybdenum

Although many reagents have been described for the photometric determination of molybdenum, few of them have either the specificity or sensitivity for the determination of microgram amounts of the element recovered from sea water or silicates by coprecipitation. In most of the earlier work on the photometric determination of traces of molybdenum in geochemical materials, the thiocyanate method has been employed. However, the mechanism of this process is complicated, and it is necessary to have very strict control of the conditions used for the reduction of molybdenum to the 5+ oxidation state if accurate results are to be obtained[16,35,36]. Tests showed that it was difficult to obtain reproducible results when methods[17,37] based on this procedure were used for the determination of less than 10 μg of molybdenum.

Another variant[38] on the thiocyanate method was also tested; in this, molybdenum(VI) is allowed to react with thiocyanate in the presence of catalytic amounts of copper giving an orange-red complex. It was found, however, that the method was too insensitive for the accurate determination of less than 5 μg of molybdenum, although it was satisfactory for amounts of molybdenum 5 times as great as this. Furthermore, iron(III) interfered seriously even when photometry was carried out on an organic extract of the coloured complex. For these reasons this method was not investigated any further.

Dithiol (toluene-3,4-dithiol) reacts with a number of metals giving insoluble complexes. Those formed by tin(II), molybdenum(VI) and tungsten(VI) have been used for the photometric determination of these elements since they are extractable by certain organic solvents, and give intensely coloured solutions. Dithiol itself is readily oxidized both in the solid state and in solution; it can, however, be prepared as required by alkaline hydrolysis of its stable diacetyl compound. Methods using dithiol are divided into two classes: (*i*) those in which the complex is precipitated and then extracted into the solvent[39-41], and (*ii*) those in which the element is extracted by a solution of dithiol in the organic solvent[42,43]. A preliminary investigation was therefore carried out in order to determine which of these processes gave the more reproducible results. Aliquots (10 ml) of a standard molybdate solution (10 μg Mo) were acidified by the addition of 5 ml of concentrated hydrochloric acid. To one set of these solutions was added 5 ml of a 0.5% alkaline solution of diacetyl dithiol: after 10 min the solution was extracted with 5 ml of *n*-butyl acetate. To another series of these solutions were added 5 ml of water and 5 ml of a 0.5% solution of diacetyl dithiol in *n*-butyl acetate, and the mixture was shaken for 10 min. The *n*-butyl acetate phases from both series of extraction were separated and their optical densities were measured at 670 mμ in a 1 cm cell. The results of these experiments showed that the first method gave more consistent results and an optical density *ca.* 8% higher than that found by the second method. This procedure was therefore selected for further study.

The effect of variation of the amount of hydrochloric acid on the reaction was investigated by treating 5 ml of standard molybdate solution (10 µg Mo) with various volumes of concentrated hydrochloric acid, and 5 ml of a 0.5% hydrolyzed solution of diacetyl dithiol (see experimental section). After 10 min the solutions were extracted with 5 ml of *n*-butyl acetate. It was found that 3–11 ml of hydrochloric acid produced the same optical density at 670 mµ in the extract (0.441 ±0.001); a volume of 5 ml was used in all subsequent work in order to minimize the extraction of tungsten which forms a similar complex at low acidities.

Similar experiments in which the hydrochloric acid volume was fixed at 5 ml and the volume of hydrolysed diacetyl dithiol reagent was varied, showed that within the range 3–15 ml the optical density was constant (0.441 ±0.001). However, in order to allow a substantial excess, in case of competition by foreign ions, a volume of 5 ml of the reagent was used in all later work.

Prevention of interference in the photometric process

Since several elements are known to cause interference in the method, the possibilities of preventing their interference by reducing or complexing them were investigated. The addition of ascorbic acid was found to prevent the interference of iron. The interference of tungsten was prevented by the addition of citric acid[16]. Interference of many of the elements which compete with molybdenum for the dithiol reagent was much reduced by use of thiourea[44]. A single solution was prepared which was 1%, 5% and 5% with respect to ascorbic acid, citric acid and thiourea respectively, and 5 ml of it was added before the addition of dithiol reagent. In the presence of this complexing reagent no interference was caused, in the determination of 10 µg of molybdenum, by 200 µg of iron or tungsten, 0.1 g of manganese, 2 mg of vanadium(V), 500 µg of copper(II), cobalt(II), nickel(II), zinc(II), lead(II), antimony(III), bismuth(III), or 100 µg of tin(II) or selenium(IV). It is thus unlikely that interferences will be encountered in the analysis of sea water, ordinary igneous or sedimentary rocks or biological materials when molybdenum is concentrated by coprecipitation with manganese dioxide. However, if samples are to be analyzed containing unusually large concentrations of any elements known to cause interference in the photometric procedure, the coprecipitated molybdenum should be separated by ion exchange as described above.

Beer's law and reproducibility

In order to determine how closely the system adhered to Beer's law, determinations were carried out on amounts of molybdenum ranging from 2–14 µg. Optical densities from these gave a straight line calibration curve with an average optical density increment per microgram of molybdenum of 0.0440 ±0.0005. Replicate determinations carried out at the 4 µg and 10 µg of molybdenum levels gave coefficients of variation of 1.2 and 0.8% respectively. The coloured complex was stable for at least 24 h.

EXPERIMENTAL

Apparatus

A Unicam S.P.500 spectrophotometer was used for all spectrophotometric measurements.

Reagents

Reducing and complexing reagent. Dissolve 1 g of ascorbic acid, 5 g of citric acid and 5 g of thiourea in water and dilute to 100 ml.

Dithiol reagent. Dissolve 0.5 g of diacetyl dithiol in 100 ml of 0.5% (w/v) potassium hydroxide solution. The reagent is stable for about 1 week if stored in a refrigerator.

Cation exchanger. ZeoKarb 225 ion-exchange resin (8% cross-linked, 52–100 mesh) was digested on the water bath several times with 3 N hydrochloric acid. It was well washed with water and packed into an 8 mm diameter ion-exchange column so as to give a length of resin of 8 cm.

Standard molybdenum solution (100 µg Mo/l). Dissolve 0.0750 g of molybdenum trioxide A.R. (dried at 250°) in 10 ml of 0.1 *N* sodium hydroxide solution, dilute to *ca.* 100 ml and add 20 ml of 0.1 *N* hydrochloric acid. Dilute to 500 ml. Prepare a working standard solution containing 2 µg Mo/ml by dilution of this stock solution with 0.1 *N* hydrochloric acid.

Determination of molybdenum in sea water and natural waters

Filter the sample as soon as possible after collection through a 0.5 µ membrane filter. Take 1 l of the filtered water, or proportionately more if its molybdenum content is less than 5 µg/l, and adjust its pH value to 2.0 by cautious addition of dilute hydrochloric acid. Add 2 ml of ethanol and 2 ml of 1 *N* potassium permanganate solution to the acidified sample, mix well and allow to stand overnight. On the following day siphon the clear supernatant liquid through a 2.5 cm diameter glass fibre filter (Whatman GF/B), centrifuge the remaining liquid and quantitatively transfer the precipitate to the filter. Wash the precipitate with a small volume of water and then dissolve it in *ca.* 15 ml of a saturated aqueous solution of sulphur dioxide. Evaporate the resultant solution to *ca.* 6 ml in a beaker on a hot plate.

If the water sample contains appreciable quantities of elements coprecipitated by manganese dioxide it is advisable to separate molybdenum by ion exchange as described below; however, this is not necessary in the analysis of sea water samples. Dilute the solution of the precipitate to *ca.* 50 ml and pass it through a column 0.8 cm in diameter and 8 cm long packed with ZeoKarb 225. Elute molybdenum with 100 ml of 0.3% (w/v) hydrogen peroxide, and evaporate the eluate to dryness in a platinum basin. Take up the residue in a few drops of 2 *N* ammonia solution, and dilute to *ca.* 6 ml with water.

Transfer the solution of the residue, or the solution of the manganese dioxide precipitate if ion exchange has not been used, to a 50-ml separating funnel, using not more than 5 ml of water to complete the transfer. Add 5 ml of concentrated hydrochloric acid and 5 ml of the reducing and complexing reagent, and mix well. If the resulting solution is yellow, add a further 3 ml of this reagent. Add 5 ml of the dithiol reagent and shake well. After 10 min, extract the greenish coloured molybdenum dithiol complex with 5 ml of *n*-butyl acetate. Measure the optical density of the extract at 670 mµ in a 1-cm cuvette against a compensator cell containing *n*-butyl acetate. For sea water samples, carry out a reagent blank in the same manner on 1 l of sea water which has been stripped of molybdenum by coprecipitation with manganese dioxide: the reagent blank normally has an optical density of *ca.* 0.006. Calibrate the method by examining 1-l aliquots of the stripped water after spiking with 5 ml of the dilute standard molybdenum solution (10 μg Mo). Carry out blanks and calibrations for non-saline waters using redistilled water in place of the stripped sea water.

Determination of molybdenum in silicates

Weigh out accurately 0.5–1.0 g of the powdered sample (ground to pass an 80-mesh sieve). Add 4 ml of 60% (w/w) perchloric acid and 25 ml of 40% (w/w) hydrofluoric acid. Heat the covered crucible on a water bath overnight. On the following day remove the lid and continue heating until no further fumes of hydrofluoric acid are evolved. Continue the evaporation under an infrared heater until most of the perchloric acid has been removed. Add a further 5 ml of perchloric acid while stirring with a platinum rod. Again evaporate almost to dryness under the infrared heater, but do not bake. Add a further 3 ml of perchloric acid and about 45 ml of water and heat on the water bath until the cake has dissolved. Transfer the clear solution to a 250-ml Erlenmeyer flask and dilute to *ca.* 200 ml. Adjust the solution to pH 2.0 by cautious addition of 4 *N* ammonia solution while stirring vigorously. Add 2 ml of ethanol and 2 ml of 1 *N* potassium permanganate solution and mix well. After not less than 12 h, separate the precipitated hydrous manganese dioxide by centrifugation, wash it with 5 ml of water and then dissolve it in 15 ml of a saturated aqueous solution of sulphur dioxide. Transfer the solution to a beaker and evaporate it to *ca.* 6 ml on a water bath. If the sample is thought to contain considerable amounts of elements coprecipitated by manganese dioxide, *e.g.* bismuth, tin and antimony, separate molybdenum by ion exchange as described in the previous section and determine with dithiol. If these elements are present at concentrations less than 10 times their average concentration in igneous rocks, this separation is unnecessary and the photometric determination should be carried out directly as described for sea water. Carry out a blank determination in the same manner but omitting the sample. To calibrate the method carry out photometric determinations on 5-ml aliquots of dilute standard molybdenum and use a determination carried out on 5 ml of distilled water as the corresponding blank.

Determination of molybdenum in biological materials

Cautiously heat 10 g of the air-dried sample with 40 ml of concentrated nitric acid in a 500-ml Erlenmeyer flask loosely closed with a bulb stopper, adding more nitric acid as required. When a clear solution has been obtained remove the stopper and evaporate to small volume. Transfer the solution to a silica evaporating basin with a jet of water, add 3 ml of 60% (w/w) perchloric acid, and heat on the hot plate until dense white fumes are evolved in order to ensure the removal of all traces of nitrate ion. Dissolve the residue in *ca.* 500 ml of water, and adjust the solution to pH 2.0 by cautious addition of 2 *N* sodium hydroxide with stirring. Add 2 ml of ethanol and 2 ml of 1 *N* potassium permanganate solution. After about 12 h separate the manganese dioxide precipitate by centrifugation, dissolve it in sulphur dioxide solution and carry out the photometric determination with dithiol as described above for sea waters. Carry out a blank determination in the same manner but omitting the sample. Calibrate the method as described above for silicates.

RESULTS

Accuracy and precision of methods

Sea water. The reproducibility of the procedure (omitting the ion exchange step) was evaluated from the results of 5 replicate analyses of filtered surface water from the Irish Sea. These analyses showed that the water contained an average of 10.3 ± 0.1 μg of molybdenum/l; very similar results (10.4 ± 0.1 μg/l) were found if the ion-exchange step was included in the process. The accuracy of the process was checked by carrying out replicate analyses on samples of sea water spiked with molybdenum. The results of these experiments (Table III) showed that the recovery of molybdenum was satisfactory.

TABLE III

RECOVERY OF MOLYBDENUM FROM 1-l SAMPLES OF SPIKED SEA WATER

Molybdenum added (μg)	0	2	4	6	8	10
Molybdenum found (μg)	10.3	12.1	14.0	16.3	18.2	20.3
Percentage recovery (total)	—	98.4	98.0	100.0	99.4	100.0

Silicates. In order to assess the precision of the method, replicate analyses (5) were carried out on 2 red clay samples collected by R.R.S. Discovery. The samples were analyzed both by the direct method and after separating molybdenum by ion exchange. Samples from Stations 3498 (Lat 34° 11'N, Long 55° 32'W) and 3617 (Lat 24° 30'N, Long 64° 47'W) were analyzed by the direct method and found to contain of 7.30 ± 0.07 and 7.24 ± 0.06 μg Mo/g respectively. When molybdenum was separated by ion exchange before photometry, molybdenum concentrations of 7.32 ± 0.06 and 7.16 ± 0.05 μg/g were found respectively. It is thus apparent that the comparatively high concentrations of trace elements present in these red clay samples did not interfere in the determination of molybdenum by the direct method. The coefficient of variation of the method at a molybdenum level of 7 μg/g was *ca.* 1%.

As a check on the accuracy of the method 0.5-g samples of red clay from Discovery Station 3498 (3.65 μg Mo) were spiked with 4 μg of molybdenum and analyzed. Recoveries ranging from 97 to 100% were obtained.

Molybdenum determinations were also carried out on the U.S. Geological Survey standard granite G1 and standard diabase W1; these showed the presence of 6.3 and 0.48 μg Mo/g respectively. A review, complete up to 1961, of previous data of molybdenum in these rocks has been given by STEVENS[45] who recommended the values of 7 and 0.5 μg/g for G1 and W1 respectively; however, since the published figures showed wide variations, their recommendations were only tentative. More recent determinations by spectrographic[46], neutron activation[47] and mass spectrometric[48,49] procedures gave values of 7.3, 7.0 ± 3.0, < 0.8 and 9.5 μg Mo/g for G1 and —, 1.3 ± 0.4, < 0.8 and 0.7 μg Mo/g for W1 respectively. The results obtained in the present work agree well with those found by KURODA AND SANDELL[50] by a photometric procedure (G1 6.6 μg/g; W1 0.5 μg/g).

Biological materials. The precision of the method when applied to biological materials was tested by carrying out replicate analyses on washed and air-dried samples of *Ascophyllum nodosum* and *Laminaria digitata*. These analyses, which were carried out by the direct procedure, showed the presence of 0.91 ±0.01 and 0.45 ±0.01 µg Mo/g respectively. The recovery of molybdenum was checked by spiking 10-g samples of *Ascophyllum nodosum* (9.1 µg Mo) with 10 µg of molybdenum; on analysis 19.0, 18.7 and 18.6 µg of molybdenum were found showing that the recovery of the element is satisfactory.

SUMMARY

Coprecipitation with hydrous manganese dioxide is used for the concentration of molybdenum from natural waters (including sea water) and from solutions prepared from silicate rocks and mineralized biological materials. Molybdenum is determined photometrically with dithiol after dissolving the manganese dioxide precipitate in sulphur dioxide solution. Since only a few elements are coprecipitated by manganese dioxide, separation before photometry is not normally necessary. However, if it is thought desirable, molybdenum can be separated from most other elements by adsorbing it on a cation exchanger and eluting it with hydrogen peroxide. The method was found to have a coefficient of variation of *ca.* 1% with sea water, argillaceous sediments and biological materials at concentration levels of 10.3 µg Mo/l, 7.2 µg Mo/g and 0.9 µg Mo/g respectively. The U.S. Geological Survey Standard granite (G1) and diabase (W1) were found to contain 6.3 and 0.48 µg Mo/g respectively.

RÉSUMÉ

On utilise une coprécipitation à l'aide de dioxyde de manganèse hydraté pour concentrer le molybdène dans des eaux naturelles (y compris l'eau de mer) et dans des solutions préparées à partir de roches silicatées et de substances biologiques minéralisées. Le molybdène est dosé photométriquement à l'aide de dithiol, après dissolution du dioxyde de manganèse précipité dans une solution d'anhydride sulfureux. Il n'est généralement pas nécessaire d'effectuer une séparation avant de photométrer, peu d'éléments étant coprécipités avec le dioxyde de manganèse. Cependant, le molybdène peut être séparé de la plupart des autres éléments par adsorption sur un échangeur de cations et élution au moyen d'eau oxygénée.

ZUSAMMENFASSUNG

Es wird die Konzentration von Molybdän durch Mitfällen mit wasserhaltigem Mangandioxid beschrieben, und zwar aus natürlichen Wässern einschl. Seewasser und aus Lösungen, die aus silikatischen Gesteinen und mineralisierten biologischen Materialien hergestellt wurden. Nach Lösen des Mangandioxidniederschlags in Schwefeldioxidlösung wird das Molybdän photometrisch mit Dithiol bestimmt. Da nur wenige Elemente durch Mangandioxid mitgefällt werden, ist vor der photometrischen Bestimmung eine Trennung normalerweise nicht notwendig. Jedoch kann, falls es wünschenswert ist, Molybdän von den meisten anderen Elementen durch Adsorption an einem Kationenaustauscher und Elution mit Wasserstoffperoxid abgetrennt werden. Die Methode hat einen Variationskoeffizienten von etwa 1% beim Seewasser, Sedimenten und biologischen Stoffen bei Konzentrationen von 10.3 µg Mo/l, 7.2 µg Mo/g bzw. 0.9 µg Mo/g.

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SHORT COMMUNICATIONS

Volatilisation of iridium from boiling perchloric acid

The behaviour of submicro- and microgram amounts of iridium in boiling perchloric acid (*ca.* 200°) was investigated under several experimental conditions by means of radioactive tracer techniques. The preparation of the ^{192}Ir tracer and the distillation apparatus used have been described previously[1,2].

The first experiments were carried out with 100 μl of ^{192}Ir tracer solution (*ca.* 0.25 μg Ir) with a γ-activity of $2 \cdot 10^4$ counts/min which was heated for 1 h at $200 \pm 5°$

TABLE I

BEHAVIOUR OF IRIDIUM IN BOILING PERCHLORIC ACID

(^{192}Ir tracer = 0.25 μg Ir; activity: $1\text{–}3 \cdot 10^4$ counts/min)

No.	*Conc. H_2SO_4 (ml)*	*70% $HClO_4$ (ml)*	*Duration (min)*	*% Distilled*	*% Left*	*% Total*	*Remarks*
1	3	20 + 6	60	79	24.5	103.5	Air current
2	3	30 + 10	75	5	96.5	101.5	Air current + 100 μg Ir
3	3	20 + 12	60	0.6	98.1	98.7	Air current + 500 μg Ir
4	3	30 + 10	60	64.6	36.9	101.5	Air mixed with HCl gas
5	3	30	35	0	100	100	HCl gas without air
6	3	30	60	58.3	41.6	99.9	Oxygen
7	3	25	100	100.9	2.4	103.3	Cl_2[a]
8	3	25	60	97.1	1.6	98.9	
9	3	25	120	95.5	5.6	101.1	
10	1 dr	25	60	94.2	5.8	100.0	Cl_2 from cylinder[a]; mixed with air
11	1 dr	25 + 30	165	86.5	4.6	91.1	+ air[b] + 10 μg Ir
12	1 dr	25 + 80	225	55.8	33.0	88.8	id. + 35 μg Ir
13	1 dr	25 + 65	100	23.0	72.4	95.4	id. + 157 μg Ir
14	10(18 *N*)		60	—	—	—	id.[c]
	(+ H_2O + dr H_2O_2) 10 + 10 ml $NaBrO_3$	25 + 10	90	97.8	0.3	98.1	id.[c]
15	id.		60	(0.2)	—	—	id.[c] + 10 μg Ir
		25 + 10	180	97.8	0.4	98.4	
16	id.		60	0	—	—	id.[c] + 32 μg Ir
		25 + 15	200	95.5	0	95.5	

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[a] Via 2 water bubblers.

[b] After waiting for some hours.

[c] After peroxide fusion and bromate distillation (1 h).

in 25 ml of 70% perchloric acid and 3 ml of concentrated sulfuric acid, while an air current was drawn through the distillation apparatus. The distillate was absorbed in 2 × 5 ml of cooled 3 *N* sodium hydroxide. Under these conditions 65–90% of the ^{192}Ir activity distilled over and was absorbed quantitatively. Addition of *ca.* 100 μg of iridium carrier, prepared in the same way as the tracer, reduced the yield to a few per cent. This seemed to indicate that isotopic exchange occurred and that only small quantities of irridium can be volatilised (see Table I, no. 1–3).

The yield could not be increased if, instead of air, oxygen or air mixed with hydrogen chloride or hydrogen chloride alone were drawn through the apparatus (see Table I, no. 4–6).

If, however, air mixed with chlorine gas was used, approximately 95% of the iridium activity was normally found to distil within 1 h (Table I, no. 7–9). Chlorine was prepared from manganese dioxide and hydrochloric acid (both technical grade) and washed in 2 bubblers containing water (Fig. 1). The same results were obtained with commercial chlorine gas from cylinders provided that it was washed in the same way. Without washing the yield was only 30–75%. No improvement was observed by mixing the gas with air or oxygen, nor by U.V. irradiation.

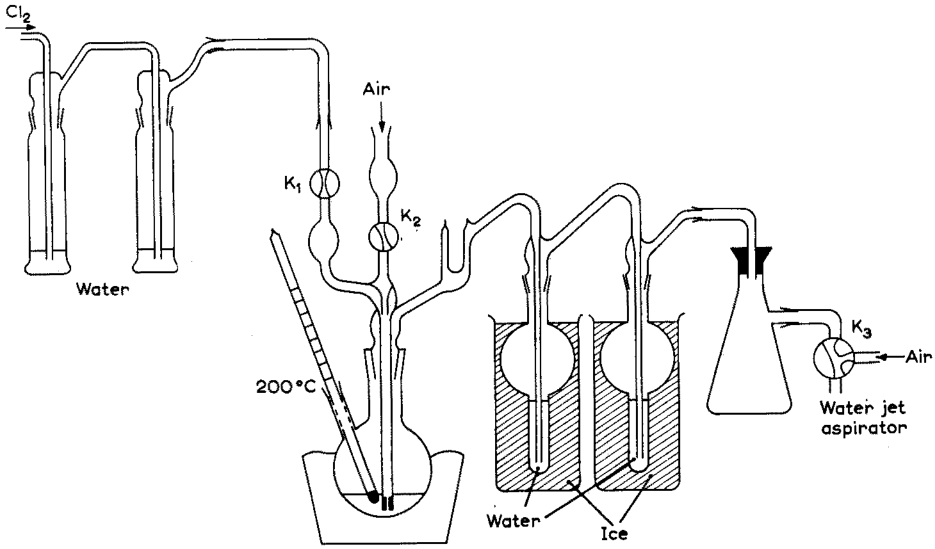

Fig. 1. Apparatus for the distillation of iridium.

Addition of iridium carrier again reduced the yield, even if the chlorine was previously washed (Table I, no. 10–13). Moreover a non-quantitative absorption of iridium was observed if the distillation was continued for a long time, and particularly if considerable quantities of perchloric acid distilled.

Finally the behaviour of iridium was investigated after fusing with sodium peroxide in a nickel crucible and after heating in sulfuric acid containing sodium bromate, *i.e.* under the conditions that osmium and ruthenium are dissolved and then distilled[1]. The distillation of iridium from boiling perchloric acid was found to be even easier, so that amounts of 10–30 µg could be volatilised quantitatively and absorbed to the extent of 95–98% (Table I, no. 14–16). To avoid crystallisation of nickel salts from the crucible, an excess of perchloric acid must always be present in the distillation flask.

By means of ^{124}Sb and ^{137}Cs tracers, it could be shown that no mechanical trailing occurred.

Experimental

Into the distillation flask (Fig. 1) are introduced: 100 µl of ^{192}Ir tracer solution, containing approximately 0.25 µg of Ir and having a sufficient γ-activity, 3 ml of concentrated sulfuric acid, and 25 ml of 70% perchloric acid. The absorption vessels are filled with 5 ml of water, and 5 ml of 3 *N* sodium hydroxide respectively, and both are cooled in an ice bath. The chlorine gas is produced from manganese dioxide and hydrochloric acid (both technical grade) and washed in 2 water-filled bottles connected to the distillation apparatus via stopcock K_1 (open). Connections are made with polythene tubing. Stopcock K_3, connected to a waterjet aspirator, is sufficiently opened so as to obtain a regular gas stream through the apparatus. To avoid a too pronounced underpressure in the chlorine gas generator, the latter is sufficiently heated and regularly provided with fresh hydrochloric acid. Stopcock K_2 is partly opened. In this way a regular air current, mixed with chlorine gas can be maintained (the glass bulb near K_1 must always show a green colour). Meanwhile, the contents of the distillation flask are boiled (*ca.* 200°) for the time indicated in Table I (>1 h).

After the distillation, the contents of the absorption vessels are transferred into 50- or 100-ml measuring flasks and counted by γ-scintillation under the same geometrical conditions as a standard containing 100 µl of the tracer solution and 50 or 100 ml of water.

The chlorine gas generator can be replaced by a cylinder. This allows a more regular gas flow.

In the alternative method, 100 µl of tracer solution of sufficient γ-activity is carefully evaporated to dryness in a nickel crucible, then covered with *ca.* 1 g of sodium peroxide and fused. This is the normal procedure for bringing metallic osmium, ruthenium and iridium into solution. After cooling, the melt is disintegrated with 10–20 ml of water, 10 ml of 18 *N* sulfuric acid and a few drops of 30% hydrogen peroxide to clarify the solution, which is then transferred to the distillation flask. An air current is drawn through the apparatus and 10 ml of 20% sodium bromate is added. The solution is boiled for 1 h ($105 \pm 5°$) while another 10 ml of 20% sodium bromate is added dropwise (under these conditions osmium and ruthenium distil practically quantitatively[1,2]). The distillate is collected in 2 × 5-ml portions of ice-cooled 9 *N* sodium hydroxide and analysed for iridium contamination. Normally a few thousandths percent are found.

Then 25 ml of 70% perchloric acid is added to the residue, while the temperature is raised again. Destruction of the residual bromate causes evolution of bromine. After complete distillation of the water, the temperature rises to about 190–200°. At this stage the air current is mixed with water-washed chlorine gas and the distillation continued for about 2 h. From time to time a few ml of perchloric acid and if required, a drop of water, are added very carefully via K_2, to prevent obstruction of the capillary tube by nickel salts. The distillate is absorbed in ice-cooled water. It has been observed that the iridium distillation starts only at *ca.* 180°, so that the "forerun" can be discarded.

After the distillation, heating is stopped and the chlorine current interrupted. During the cooling the air current is, however, maintained. Moreover, water must be added to avoid solidification of the contents of the distillation flask. Residue and distillate are counted by γ-scintillation in 50- or 100-ml measuring flasks and compared with a standard.

The behaviour of some other elements (Se, Mn, Sb, Ta, Au) was also investigated after peroxide fusion followed by distillation from sulfuric acid–hydrogen peroxide (selective distillation of osmium[3]) and from sulfuric acid–sodium bromate (selective distillation of ruthenium[1]). Some results are summarized in Table II.

TABLE II

BEHAVIOUR OF SOME ELEMENTS IN H_2SO_4–$HClO_4$–Cl_2 AT 200°, AFTER PEROXIDE FUSION AND AFTER HEATING IN H_2SO_4–H_2O_2 AND IN H_2SO_4–$NaBrO_3$ AT 105°

Tracer	*γ-activity (counts/min)*	*% dist. H_2O_2*	*% dist. $NaBrO_3$*	*% dist. $HClO_4$–Cl_2*
^{75}Se	50,000	0.1	0	0
^{54}Mn	360,000	0	0.02	0.03
^{124}Sb	100,000	0	0	0.06
^{182}Ta	100,000	0	0	0
^{198}Au + Pt	200,000	7 (p.p.b. Pt)	0.6	0.3 ($PtO_2\downarrow$)

Discussion and conclusions

The distillation of iridium from H_2SO_4–$HClO_4$–Cl_2 at 200° seems to be specific for this element. If osmium or ruthenium are present at this stage, they will, of course, form tetroxides and hence distil. It is perhaps worthwhile to remember that osmium distils from H_2SO_4–H_2O_2, H_2SO_4–$NaBrO_3$ and H_2SO_4–$HClO_4$–Cl_2–air, ruthenium from H_2SO_4–$NaBrO_3$ and H_2SO_4–$HClO_4$–Cl_2–air, and iridium from H_2SO_4–$HClO_4$–Cl_2–air.

After fusion with sodium peroxide and bromate distillation ($\geqslant$99.997% Os, 99.5–99.8% Ru, $\leqslant$0.01% Ir[1,2]), iridium can be volatilized almost quantitatively (residue $\simeq$0.5%) by heating in H_2SO_4–$HClO_4$–Cl_2–air at 200° for 2 h. Even if amounts of some 30 μg of iridium are present, *ca.* 95% can be recovered in ice-cooled water. If osmium or ruthenium is present (*e.g.* if traces of these elements are not completely distilled in the previous stage) they will be volatilized quantitatively. Other elements, such as Se, Mn, Sb, Ta, Au, Cs remain in the residue.

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Derivatives of orotic acid as potential reagents for the alkali metals

There are few satisfactory reagents for the precipitation of the alkali metal ions and even fewer which have any real degree of selectivity within the alkali metal group. The double uranyl acetate reagents have many advantages for the selective precipitation of sodium, but lack high sensitivity. 5-Benzaminoanthraquinone-2-sulphonic acid[1] has an unusually high sensitivity towards sodium ions but no selectivity. Other organic reagents, such as dihydroxytartaric acid[2] and lithium tetra-*p*-tolylborate[3], are somewhat limited in their application. This situation lends general interest to the reactions of the pyrimidine derivative, uracil-4-carboxylic acid, otherwise known as orotic acid, which has recently been recommended by Selleri and Caldini[4] as a precipitant for sodium and potassium. These workers have established the optimal conditions for the quantitative precipitation of these ions from solutions of their salts using as reagents the alcohol-soluble dialkylethanolammonium salts of orotic acid. The precipitations are done in a strongly methanolic or ethanolic medium (about 80%, v/v); this lowers the solubility of the sodium and potassium orotates to a suitable level for quantitative work. The advantages claimed for these orotate reagents are: (*i*) no interference from lithium, the alkaline-earth metals, iron (III), aluminium, cobalt, copper and nickel; (*ii*) the determinations can be done on solutions of a wide range of common salts containing sodium and potassium including phosphates, thiosulphates, oxalates, and tartrates; and (*iii*) the ammonium ion does not interfere under the prescribed conditions.

These important aspects of orotic acid as an alkali metal precipitant have led in the present work to a study of the behaviour of a number of other pyrimidines related to orotic acid in order to establish whether these new compounds show improved characteristics with respect to the precipitation of the alkali metal ions. An increase in both sensitivity and selectivity would be particularly desirable for the wider application of this type of reagent in alkali metal analysis.

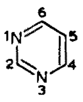
Of the other alkali metals, Selleri and Caldini mention only lithium as a non-interference in the precipitation of sodium and potassium when operations are done in an aqueous medium. A qualitative examination of the behaviour of the dimethylethanolammonium orotate reagent towards solutions of Li^+, Na^+, K^+, Rb^+ and Cs^+ indicated that the reagent lacked any useful degree of selectivity and could probably be used for the determination of the last two ions. During the course of the present investigation, Babbie and Wagner[5] actually described the use of the dimethylethanolammonium salt in methanol for the quantitative precipitation of rubidium and caesium, which conclusively indicates the completely unselective behaviour of these orotic acid reagents.

In the present study, several derivatives of orotic acid and other related compounds have been synthesised in order to establish whether or not substitution in the orotate molecule would give rise to a new series of more selective reagents.

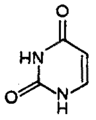
In view of the differences which exist in the numbering of the pyrimidine ring system, the following convention for pyrimidine (I) has been used.

On this basis, uracil (II) is 1,3-dihydro-2,6-dioxopyrimidine and orotic acid is 2,6-dihydroxypyrimidine-4-carboxylic acid (III), the oxo-form, uracil-4-carboxylic acid (IV) predominating in neutral aqueous solution.

The orotic acid derivatives which have been examined can be divided into two

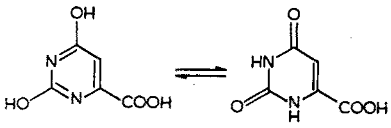


(I)



(II)

main groups: (*a*) the N-substituted orotic acids and (*b*) the C_5-substituted orotic acids. In addition, the isomeric uracil-5-carboxylic acid has also been studied. These



(III) (IV)

compounds have in general been prepared both by total synthesis and by appropriate substitution in orotic acid itself. The latter method has greatest application in the preparation of the C_5-substituted acids, because the 5-position is not so electron-deficient as the 2-, 4- or 6-positions. Thus the 5-position is reasonably reactive towards

TABLE I

REACTIONS OF THE ALKALI METALS WITH PYRIMIDINECARBOXYLIC ACIDS

Compound	NH_4^+	Li^+	Na^+	K^+	Rb^+	Cs^+
Orotic acid	−	+	+	+	+	+
Uracil-5-carboxylic acid	−	+	+	+	+	+
5-Methylorotic acid	−	−	+	+	+	+
5-Ethylorotic acid	−	−	+	−	−	−
5-Ethoxyorotic acid	−	−	+	+	+	+
5-Isopropylorotic acid	−	−	−	−	−	−
5-Butylorotic acid	−	−	−	−	−	−
5-Phenylorotic acid	−	−	+	+	+	+
5-Phenoxyorotic acid	−	−	+	+	+	−
5-Fluoroorotic acid	−	−	+	+	+	+
5-Chloroorotic acid	−	−	+	+	+	+
5-Bromoorotic acid	−	−	+	+	+	+
5-Iodoorotic acid	−	−	+	+	+	+
5-Nitroorotic acid	−	−	+	+	+	+
5-Aminoorotic acid	−	−	+	+	+	+
5-Benzaminoorotic acid	−	−	+	+	+	+
5-Cyclohexylaminoorotic acid	−	+	+	+	+	+
1-Phenylorotic acid	−	−	−	−	−	−
1-Phenyluracil-5-carboxylic acid	−	−	+	+	−	−
1-Methylorotic acid	−	−	+	+	+	−
3-Methylorotic acid	−	−	+	−	−	−
1,3-Dimethyluracil-5-carboxylic acid	−	+	+	+	−	−
1-Methyluracil-5-carboxylic acid	−	+	+	+	+	−
Uracil-3-acetic acid	−	+	−	−	−	−
5-Methyluracil-3-acetic acid	−	−	−	+	−	−

electrophilic reagents, especially if other electron-releasing groups are also present anywhere in the ring. These acids, in the form of their N,N-dimethylethanolammonium salts, were tested qualitatively on solutions of lithium, sodium, potassium, rubidium, caesium and ammonium chlorides. The results of these tests are given in Table I. By a careful observation of the formation of a precipitate, and the time taken for the precipitation to be completed, an approximate indication of the comparative solubilities of the various alkali metal salts can be obtained. With the more promising reagents, absolute measurements of the solubilities of the individual salts have been made; these are given in Table II.

TABLE II

SOLUBILITIES OF ALKALI METAL SALTS OF VARIOUS PYRIMIDINECARBOXYLIC ACIDS (g/l at 25°)

Reagent	*Li*		*Na*		*K*		*Rb*		*Cs*	
	80%[a]	*90%*[b]	*80%*	*90%*	*80%*	*90%*	*80%*	*90%*	*80%*	*90%*
Orotic acid	1.08	0.33	0.08[c]	0.03[c]	0.07[c]	0.03[c]	0.21[d]	0.15[d]	1.55[d]	0.22[d]
Uracil-5-carboxylic acid	0.54	0.19	0.08	0.03	0.14	0.06	0.32	0.08	0.63	0.21
5-Methylorotic acid	—	—	0.91	0.26	1.57	0.78	3.47	1.41	2.81	0.85
1-Phenyluracil-5-carboxylic acid	—	—	1.25	0.48	0.46	0.11	—	—	—	—
5-Aminoorotic acid	—	—	0.14	0.08	0.15	0.07	0.34	0.09	—	—
5-Chloroorotic acid	—	—	1.15	0.33	0.65	0.14	1.15	0.20	1.58	0.32
5-Bromoorotic acid	—	—	3.34	0.78	1.09	0.44	1.05	0.26	1.33	0.28
5-Iodoorotic acid	—	—	2.41	1.54	1.44	1.01	1.48	0.86	0.99	0.36

[a] Solubilities in 80% ethanolic solution. [b] Solubilities in 90% ethanolic solution. [c] Solubility in water (25°) is 2.94 g/l for sodium orotate and 2.57 g/l for potassium orotate[4]. [d] Solubility in water (20°) is 5.59 g/l for rubidium orotate, and 30.82 g/l for caesium orotate; in 70% methanol, the corresponding figures are 0.49 and 3.83 g/l, and for 100% methanol, the values are[5] 0.08 and 0.31 g/l.

Experimental

Preparation of reagents. Orotic acid and uracil-5-carboxylic acid were obtained commercially. Full details of the preparation of the other substances are given elsewhere[6]. The reagents were used in the form of their N,N-dimethylethanolammonium salts, prepared in the manner described by SELLERI AND CALDINI. Each reagent solution was 0.1 *M* in ethanol (80%, v/v).

Alkali metal solutions. Solutions containing 10 mg/ml were prepared by dissolving the appropriate weight of pure, dry alkali metal chloride in water.

Method of test. To 1 ml of the aqueous solution of alkali metal chloride, 5 ml of 0.1 *M* reagent solution were added. The solution was mixed thoroughly and examined for formation of a precipitate.

Determination of solubilities. Solutions of each reagent (40 ml of 0.1 *M*) (Table II) in ethanol were placed in 100-ml conical flasks and solutions of the appropriate alkali metal chloride (*ca.* 0.5 g) dissolved in 10 ml of water were added. The resultant precipitates were aged for several hours at 3° and were then filtered off on sintered glass crucibles. The precipitates were washed 4–5 times with 2-ml portions of 70% ethanol and twice more with 2-ml portions of 95% ethanol. The precipitates were then dried at 105° for 1 h. The composition of the precipitates was determined by ultimate analysis and sulphated ash. In every case, the normal salt was indicated.

An excess of the alkali metal precipitates was suspended in 80 and 90% ethanol in 50-ml stoppered flasks. The flasks were placed in a constant-temperature water-bath at 25 ± 0.2°. The flasks were thoroughly shaken at intervals and kept under these conditions for at least four days to allow equilibrium to take place. The supernatant liquid in each flask was decanted off and filtered, and a 20-ml aliquot was transferred to a tared evaporating dish. The solutions were evaporated to dryness on a water-bath; the residues were dried in the oven at 105° for 1 h, cooled and weighed. The solubilities of the respective salts were calculated from the weights of these residues.

Discussion

Very few of the compounds show any useful degree of selectivity or sensitivity in their action towards the alkali metals. However, uracil-3-acetic acid gives a selective reaction with lithium, 5-ethylorotic acid with sodium, and 5-methyluracil-3-acetic acid with potassium. This last reagent is especially interesting because of its ability to distinguish very readily between potassium and rubidium. A serious disadvantage of the use of these three reagents is that precipitation occurs only in solutions containing about 90% ethanol. In fact, the solubilities of their salts in solutions of lower ethanol concentration are far too high for any quantitative analytical use to be possible.

The solubility measurements, together with the observations made during the qualitative precipitation tests, have shown that none of the derivatives of orotic acid is as sensitive as orotic acid itself towards the alkali metals and that substitution in the orotic acid molecule usually results in an all-round increase in the solubility of the corresponding alkali metal salts; any increase in selectivity is gained only at the expense of sensitivity, and this only to an undesirable extent from the standpoint of analytical utility.

Of the reagents that are not substituted orotic acids, uracil-5-carboxylic acid and its derivatives seem to show promise. Uracil-5-carboxylic acid appears to be only slightly inferior to orotic acid for the precipitation of sodium, potassium and rubidium, but should prove rather better for the determination of lithium and caesium. It has the disadvantage of being less readily available than orotic acid.

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Spectrophotometric determination of traces of thiourea in ammonium thiocyanate

A spectrophotometric method for the determination of traces ($1 \cdot 10^{-5}$–$7 \cdot 10^{-4} M$) of thiourea present in ammonium thiocyanate was required. Earlier methods described in the literature[1-4] deal with the determination and separation of macro amounts of these compounds. The method proposed below is based on measuring absorbances in the ultraviolet region. The method has the advantage that trace amounts of thiourea can be determined accurately in the presence of large amounts ($2 \cdot 10^{-2} M$) of thiocyanate.

Experimental

AnalaR-grade thiourea and ammonium thiocyanate were used. A Hilger UVISPEK H 700/304 was used with a quartz prism, a slit width of 1 mm (50 divisions) and 1-cm matched silica cells. Known mixtures of freshly prepared standard solutions of thiourea and ammonium thiocyanate were prepared and the absorbances of the solutions were measured at 270 and 245 nm.

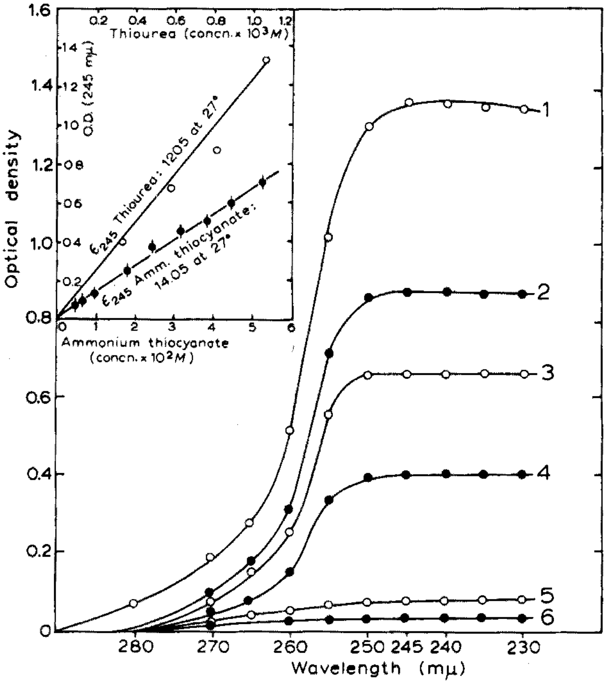

Fig. 1. Absorbance curves for thiourea and ammonium thiocyanate in U.V. (245 nm) at 27°. (1)–(4): thiourea; (1) $11.78 \cdot 10^{-4} M$, (2) $8.25 \cdot 10^{-4} M$, (3) $5.89 \cdot 10^{-4} M$, (4) $3.53 \cdot 10^{-4} M$, (5) and (6): ammonium thiocyanate; (5) $5.25 \cdot 10^{-3} M$, (6) $2.52 \cdot 10^{-3} M$.

From the absorbance curves (Fig. 1) the extinction coefficients at 245 and 270 nm (27°) were calculated to be 1205 and 127.6 respectively for thiourea, and 14.05 and

ABLE I

TERMINATION OF TRACE QUANTITIES OF THIOUREA IN AMMONIUM THIOCYANATE

oncentrations are expressed as $M \cdot 10^3$)

ncentration the ixture	*O.D. (nm)*				*Thiourea*				
	245 obs.	*245 SCN*	*245 corrected*	*270 calcd.*	*Present*	*By calculation*		*Applying correction*	
						Found	*% Error*	*Found*	*% Error*
.3230	0.748	0.040	0.708	0.07926	0.5890	0.5887	0.051	0.5877	0.22
.6087	0.261	0.051	0.210	0.02769	0.1767	0.1741	1.47	0.1743	1.36
.9994	0.477	0.052	0.3584	0.05057	0.3584	0.3513	1.98	0.3447	3.82
.2866	1.070	0.080	0.990	0.11341	0.8246	0.8142	1.26	0.8217	0.35
.4286	1.072	0.080	0.992	0.11362	0.8246	0.8175	0.86	0.8233	0.16
.5776	0.627	0.120	0.507	0.06653	0.4136	0.4080	1.35	0.4112	0.58
.2004	0.910	0.160	0.750	0.09653	0.6204	0.6190	0.23	0.6084	1.9

1.5 respectively for thiocyanate. With the simultaneous spectrophotometric technique[5] and with these values for the extinction coefficients, the following expressions were derived:

$$C_{\text{thiourea}} = 0.1 \cdot \text{O.D.}_{245} - 0.9363 \cdot \text{O.D.}_{270}$$

$$C_{\text{thiocyanate}} = 80.321 - \text{O.D.}_{270} - 8.507 \cdot \text{O.D.}_{245}$$

The results obtained for various compositions of the mixture, using the above equations, are shown in Table I.

The necessary correction for the small absorbance of ammonium thiocyanate at 245 nm (Fig. 1) can also be applied directly (Table I, final 2 columns).

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Spektralphotometrische Bestimmung kleiner Titanmengen mit Adrenalin

Bei der spektralphotometrischen Titanbestimmung benutzt man meist die Farbreaktionen mit Wasserstoffperoxyd[1], Chromotropsäure[1] und Tiron[1]. Ausserdem wurde eine ganze Reihe weiterer organischer Reagenzien vorgeschlagen, z.B. Salicyl-[1], Sulfosalicyl-[1], Salicylhydroxam-[2], Gallus-[1] und Pyrogallussäure[3], Brenzkatechin[1], Thymol[1], Phenylfluoron[4], Arsenazo[5], Askorbinsäure[1], Diantipyrinmethan[6], u.a.

Wir fanden, dass auch Adrenalin mit Lösungen von Titan(IV)-Salzen unter Bildung einer orangen bis roten Farbe reagiert. Auf dieser Reaktion beruht eine empfindliche spektralphotometrische Bestimmung über die im folgenden berichtet wird.

Geräte und Chemikalien

Die Extinktionsmessungen wurden teils mit Hilfe des Spektralphotometers Coleman Maywood 111 (USA), Type Junior, teils mit dem Spektralphotometer Prema K 58 (ČSSR) ausgeführt.

Die Reagenzlösung, 3%ige Adrenalinlösung (Präparat Spofa) in konzentrierter Schwefelsäure, wurde stets vor dem Gebrauch in kleinen Mengen frisch hergestellt.

Die Titan-Stammlösungen wurden durch Aufschluss einer abgewogenen Menge von *ca.* 0.2 g Titanoxyd (spektralreines Präparat Merck) im Quarztiegel mit 3 g $KHSO_4$ und durch Lösen der abgekühlten Schmelze in konzentrierter Schwefelsäure gewonnen. Durch entsprechendes Verdünnen der Stammlösung wurden Standardlösungen erhalten.

Die Stamm- und Standardlösungen von Niob und Tantal wurden in der gleichen Weise hergestellt. Das Niobpentoxyd war frei von Tantal (spektral überprüft) und enthielt nur Spuren Titan. Das Tantalpentoxyd war frei von Niob und Titan.

Studium der Farbreaktion

Mischt man Titansalzlösungen in konzentrierter Schwefelsäure mit Adrenalinlösung, so ergibt sich eine bräunlich-rote Färbung. Bei Verdünnen dieser Lösung mit Wasser verringert sich die Farbintensität bis zum gänzlichen Verschwinden bei ungefähr 80%iger Schwefelsäure. Die Farbe ist nicht beständig und ändert sich mit

TABELLE I

BESTÄNDIGKEIT DER VERFÄRBUNG DES TITAN–ADRENALIN-KOMPLEXES

Zeit nach dem Mischen der Lösungen in Stunden	*Extinktion bei der Wellenlänge $\lambda = 500$ nm*		
	3.5 μg Ti/ml	*4.5 μg Ti/ml*	*6 μg Ti/ml*
0	0.125	0.165	0.210
0.25	0.127	0.164	0.212
0.50	0.128	0.166	0.215
1.0	0.132	0.168	0.219
2.0	0.136	0.175	0.226
3.0	0.141	0.183	0.233
18.0	0.259	0.310	0.385

der Zeit. Die Ergebnisse für die zeitliche Abhängigkeit zeigt die Tabelle I. Aus der Tabelle ergibt sich, dass eine Stundelang nach dem Mischen der Titansalzlösung mit dem Reagenz die Extinktion praktisch unverändert bleibt, dann aber sich langsam erhöht. Die Extinktion kann also innerhalb der ersten Stunde nach dem Mischen der Lösungen gemessen werden.

Durch Absorptionmessungen im Bereich von 400 bis 700 nm fanden wir, dass der rote Titan–Adrenalin-Komplex zwischen 495 bis 500 nm maximal absorbiert (Abb. 1). Die verwendeten Lösungen wurden durch Pipettieren der entsprechenden Mengen von Standardlösungen (50 μg Ti/ml) in einen 10-ml Messkolben durch Zugabe von 1 ml 3%ige Adrenalinlösung in konzentrierter Schwefelsäure und durch Auffüllen mit H_2SO_4 hergestellt.

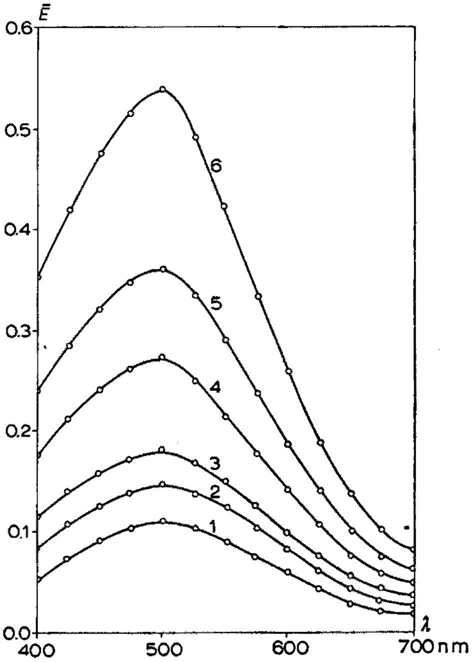

Abb. 1. Extinktionskurven des Titan–Adrenalin-Komplexes. Titankonzentration: (1) 3; (2) 4; (3) 5; (4) 7.5; (5) 10; (6) 15 μg/ml.

Die Farbintensität ist nicht nur vom Titangehalt in der Lösung abhängig, sondern auch von der Adrenalinkonzentration. Die Extinktion der Lösung strebt mit zunehmender Reagenzkonzentration einem Grenzwert zu, der erst bei mehr als hundertfachem Überschuss vom Reagenz erreicht wird. Eine weitere Erhöhung der Reagenzkonzentration im Verhältnis zur Titankonzentration sichert den linearen Verlauf der Eichkurve auch bei höheren Titankonzentrationen. Wir verwendeten eine 3%igen Reagenzlösung, die den maximalen Extinktionswert noch für 20 μg Ti/ml Lösung ergibt. Die Extinktionswerte für die Eichkurve wurden gewonnen indem sofort nach dem Auffüllen und Durchmischen die Extinktion der Lösung gemessen wurde. Die Gültigkeit des Lambert–Beerschen Gesetzes wurde im Konzentrationsbereich 0.5–20 μg Ti festgestellt. Den Verlauf der Eichkurve für die Titanbestimmung zeigt Abb. 2, in dem auch die Eichkurven des Niobs und Tantals angeführt sind. Die Farbkomplexe des Niobs und Tantals mit Adrenalin in konzentrierter Schwefelsäure verhalten sich ganz ähnlich wie der des Titankomplexes. Der Niobkomplex ist orange gefärbt und hat ein Absorptionsmaximum bei 435 nm. Der Tantalkomplex ist gelb und hat eine maximale Absorption bei 405 nm. Nimmt man die absoluten Extinktionswerte und setzt die Empfindlichkeit der Reaktion mit Tantal gleich 1, so steigt die Empfindlichkeit in der Reihe Ta, Nb, Ti im Verhältnis von etwa 1:2:40.

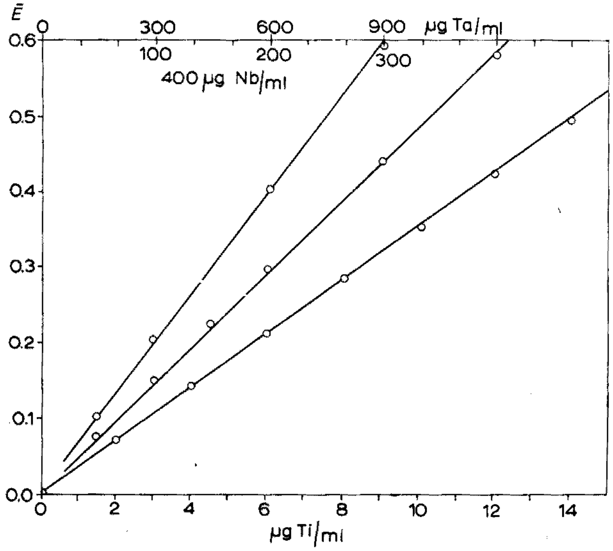

Abb. 2. Eichkurven zur spektralphotometrischen Bestimmung von: (1) Titan, λ=500 nm; (2) Niob, λ=435 nm; (3) Tantal, λ=405 nm.

Diskussion der Ergebnisse

Aus dem oben angeführten folgt, dass Niob und Tantal bei der Titanbestimmung stören, was die Brauchbarkeit der Methode im Bereich der Hüttenanalysen einschränkt, da hier gewöhnlich Titan, Niob und Tantal im Gemisch vorkommen und sich nur schwierig trennen lassen. Eine geeignete Maskierung der übrigen 2 Elemente ist in schwefelsaurem Milieu nicht möglich. Ausser Tantal und Niob stört die Gegenwart von Wolfram, Molybdän, Vanadin, Fluorid und Wasserstoffperoxyd. Einige Metalle (z.B. Eisen, Nickel, Kobalt, Aluminium) verursachen auf Grund der Schwerlöslichkeit ihrer Sulfate in konzentrierter Schwefelsäure Trübungen. Die rote Farbe, die das Titan mit Adrenalin in konzentrierter Schwefelsäure bildet, ist trotzdem analytisch zur spektralphotometrischen Titanbestimmung in den Fällen ausnutzbar, bei denen Tantal und Niob abwesend sind. Andere eventuelle Begleitelemente lassen sich durch übliche analytische Verfahren vorher abtrennen.

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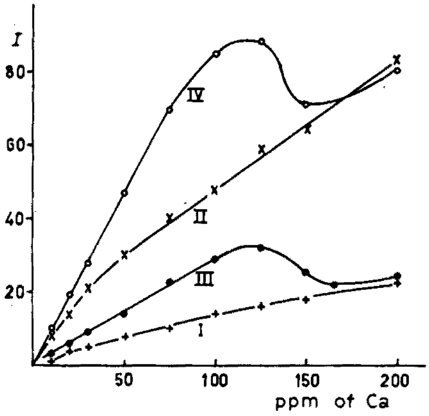
An unusual effect of iron in the flame-photometric determination of calcium

For a special purpose, calcium had to be determined in the 0–200 p.p.m. range in a 0.4 *N* sulphuric acid medium with a "Kipp" flame photometer (with separate atomizer) using propane–air as fuel. In this medium the presence of iron almost doubled the intensity of the emission of calcium.

To obtain some knowledge about the mechanism of the process involved, spectra of the flame (using the Kipp burner and atomizer assembly with propane–air) were scanned with an "Optica CF4" spectrophotometer. In the spectrum the CaOH bands at 554 and 620 nm were rather strong, but the resonance line at 422.7 nm could barely be detected. As was expected the iron lines at 393 and 397 nm could not be detected at all.

Measurements with this set-up gave the following results. Addition of *n*-butanol (4%, v/v) increased the sensitivity in the range of 0–200 p.p.m. of calcium by a factor of about 3, without influencing the background (curves I and II in Fig. 1). The presence of 60 p.p.m. of iron increased the sensitivity by a factor of about 2 up to about 100 p.p.m. of calcium, regardless of whether butanol was present or not (curves III and



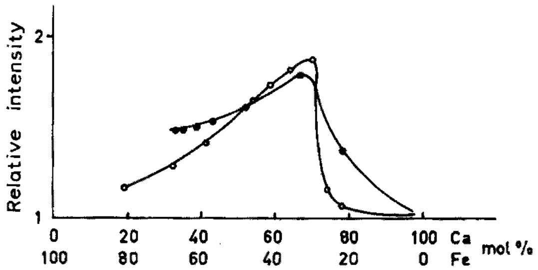


Fig. 1. Emission of Ca standard series in a medium of: (I) 0.4 *N* H_2SO_4; (II) 0.4 *N* H_2SO_4 + 4% butanol; (III) 0.4 *N* H_2SO_4 + 60 p.p.m. of Fe; (IV) 0.4 *N* H_2SO_4 + 4% butanol + 60 p.p.m. of Fe.

Fig. 2. Influence of the Ca:Fe mole ratio on the relative emission.

IV in Fig. 1). At higher calcium concentrations this increase diminished rather sharply; at about 150–170 p.p.m. it had disappeared completely (curves III and IV in Fig. 1). The presence of 30 p.p.m. of iron produced a similar increase, but here, the effect diminished at about 80 p.p.m. of calcium and from *ca.* 80–200 p.p.m. of calcium the curve was very close to curve II. Iron had no detectable influence upon the background within the concentration range tested. The CaOH bands at 620 and 554 nm and, as far as could be measured at the low intensity found, the resonance line at 422.7 nm showed the same effect.

The data (net emission intensity against concentration) are shown in Fig. 1. The form of curves I and II in Fig. 1 suggests an influence of dissociation processes, which is not shown by the other curves. The sharp break in the curves points to the presence of a compound with a rather well defined Ca:Fe mole ratio. The data, including some based on experiments not reported here, are presented in Fig. 2 plotted as relative intensity (Ca emission with Fe present over Ca emission without Fe) against the Ca:Fe mole ratio.

Addition of magnesium in the 100-p.p.m. range masked the influence of iron completely; strontium however, had only a small influence on the effect of iron. Although of no direct importance it should be added that iron had a pronounced effect on the stability of the flame, which resulted in highly reproducible data. Using the burner-atomizer assembly from "Optica" with an oxyhydrogen flame only the butanol, and not the iron, had an enhancing effect.

YOFÈ AND FINKELSTEIN[1] used iron as a releasing agent in eliminating the depressing effect of phosphate on the emission of calcium. It seemed interesting to check whether the same mechanism was responsible for the phenomenon described here, by investigating the influence of iron on the emission of calcium in the absence of sulphate.

Standard series of calcium, with and without 4% of butanol and with concentrations of 0, 30 or 60 p.p.m. of iron were therefore measured with the Kipp apparatus, sulphuric acid being absent. It was found that the emission intensity of calcium using butanol was nearly 4 times higher than samples without butanol. Iron increased the calcium emission by about 30% over the whole range from 10–200 p.p.m. whether butanol was present or not. It made no difference whether 30 or 60 p.p.m. of iron was introduced in the standard series.

In order to obtain an idea of the order of magnitude of the negative influence of sulphate on the emission of calcium under the conditions described, increasing amounts of sulphuric acid were added to solutions of 100 p.p.m. of calcium, with or without butanol. Without butanol, sulphuric acid reduced the intensity of the emission of calcium to about 25% and with butanol to about 50% of the original value.

Discussion

In a sulphuric acid medium the addition of iron increases the emission of calcium by nearly 100%. The data in Fig. 1 suggest that the increase would be extended to greater quantities of calcium if more iron were present. The data in Fig. 2 seem to imply that a Ca:Fe mole ratio of 2 or less is a prerequisite for this phenomenon. If more calcium is present this iron influence fails to appear (see Fig. 1).

It seems reasonable to conclude that, when the Ca:Fe mole ratio is smaller than 2, a Ca–Fe compound is formed which prevents sulphate from exerting its well-known negative influence. Whereas barium, strontium and lanthanum and other releasing agents[2–5] block the negative effect of sulphate by forming compounds with it (using a direct consumption burner and a hot flame), the iron seems to have the same result by forming a compound with calcium (with the Kipp apparatus and propane–air as fuel). This would also explain why low concentrations of iron have such a pronounced effect: it has nothing to do with the amount of sulphate present but only with the Ca:Fe mole ratio.

Sulphate reduces the original emission intensity of calcium by about 75%; addition of iron nearly doubles this emission, which means that sulphate still reduces the original value by 50%. However, if butanol is present, sulphate reduces the calcium emission by about 50% and iron seems to restore quantitatively the original calcium emission. If no sulphuric acid is present iron increases the emission of calcium by about 30%. Since these observations were made at 620 nm, this means that iron promotes the formation of CaOH in the flame. This effect was observed over the whole range of 10–200 p.p.m. of calcium regardless of whether 30 or 60 p.p.m. of iron was present. This particular effect of iron is, however, not observed in the presence of sulphuric acid, which can be seen in the last part of the curves of Fig. 1.

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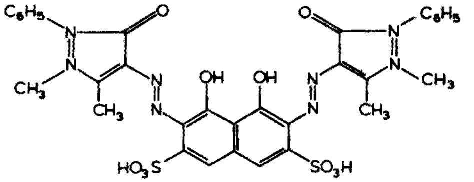
Spectrophotometric determination of lanthanides and yttrium with diantipyrylazo

Many 2,7-bisphenylazo derivatives of chromotropic acid have been used as chromogenic reagents in spectrophotometry[1]. Diantipyrylazo, *i.e.* 2,7-bis(4'-antipyrylazo)chromotropic acid (I) is the first known heterocyclic 2,7-bisazo derivative of chromotropic acid[2]. Its chromogenic properties differ very strongly from the analogous properties of the bisphenylazo derivatives. The interval of pH for spectrophotometric application of diantipyrylazo is 3–12. Diantipyrylazo is a selective photometric reagent for the determination of lanthanides and yttrium.


(I)

Recommended procedure

Adjust the acidity of the sample solution using 0.1 *M* hydrochloric acid and 0.1 *M* sodium hydroxide to pH 4–5 with methyl red as indicator. Place an aliquot of the sample solution, containing 0.05–0.4 μmole of lanthanides and yttrium, in a 25-ml volumetric flask. Add 1 ml of 10^{-3} *M* potassium cyanide and 0.5 ml of 10^{-3} *M* ammonium fluoride and mix. Add 10.0 ml of aqueous $1.0 \cdot 10^{-4}$ *M* diantipyrylazo solution (prepared by dissolution of 74.9 mg of the reagent in 1 l of water), dilute with water to the mark and mix. Measure the absorbance in 1-cm cells at 645 mμ *vs.* a reagent blank.

Applications

If $1 \cdot 10^{-4}$–1.0 mmole of uranium(VI) is present in the sample aliquot, 1 ml of 0.1 *M* disodium-EDTA solution must be added and uranium(VI) extracted with four 10-ml portions of acetylacetone–chloroform (1:1), in each case by 2–3 min of vigorous shaking. The acidity conditions of the extraction are analogous to those above. The aqueous phase is evaporated to dryness and the residue is heated to 500–600°. Then the residue is dissolved in 3 ml of 0.1 *M* hydrochloric acid, the pH of solution is adjusted to 4–5 with 0.1 *M* sodium hydroxide using methyl red as indicator, and the procedure given above is applied.

The determination of lanthanides and yttrium in thorium is carried out as follows. The acidity of an aliquot of sample solution containing 0.1–200 μmole of thorium is adjusted to pH 1.0–1.5. The solution is extracted with four 10-ml portions of 0.5 *M* thenoyltrifluoroacetone in benzene, in each case by 3–5 min of vigorous shaking. The acidity of the aqueous phase is adjusted with 0.1 *M* sodium hydroxide to pH 4–5, and the determination is completed as described above.

The net analytical molar absorptivities for individual lanthanides and yttrium on complex formation with diantipyrylazo are given in Table I.

TABLE I

NET ANALYTICAL MOLAR ABSORPTIVITIES FOR INDIVIDUAL METAL IONS AT 645 mµ AND pH 5.5

Metal ion	*Molar absorp. (cm^2/mmole)*	*Metal ion*	*Molar absorp. (cm^2/mmole)*
Y	29,400	Tb	33,500
La	45,000	Dy	31,000
Ce(III)	20,600	Ho	30,000
Pr	23,000	Er	29,400
Nd	23,200	Tm	28,800
Sm	25,000	Yb(III)	23,000
Eu(III)	27,600	Lu	21,000
Gd	34,400		

TABLE II

DETERMINATION OF LANTHANIDES AND YTTRIUM

Foreign ion added (µmole)		*Lanthanides and yttrium*			*Relative error (%)*
			Taken (µmole)	*Found (µmole)*	
Cu(II)	0.10	La	0.100	0.103	+3
	0.15		0.200	0.210	+5
Al	0.10	Y	0.100	0.098	−2
	0.20		0.200	0.212	+6
Ga	0.05	Gd	0.100	0.099	−1
	0.10		0.100	0.105	+5
In	0.001	La	0.200	0.196	−2
	0.002		0.200	0.210	+5
	0.003		0.200	0.226	+13
Pb(II)	0.05	Pr	0.100	0.101	+1
	0.06		0.100	0.105	+5
V(V)	1.50	Lu	0.100	0.097	−3
Nb(V)	1.50		0.100	0.104	+4
Cr(III)	1.50	Yb	0.200	0.204	+2
	2.00		0.200	0.208	+4
Fe(III)	1.50	La	0.100	0.098	−2
	2.00		0.100	0.106	+6
	3.00		0.100	0.108	+8
Co(II)	0.5	Y	0.300	0.297	−1
	1.0		0.300	0.285	−5
Ni	0.05		0.100	0.098	−2
	0.10		0.100	0.095	−5
EDTA	0.1	La	0.200	0.196	−2
	0.3		0.200	0.192	−4
	0.5		0.200	0.190	−5
U(VI)[a]	900.0	Gd	0.100	0.098	−2
	900.0	Yb	0.050	0.051	+2
	500.0		0.050	0.049	−2
Th[b]	100.0	La	0.100	0.103	+3
	150.0		0.100	0.102	+2
	200.0		0.100	0.100	±0

[a] Extraction of uranium(VI) with acetylacetone–chloroform was applied.

[b] The extraction of thorium with TTA was applied.

The following amounts, in µmole per 25 ml of solution, of other ions interfere: copper(II) 0.15, scandium 0.10, aluminium 0.20, gallium 0.10, indium 0.10, thallium(III) 0.10, titanium(IV) 0.10, zirconium 0.10, hafnium 0.10, germanium(IV) 5.0, tin(II) 0.10, lead(II) 0.06, vanadium(V) 2.0, niobium(V) 2.0, bismuth 0.2, chromium(III) 2.0, molybdenum(VI) 0.2, tungsten(VI) 0.2, magnanese(II) 2.0, iron(III) 2.0, cobalt(II) 1.0, nickel 0.1, palladium(II) 2.0, thorium 0.1, uranium(VI) 0.06, fluoride 0.7, cyanide 1.5, phosphate 0.5, sulphate 1.0, EDTA 0.5, citrate 0.6 and tartrate 0.6.

The aqueous solutions of diantipyrylazo are stable for some months. The complexes of the reagent with lanthanides and yttrium are stable in solution under normal conditions for 10 h. The deviations in the individual determinations do not exceed ±5% relative. The molar ratio between metal and ligand in the complexes of lanthanides is 1:1. Some characteristic results of analyses are given in Table II.

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The Boedeker reaction. Part III. The detection of sulphite ion

Nitroprusside and sulphite ions in aqueous solution interact to give[1–5] the red, highly-dissociated sulphitonitroprusside ion, $Fe(CN)_5NOSO_3^{4-}$. The addition of zinc ions results in the formation of sparingly soluble zinc sulphitonitroprusside, and markedly increases the sensitivity of the reaction[1,2]. According to Charlot, 100 p.p.m. of sulphite ion is detectable in aqueous solution in this way[6].

We have observed two new aspects of the Boedeker reaction. First, the amount of sulphitonitroprusside ion formed in solution is increased not only by the addition of zinc ions, but also by the addition of alkali metal ions[5]. This effect of alkali metal ions appears to be due to the formation of ion-pairs of the type $Fe(CN)_5NOSO_3M^{3-}$, where M is an alkali metal. The effect is more pronounced, the larger the alkali metal ion. Secondly, the sensitivity of the reaction involving zinc ion has been shown to be further improved by the addition of pyridine; this is believed to be due to the low solubility of $(Zn\,py_x)_2Fe(CN)_5NOSO_3$.

In the present communication the analytical aspects of the Boedeker reaction are reassessed. A method is described by which 5 p.p.m. of sulphite ion in aqueous solution may be detected; interference by sulphide ion is avoided.

Intensification by potassium ions

The addition of alkali metal salts to solutions containing sodium nitroprusside and sodium sulphite increases the sensitivity of the reaction many times. Although this intensification of the colour is greatest with caesium salts, the use of a potassium salt is more practicable.

Concentrated potassium chloride solution (12.5 ml, 2.13 *M*) and 20% sodium nitroprusside solution (1 ml) were added to an aliquot of sulphite solution and the mixture diluted to 25 ml. It was found possible to detect a minimum of 160 p.p.m. of sulphite ion in 10 ml of the sulphite solution.

Intensification by zinc ions

Both zinc sulphitonitroprusside and zinc nitroprusside remain in colloidal solution when the nitroprusside concentration is less than 0.008 *M* and the zinc is added last in the form of a highly concentrated solution of zinc acetate.

A mixture of 2 ml of 0.04 *M* sodium nitroprusside and an aliquot of sulphite solution was diluted to 23 ml. The solution was mixed thoroughly, and 2 ml of 1 *M* zinc acetate solution were added. A minimum of 80 p.p.m. of sulphite ion was detectable in 10 ml of sulphite solution.

Intensification by zinc ions in the presence of pyridine

In the presence of zinc ions and pyridine, the coloured species—probably a pyridinezinc(II) sulphitonitroprusside—can be kept in colloidal solution by the addition of gelatin. The colour intensity of these gelatin-protected solutions reaches a maximum after 15 min and remains constant for several hours. The optimum concentration of pyridine and zinc are 0.30 *M* and 0.045 *M* respectively.

Curves obtained by applying the method of continuous variations[7] indicated that with a slight excess of nitroprusside about 93% of the sulphite added was converted to sulphitonitroprusside. They also gave a value of 3800 for the molar extinction coefficient at the wavelength of maximum absorption (490 mμ), a value identical with that obtained for the sulphitonitroprusside–potassium ion-pair[5].

Unfortunately, the application of this modification of the Boedeker reaction to quantitative work was not completely successful, owing to the gradual formation of a white crystalline precipitate, which is believed to be a pyridinezinc(II) acetate, in the reaction mixture. The formation of this precipitate often occurred before the colour intensity of the solution had been measured, *i.e.* within 15 min. Substitution of cadmium acetate or other cadmium or zinc salts for the zinc acetate did not resolve the problem. The substitution of β-picoline or hexamine (which also cause colour intensification) for pyridine was also unsuccessful. The addition of alcohol appeared to delay the formation of the precipitate to some extent, and was advantageous in limiting bubble formation in the gelatin solutions.

Sensitivity tests

The sensitivity of this modification of the Boedeker reaction was determined using the following reagent solutions.

Solution A. Sodium nitroprusside (A.R., 0.50 g) was dissolved in about 50 ml of water, and 2 ml of 0.01 *M* EDTA were added (to inhibit Prussian Blue formation in the aged solution). Pyridine (A.R., 67 ± 2.5 ml) and ethanol (360 ± 10 ml) were then added and the solution was diluted to about 750 ml with water. Finally, a solution of 1.25 g of gelatin in 150 ml of water was added, and the resulting solution was diluted to 1 l with water and mixed thoroughly. The straw-coloured solution was stored in an amber glass bottle. The solution became yellow over a period of time, but was usable for at least three months.

Solution B. Zinc acetate dihydrate (220±10 g) was dissolved in 800 ml of water.

Two procedures were used: (*1*) Solution A (20 ml) was added from a burette to a 50-ml volumetric flask, and an aliquot of sulphite solution was added. The mixture was diluted to about 45 ml and mixed, then solution B (2.5 ml) was added from a pipette, and the solution was diluted to 50 ml and mixed thoroughly. When the maximum volume of sulphite solution (25 ml) was used, 1 p.p.m. of sulphite ion was just detectable. The optical densities of a series of solutions which remained clear after 15-min standing, are given in Table I. These measurements were made on a Spekker Absorptiometer fitted with an Ilford 603 filter. A plot of optical density against sulphite concentration was linear.

TABLE I

SENSITIVITY OF THE PYRIDINE-INTENSIFIED REACTION

(25 ml of sample)

Sulphite concn. in sample solution ($M \times 10^{-4}$)	1.10	2.19	3.29	4.38	5.48
Optical density	0.153	0.312	0.483	0.637	0.808

(*2*) Two drops of solution A and two drops of sulphite solution were mixed on a spot tile. One drop of solution B was added and the solution stirred. An immediate reaction was given by 10 p.p.m. of sulphite in the sulphite solution and after the solution had been allowed to stand for 10 min, 5 p.p.m. of sulphite was readily detectable and 2.5 p.p.m. of sulphite just detectable.

Effect of pH

The sample solution should be approximately neutral. When 10-ml aliquots of sample solution were tested by procedure (*1*), it was found that if the pH of the sample solution exceeded 10, zinc hydroxide was precipitated in the test solution, and if the pH of the sample solution was less than 4, the reaction was less sensitive, as bisulphite ion does not react with nitroprusside ion[8].

Interfering substances

A number of organic compounds, including thiols, amines and ketones give coloured compounds with the nitroprusside ion, but usually only in strongly alkaline solution[9].

The only important source of interference is the sulphide ion, which reacts in rather an unusual way with the reagents. When sulphide is added to solution A, a blue–red colour develops over a period of time, but when solution B is added the test solution becomes red in colour and no further reaction occurs. When solution B is added first to the sulphide solution, zinc sulphide is precipitated, and this does not react with solution A. Sulphite ion reacts normally under this reversed order of addition, although there is the possibility of some slight coprecipitation with zinc sulphide[10]. Thus, as the reaction of sulphite ion with solution A is so insensitive, the presence of sulphide ion can be detected readily and its interference avoided by adding the reagents in reverse order.

Thiosulphate ion (200 p.p.m.) in the sample solution causes a slight turbidity but does not interfere. Up to 400 p.p.m. of sodium hypophosphite can be tolerated without loss of sensitivity. Large amounts of iron(II), tin(II), ferrocyanides and arsenates give white precipitates with the reagents.

Discussion

The use of pyridine—with zinc acetate and sodium nitroprusside—in the test for sulphite ion, results in a much greater sensitivity. Indeed, about 93% of the sulphite is combined with the nitroprusside under these conditions. Any sulphide or interfering organic compounds present react with the sodium nitroprusside before the addition of the zinc and cannot be confused with sulphite ion. Interference by sulphide can be eliminated by reversing the order of addition of the reagents.

Quantitatively reproducible results are obtainable when the reagent solutions are prepared within the limits quoted, but for qualitative work the reagent solutions need not be prepared so exactly.

The procedure cannot at present be recommended as a spectrophotometric method of determining sulphite owing to the uncertainty of obtaining clear, measurable solutions.

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The use of air as carrier gas in the electron capture detector

The electron capture or electron absorption detector is one of the most sensitive detectors used in gas chromatography. It has been extremely successful in the determination of traces of pesticide residues in materials of biological origin[1], mainly because of its very high sensitivity to compounds containing halogens and/or phosphorus atoms and its relatively low sensitivity to hydrocarbons. It was felt that perhaps this selectivity could be utilized to distinguish between the hydrocarbons generally present in the air and phosphorus-containing pesticides.

In gas chromatography nitrogen or a counting gas is generally used as the carrier[2]. However, in order to utilize the electron capture detector in an automatic field type apparatus, air must be used as the carrier gas. The background signal with nitrogen or counting gas is very low because these gases do not capture electrons to any appreciable extent. Although oxygen is a weak electron absorber, the presence of a large amount of a weak absorber would be expected to increase the background signal, which indeed it does. At the outset of this work it was felt that, due to the very high sensitivity of this detector, it still might be possible to detect pesticides directly in sufficiently low concentration to make it a suitable means of detection.

There is no published work on the use of air as a carrier gas. Some work has been published in which air was injected into a nitrogen stream[2], but since the electron capture characteristics of oxygen–nitrogen mixtures are not linear with concentration, the literature was not particularly helpful in predicting the behavior of this system.

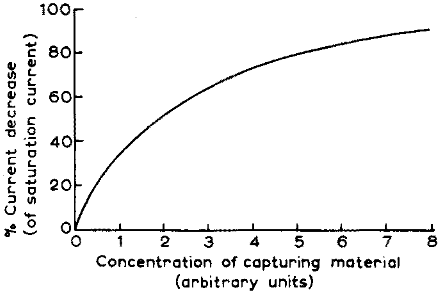
A parallel plate detector of the LOVELOCK design (Micro-Tek Inc., Baton Rouge, Louisiana) was used for this work. For pulsed operation an Ionics pulser, also of LOVELOCK design was used. A battery was generally used for the d.c. mode of operation.

The first investigations were carried out using halogen compounds as test substances, because the results could be compared more readily to literature data. Some investigators doubt that any meaningful quantitative data have been obtained with the phosphorus-containing pesticides owing to the decomposition and hold up in the chromatographic column[3].

Chloroform was used most often as a test substance because its high volatility made vaporization of the sample easy, and the detector is known to be very sensitive for chloroform. The apparatus was essentially a gas chromatograph without a column. The sample was injected through a rubber septum into a vaporizer, passed through a splitter, and then through a length of metal tubing into the detector. The quantity of material which passed through the detector was calculated assuming that the sample split was the same as the carrier gas split. With air as the carrier gas and a d.c. mode of detection the minimum detectable amount of chloroform was about $3 \cdot 10^{-6}$ g. LOVELOCK reported an experiment with argon–methane counting gas and a pulsed mode of operation in which he was able to detect approximately $3 \cdot 10^{-13}$ g of chloroform[2]. The d.c. mode of operation is generally slightly more sensitive. It was apparent from these first experiments that the use of air seriously curtailed the sensitivity of the detector.

A typical plot of detector current *vs.* concentration of capturing material is shown in Fig. 1. The analytically useful portion of the curve lies below 30% current decrease. Electron capture detectors in gas chromatographs operate in this region. At

30 V d.c. a typical saturation current using nitrogen was approximately $5 \cdot 10^{-9}$ A. A typical saturation current for air under the same conditions was $3 \cdot 10^{-10}$ A. This corresponds to a 94% reduction in the saturation current. Reference to Fig. 1 shows that the detector is operating on the non-linear portion of the current *vs.* concentration curve, and consequently only large changes in concentration can be detected.



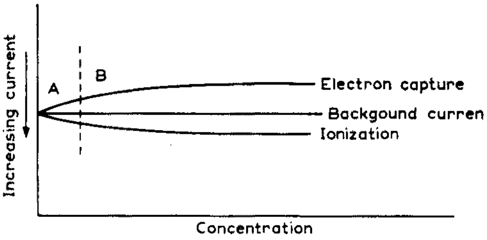


Fig. 1. Relationship between detector current and capturing material concentration.

Fig. 2. Possible relation between concentration, ionization and electron capture. (A) Ionization predominates; (B) electron capture predominates.

Experiments were also performed using the pulsed mode of operation. Pulsing intervals of 5, 15 and 50 µsec were used. When the detector is used in a normal manner in a gas chromatograph, the sensitivity increases as the interval between pulses is increased up to the point where the natural recombination between electrons and positive ions limits any further increase. This effect is shown in Fig. 2 in ref. 2. When air was used as the carrier gas just the opposite was true. With a 5-µsec interval the signal was slightly less than that obtained with d.c. With a 15-µsec interval the signal was greatly reduced, and with a 50-µsec interval no signal was observed. Trimethyl phosphate was used as the test vapor in these experiments. There is no published account of this type of behavior, but these observations can probably be rationalized on the basis of results reported for argon–oxygen mixtures (see Fig. 3 in ref. 2). The presence of oxygen lowers the equilibrium concentration of electrons, but the rate at which this equilibrium is attained increases with increasing oxygen concentration. In the case of air the electrons removed by the pulse are "replaced" very rapidly. When the pulse interval is as long as 50 µsec, equilibrium is re-established between pulses, and there is no recordable evidence of electron capture.

A second series of experiments was performed using an air dilution apparatus as a source of vapor of known concentration. The detector was connected to the generator through a 3-way stopcock so that Sarin vapor (isopropyl methyl phosphonofluoridate) or air could be sampled alternately. Laboratory air or air plus Sarin vapor was drawn through the detector by means of vacuum at about 140 ml/min. A series of sodium hydroxide scrubbers was placed between the detector and the vacuum line to remove the Sarin after it had passed through the detector. For most of this work a potential of 20 V d.c. was impressed across the electrodes.

In any of the ionization detectors used in gas chromatography electron capture and ionization both occur[3]. The electron capture detector is designed so that the effect of ionization is minimized. In this second experiment it became apparent that ionization was playing an important and in some cases the dominant role. Whether ionization or electron capture predominated depended upon the experimental conditions. An obvious disadvantage in this state of affairs is that these processes are mutually antagonistic, each reducing the sensitivity of the other.

BARNEY *et al.*[3] studied the behavior of Systox isomers in the same type of detector as used in this work. Both isomers captured when the detector was operated normally for both the d.c. and pulsed modes. When the detector was operated in this reverse of fashion the thiono and the thiolo isomers produced a signal for both the d.c. and pulsed modes, but the thiolo isomer gave an increase in current at all amounts tested (at 30 V). The response of the detector to the thiono isomer was dependent upon the amount of the isomer in the detector. Electron capture occurs when the concentration of isomer is small, and ionization occurs when the amount is large at 30 V. The response also depended upon the polarizing voltage. For the thiono isomer electron capture predominated below 15 V, and for the thiolo isomer electron capture predominated below 10 V. Similar results were obtained with Sarin. Negative signals, *i.e.* an increase in current, were obtained, but they were not due simply to the presence or absence of Sarin vapor. If air was first passed through the detector followed by Sarin vapor, a signal was obtained. When air was reintroduced the current fell back to the original value. However, similar results were obtained when the sequence was Sarin, air, and Sarin. Raising the detector temperature to 50–70° eliminated this behavior (which was possibly a contact potential phenomenon).

When low concentrations of Sarin vapor, approximately 2 μg/l of air were passed through the detector the current increased, indicating ionization. High concentrations of Sarin, 10–20 mg/l, resulted in electron capture. The transition concentration was not determined. There is no report of this type of behavior in the literature. If one assumes that the relationship between concentrations and ionization and electron capture is in general as shown in Fig. 2, then the experimental results are consistent.

In another series of experiments, the pulser power supply was connected to the detector and the test substances were introduced by holding a bottle of the substance near the air inlet. At 5-μsec pulsed intervals, chloroform, petroleum ether, trimethyl phosphate, and Sarin from a bottle exhibited electron capture, Sarin from the dilution generator produced an increase in the current (ionization). At 15-μsec pulsed intervals petroleum ether increased the current, and at 50-μsec intervals chloroform caused an increase in current.

Apparently ionization and electron capture were occurring simultaneously. When longer pulse intervals were used, the electron capture was not detected because of the rapid re-establishment of the electron equilibrium, so only the ionization was detected.

It might be concluded from these experiments that as expected, the use of air as a carrier for an electron capture detector caused a large reduction in sensitivity. This reduction of sensitivity was so great that it seems improbable that an electron capture detector would be suitable for the detection of low concentrations of atmospheric pesticide contaminants under these conditions.

With low concentrations of Sarin, ionization predominates over electron capture. This particular phenomenon has not been reported in the literature. The fact that ionization can predominate over electron capture in poorly designed detectors has been known for several years[3]. However, there are not yet adequate data available to determine whether the ionization observed in our case was due to detector geometry or the presence of large amounts of oxygen. Preliminary experiments have shown that the electron capture detector might be used to detect and roughly estimate the concentration of large amounts of pesticides.

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Reactions of mercury(II) cyanide with heavy metal sulfides*

Some studies dealing with possible new applications of mercury(II) cyanide in inorganic analysis included an investigation of the behavior of heavy metal sulfides when suspended in aqueous solutions of this slightly ionized compound. The solubility product of mercury(II) sulfide is extremely small and accordingly it was expected that only those sulfides that themselves have very low solubilities would remain unchanged under these conditions, whereas other sulfides would yield mercury(II) sulfide.

This expectation was realized with yellow cadmium sulfide as revealed by an immediate blackening:

$$CdS + Hg(CN)_2 \rightarrow Cd(CN)_2 + HgS \qquad (1)$$

However, reaction (1) is merely an initial reaction that is followed by others. This fact is revealed by the release of hydrogen cyanide, even at room temperature, in sufficient amounts to give a positive response to characteristic color tests for this volatile compound. Furthermore, it was found that the liquid obtained by filtering or centrifuging after warming cadmium sulfide with a solution of mercury(II) cyanide contains Cd^{2+} ions as shown by the precipitation of cadmium carbonate on the addition of sodium carbonate. Obviously the cadmium cyanide produced initially undergoes hydrolysis:

$$Cd(CN)_2 + 2\ H_2O \rightarrow Cd(OH)_2 + 2\ HCN \qquad (2)$$

which is in conformity with the behavior of freshly precipitated cadmium cyanide.

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* (Translated by RALPH E. OESPER, University of Cincinnati)

The formation of water-soluble cadmium salts results from the reactions:

$$Cd(CN)_2 + Hg(CN)_2 \rightarrow Cd^{2+} + [Hg(CN)_4]^{2-} \qquad (3)$$

$$Cd(OH)_2 + Hg(CN)_2 \rightarrow Cd^{2+} + [Hg(OH)_2(CN)_2]^{2-} \qquad (4)$$

It is possible that reactions analogous to (1)–(4) also are given by other heavy metal sulfides.

From the analytical standpoint it was of interest whether the formation of hydrogen cyanide could be employed for a differentiation of heavy metal sulfides. Accordingly the following experiments were tried: about 10 mg of carefully purified and dried sulfide was treated in a test tube with 1 ml of a 5% solution of mercuric cyanide and the mouth of the tube was covered with a disk of filter paper moistened with hydrogen cyanide reagent. The test tube was held in boiling water for about 2 min and the paper observed for the appearance of a blue stain that is characteristic for hydrogen cyanide. The *reagent solution*[1] consists of a freshly prepared solution of 5 mg of copper ethylacetoacetate along with 5 mg of tetrabase in 4 ml of chloroform. The results were:

I. *Strong evolution of hydrogen cyanide*: ZnS, CdS, Fe_2S_3, MnS, PbS, Bi_2S_3, SnS, SnS_2, UO_2S, As_2S_3, MoS_3.

II. *No evolution of hydrogen cyanide*: PdS, Ag_2S, CoS, NiS, CuS, As_2S_5.

The absence of the HCN-production in the latter instances may be ascribed to the lack of reactivity of these sulfides with mercury(II) cyanide. This assumption is supported by the behavior of silver sulfide. When this sulfide was warmed with a solution of mercury(II) cyanide and then digested with ammonia, no silver could be detected in the filtrate as should have been the case if silver cyanide had been formed.

Rapid reaction of the sulfides in *both* categories with mercury(II) cyanide can be achieved by dry heating (pyrolysis) of an intimate mixture of the reaction partners, in a glycerol bath at 180°. This is demonstrated by the evolution of a volatile product which gives a blue coloration with hydrogen cyanide reagent. Surprisingly it was found that HgS behaves like the other heavy metal sulfides. We assume therefore that the initial pyrolytic reaction:

$$MeS + Hg(CN)_2 \rightarrow Me(CN)_2 + HgS$$

leads to HgS. The latter pyrolytically reacts with excess $Hg(CN)_2$ to form a volatile CN-containing compound in amounts which can be detected by the bluing of the HCN reagent. This volatile product is neither dicyanogen nor dicyanogen sulfide because these compounds could not be detected by means of characteristic spot tests[2,3]. Due to the fact that the formation of elemental mercury has been observed (insolubility in alkali sulfide), a plausible assumption may be that first thiocyanogen is produced according to:

$$2\ HgS + Hg(CN)_2 \rightarrow 3\ Hg^0 + (CNS)_2$$

which then reacts with excess $Hg(CN)_2$ to form cyanogen thiocyanate[4]:

$$Hg(CN)_2 + 2\ (CNS)_2 \rightarrow Hg(CNS)_2 + 2\ CNCNS$$

The vapors of $(CNS)_2$ and CNCNS in contact with the HCN reagent produces bluing.

Analytical applications may be expected from the reaction of mercury(II) cyanide with heavy metal sulfides either by the wet method or by pyrolysis with production of hydrogen cyanide or thiocyanogen that are readily detected. For example, minute amounts of cadmium sulfide react with aqueous solutions of mercury(II) cyanide, permitting a ready detection[5] of this sulfide in the presence of CuS, CoS or NiS. Also, lead sulfide can be detected in the presence of silver sulfide through the production of hydrogen cyanide. The pyrolysis with mercury(II) cyanide seems to be suitable for revealing sulfidic minerals, as was demonstrated by the behavior of molybdenite (MoS_2).

It should be noted that the pyrolytic reactions between heavy metal sulfides and mercury(II) cyanide, which proceed at relatively low temperatures (140–180°) are solid body reactions that occur at the contact sites of the participants. Although the yields of such reactions are small, their occurrence can be detected through the highly sensitive test for volatile CN-compounds formed, by means of the HCN reagent. It must be taken into consideration that mercury(II) cyanide has a low but significant vapor tension at the reaction temperature and consequently the vapors of $Hg(CN)_2$ reach the active sites on solid metal sulfides.

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Some observations on the determination of metals by atomic absorption spectroscopy combined with extraction

Solvent extraction is recognized as a powerful technique for accomplishing analytical separations. In atomic absorption spectroscopy, this technique can be of great value in making the determination more sensitive by selective extraction from the matrix elements and in eliminating the interfering elements. However, highly selective extraction is not necessary; many extractive methods, formerly dismissed as unsatisfactory for spectrophotometry, may be satisfactory for atomic absorption spectroscopy. Recently, many workers have applied the extraction technique in conjunction with atomic absorption spectroscopy.

The present paper presents certain results of comparative tests made to investigate the effect of complexing agents on the absorption.

Experimental

Apparatus. A Techtron AA-100 atomic absorption spectrophotometer was used. An air–acetylene flame (10 cm) was used and the flow rate of sample solution was 9 ml/min. Lamp currents and analytical lines used are listed in Table I. A Hitachi EPU-2 spectrophotometer with atomic absorption attachment RA-1 was also used for comparison.

A mechanical extraction device was used for extraction of complex.

TABLE I

LAMP CURRENTS AND WAVELENGTHS USED

Element	*Lamp current (mA)*	*Wavelength (Å)*
Cd	5	2288
Ag	4	3281
Mn	5	2795
Cu	4	3247
Ni	5	2320
Fe	4	2483
Pd	10	2476
Pb	5	2171

Reagents. Pure analytical reagents were used throughout this work. Methy isobutyl ketone (MIBK) was redistilled.

Extraction method. The following complexes were extracted and compared: diethyldithiocarbamate (DDTC)[1], dithizonate[2,3] and iodide[4] for silver and cadmium; cupferrate[5], DDTC[1], hydroxyquinolinate[6] and thenoyltrifluoroacetate[7] for manganese; cupferrate[5,8], DDTC[1], dithizonate[4], hydroxyquinolinate[6] and salicylaldoximate[9] for copper and nickel; cupferrate[5], hydroxyquinolinate[6] and chloride[5] for iron; DDTC[1] and dithizonate[3] for palladium and DDTC[1], dithizonate[3], hydroxyquinolinate[3] and iodide[4] for lead.

Each complex was extracted twice with 10-ml portions of MIBK from 30 ml of buffered solution and the combined extract was diluted to 25 ml with MIBK. The absorption was measured by spraying this into the flame. Extraction was made as complete as desired by this technique.

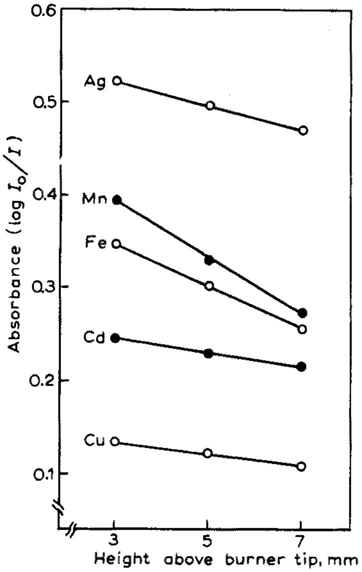
Results and discussion

The number of solvents that can be successfully used in atomic absorption spectroscopy is limited. The solvent must be completely combustible and must have no absorption against the radiation from the hollow-cathode lamp. Ketones and esters behave satisfactorily in the flame. In flames, methyl isobutyl ketone is a highly suitable solvent in every respect[10], and it was therefore chosen for the present work. *n*-Butyl acetate and isoamyl alcohol were also tested for comparison.

The effect of the height of the light path in the flame is shown in Fig. 1; the height above the burner tip to the lower part of the light beam was measured. As shown in Fig. 1, absorption was higher in the lower portion of flame. The effect of height was larger for manganese and iron than for other elements. Similar results were obtained for aqueous solutions.

The effect of flame state on absorption was also tested. Lower acetylene flow rates were necessary in spraying the organic solvent. A slightly reducing flame was adequate for measurement; air pressure was set at *ca.* 15 psi on the regulator and the acetylene flow rate was *ca.* 0.2 l/min. In this case, the flame was about 15 mm in height without spraying the organic solvent.

The effect of the complexing agent on the absorption is summarized in Fig. 2. For cadmium, silver, iron or palladium, the different complexing agents tested had no effect. However, the complexes were divided into 2 groups for manganese, copper,



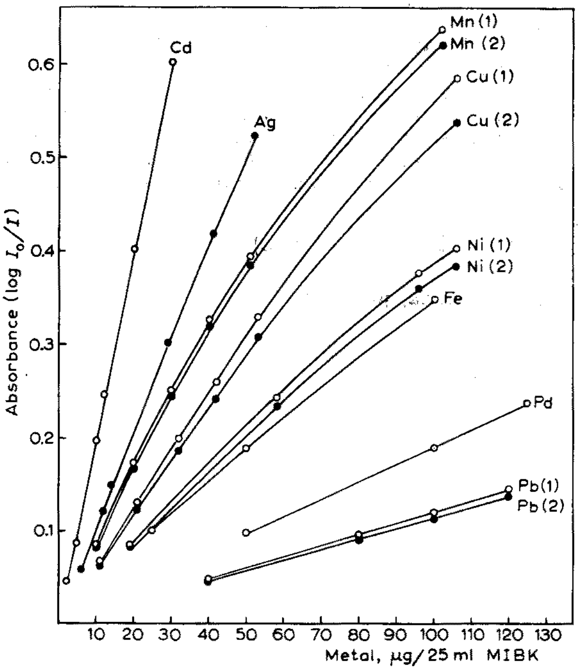


Fig. 1. Effect of height of light path in flame.

Fig. 2. Relation between metal concentration and absorption. Cd, Ag and Pb(I): DDTC, dithizonate and iodide. Mn(I): Cupferrate. Mn(2): DDTC, hydroxyquinolinate and thenoyltrifluoroacetonate. Cu(I) and Ni(I): Cupferrate, DDTC and dithizonate. Cu(2) and Ni(2): Hydroxyquinolinate and salicylaldoximate. Fe: Cupferrate, hydroxyquinolinate and chloride. Pd: DDTC and dithizonate. Pb(2): Hydroxyquinolinate.

nickel and lead. The hydroxyquinolinate and salicylaldoximate complexes gave a slightly lower absorption for copper, nickel or lead than that obtained with other complexes. Cupferrate gave a slightly higher absorption for manganese than did the other complexes; the origin of this effect is uncertain.

Similar results which confirmed the above results were obtained in the use of the Hitachi atomic absorption apparatus.

The extraction method is effective in atomic absorption spectroscopy. A three-fold increase in sensitivity was obtained with methyl isobutyl ketone extracts, relative to aqueous solutions. The absorptions with *n*-butyl acetate or isoamyl alcohol extracts were lower than those with methyl isobutyl ketone extracts; this may result from the physical properties of the solvents in spraying. The same tendency was observed in the case of magnesium extraction[10].

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BOOK REVIEWS

Methods of Biochemical Analysis, Edited by DAVID GLICK, Vol. 13, Interscience Publishers–J. Wiley & Sons, Inc., New York, 1965, ix+488 pp., price 110 s.

The 13th volume in this series can best be reviewed by giving a brief account of each of the 7 articles it contains.

S. BLACKBURN contributes an account of the determination of amino acids by high-voltage electrophoresis. The author advocates this method as an alternative to that of MOORE AND STEIN on the grounds of its speed and the number of analyses which can be carried out simultaneously. It is particularly suitable for the determination of acid sequences in proteins. The types of apparatus available are discussed and the recommended type (Gross) described, together with the effect of buffer composition and the temperature of the cooling liquid on separations using the apparatus. The determination of the separated acids by elution or direct photometric methods is considered and finally a recommended procedure is described in detail.

In the second article H. WALDMANN-MEYER discusses mobility determination by zone electrophoresis at constant current. This technique has already been used for the characterisation of enzymes and pathological proteins and for the study of ion binding by proteins. The theoretical basis of the technique is considered in detail and the apparatus and experimental procedure fully described.

In the next article J. HERMANS, JR., describes spectrophotometric and polarimetric methods for the study of reversible denaturation of proteins and discusses at length the interpretation of results to yield thermodynamic data.

K. C. HOLMES AND D. M. BLOW contribute a lengthy review on the use of X-ray diffraction in the study of protein and nucleic acid structure. The principles of this technique, experimental procedures for the measurement of X-ray intensities and the interpretation of results are all considered in detail. A final section deals with diffraction by fibrous proteins and nucleic acids.

A review by S. JACOBS deals with nitrogen determination in biological materials. The Dumas and Kjeldahl methods in their more recent modified forms are considered in some detail, together with methods for determining ammonia with and without prior separation from the digest. The author concludes that a sealed tube digestion modification of the Kjeldahl procedure combined with a sensitive colorimetric method for the estimation of ammonia should be capable of precise nitrogen determinations.

E. AMADOR AND W. E. C. WACKER contribute an exhaustive review of enzymatic methods used in the diagnosis of disease. This is a timely account since techniques of this kind have only recently come to be widely used and their full potentialities are still to be realised. The enzymes dealt with include dehydrogenases, reductases, transaminases, phosphatases, esterases, peptidases, isomerases, aldolases, kinases, nucleases, oxidases, sulphatases, hydrases, transphosphorylases, glycosidases, polysaccharidases, transferases, deaminases, deamidinases and transamidases. In the majority of cases experimental details for the tests are given.

In the final article I. E. BUSH deals with applications of the R_M treatment in chromatographic analysis. The validity of the concept of the additivity of ΔR_M values is examined in detail and it is concluded that the R_M theory is confirmed over the range of values in which reliable predictions are to be expected. This article is a valuable contribution to the theoretical treatment of chromatography.

In conclusion the reviewer must again, on behalf of all workers in the field of biochemical research, welcome this latest volume in this important series.

H. G. BRAY (Birmingham)

Anal. Chim. Acta, 36 (1966) 261–262

W. KOCH, *Metallkundliche Analyse*, Verlag Stahleisen, Düsseldorf–Verlag Chemie, Weinheim/Bergstrasse, 1965, 497 S., Ganzleinen DM 135.—.

The isolation, identification and analysis of components present in metallic alloys has been the subject of much investigational work over many years. Professor WALTER KOCH of the Max Planck Institut has been one of the most outstanding workers in this field for over 25 years. In this comprehensive treatise he gathers together the fruits of his work in an easily available form.

After a critical evaluation of the older chemical and electrolytic procedures Professor KOCH discusses the electrochemical bases affecting the decomposition of iron alloys and, more briefly, of non-ferrous alloys. Practical procedures for the isolation of phases follow. These include sampling methods, chemical and electrolytic methods and the application of micromanipulation. Enrichment and separation of the phases can be achieved by methods based on differences of solubility or by halogenation followed by vacuum sublimation. Physical procedures can also be used, including centrifugation, flotation, the use of liquids of known density, magnetic separations and separations using a micromanipulator.

The determination of the components in the isolated material is described in detail. Analytical methods are given for the examination of oxide inclusions, carbides, intermetallic phases, other components and of the electrolyte itself. All types of modern chemical techniques such as solvent extraction and ion-exchange separations and spectrophotometry have been applied, both on the semi-micro and micro scales, as well as ultraviolet emission spectroscopy, flame spectrophotometry and X-ray fluorescence spectrometry.

Besides analytical methods other techniques are now available for the examination of the isolated material and Professor KOCH gives instructions for the use of microscopy, electron microscopy, X-ray diffraction, electron diffraction and the examination of magnetic properties. The characteristic properties of virtually all the components likely to be encountered in irons and steels — oxides, sulphides, nitrides, carbides, silicates, intermetallic compounds, etc. — are described and fully documented, with illustrations.

As might be expected the emphasis is on ferrous alloys, although some attention is given to non-ferrous metals. The book will be invaluable to chemists and metallurgists concerned with the investigation of alloy components and it is to be hoped that it will be translated into other languages, thus making available to a wider circle the mass of information it contains.

W. E. CLARKE (Alvechurch)

Anal. Chim. Acta, 36 (1966) 262

A. BERKA, J. VULTERIN AND J. ZÝKA, *Newer Redox Titrants*, Translated by H. WEISZ (International Series of Monographs on Analytical Chemistry, Vol. 22), Pergamon Press, Oxford, 1965, ix + 245 pp., price 60 s.

Some 30 oxidants or reductants which have been proposed for titrimetric analysis, but which are relatively unfamiliar, are described in this book. Each of them is dealt with in a separate chapter. This first summarizes the literature, then describes the preparation and standardization of the reagent, and the preparation and use of the indicator or indicators; and then the determinations for which the reagent has been proposed or tested are reviewed.

With the proliferation of analytical methods during the past quarter of a century, it is inevitable that specialised monographs of this kind should be produced. These enable the analyst to become familiar with advances in various fields without the necessity for lengthy and time-consuming literature searches. This book certainly gives the impression of having covered the literature thoroughly. The number of references for each chapter ranges from 10 for tungsten(V) and tungsten(IV) to over a 100 for chromium(II) (averaging about 45).

It should be made clear that this is a source-book rather than a laboratory manual. In most cases it is doubtful if the titrant could be used for the determinations listed without following up the references and consulting the original literature. But the references are there, and therefore the original literature is readily traced.

One would, perhaps, have liked to see a more critical appreciation of the usefulness of the various titrants. Thus, although it is interesting to know that about a dozen of these reagents can be used for the determination of arsenic, this is of little help in deciding whether any of them is likely to be as satisfactory as or more satisfactory than more conventional oxidants. It can, of course, be argued that such an extension of the monograph would have made the book much larger than the authors intended, resulting, among other things, in a further increase in the already rather high price.

The translation is on the whole very good, and only an occasional unusual construction betrays that it is in fact not by an English writer.

C. L. WILSON (Belfast)

Anal. Chim. Acta, 36 (1966) 263

T. M. SUGDEN AND C. N. KENNEY, *Microwave Spectroscopy of Gases*, Van Nostrand Series in Physical Chemistry, D. Van Nostrand, London, 1965, ix + 332 pp., price 35 s. (paperbound), 70 s. (clothbound).

This book is a lucid account of the application of microwave spectroscopy to the determination of molecular structure. The first quarter of the text describes the quantum mechanical treatment of molecular rotation and concludes with a short account of the methods used to extract details of the molecular geometry from the spectroscopic data. This is followed by an extended discussion on the origins of hyperfine structure. These include nuclear electric quadrupole effects (which give valuable

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information concerning the distribution of electrons about the nuclei), the Stark Effect (which allows the measurement of the electric dipole moments), and inversion and restricted rotation. The remainder of the book contains a discussion of experimental methods peculiar to the microwave region, several mathematical appendices and an exhaustive bibliography of experimental measurements made up to 1963.

The book is well written, well referenced and well produced and should be required reading for all spectroscopists.

J. P. SIMONS (Birmingham)

Anal. Chim. Acta, 36 (1966) 263–264

P. JAULMES, *Précis de Chimie Analytique. Tome I. Analyse qualitative minérale*, Collection de précis de pharmacie sous la direction de M.-M. JANOT, Masson, Paris, 1965, 366 pp., prix 46 F.

Bien que cet ouvrage soit particulièrement destiné aux étudiants en pharmacie, il rendra de grands services à ceux qui commencent leurs études en chimie. Présenté de façon claire et concise, débarrassé de détails inutiles, l'auteur donne en 89 pages les bases fondamentales de la chimie analytique moderne: acides et bases, produits de solubilité et solubilité, oxydo-réduction et complexes et les principales méthodes de séparation. La façon de présenter chaque chapitre et la logique avec laquelle on passe de l'un à l'autre est fort plaisante et l'étudiant peut comprendre aisément les diverses réactions, leurs mécanismes, les conditions dans lesquelles on fait telle ou telle identification lorsqu'on aborde les 2me et 3me partie de cet ouvrage qui traitent des conditions d'analyse des ions.

Une très petite critique à l'auteur. On utilise de plus en plus en pharmacie les dosages en milieu non aqueux basés en particulier les titrations acide–base. Or il est évident que la théorie classique n'est pas capable d'expliquer le mécanisme des réactions qui s'y passent. La théorie du proton (Brönsted) par contre, rend compte de façon parfaite de celui-ci. Le principe de cette théorie est donné, mais alors pourquoi revenir par la suite à cette théorie classique qui a fait son temps. Il est vrai que beaucoup d'auteurs, particulièrement en biologie, n'ont pas encore adopté Brönsted et c'est probablement la raison pour laquelle Monsieur JAULMES ne l'a pas généralisée.

L'auteur a tenu à développer les représentations graphiques qui prennent une importance croissante et rendent plus compréhensibles les phénomènes ox–red, acides–bases et ceux qui font intervenir les complexes. En résumé, un très bon ouvrage à recommander.

D. MONNIER (Genève)

Anal. Chim. Acta, 36 (1966) 264

JOHN T. STOCK, *Amperometric Titrations*, Interscience Publishers–J. Wiley, Inc., New York, 1965, xiv+730 pp., price 189 s.

The technique of amperometric (or polarometric) titrations in which the current flowing at a properly chosen potential is measured as a function of the volume of the titrant, has become widely used during the last decade; hence it is timely for a monograph to be written on this subject. The monograph consists of two parts: the first quarter is devoted to theoretical principles, descriptions of apparatus and to general techniques, in particular the methods for evaluation of titration curves. The scope of the methods discussed is rather broad–in addition to the classical methods using a polarizable indicator and an unpolarizable reference electrode, biamperometric and bipotentiometric titrations and even techniques using alternating current are also discussed. A critical assessment of any advantages of the biamperometric method compared to the classical method would have been valuable; apart from some simple applications it seems to be questionable whether the modest simplification in instrumentation with the biamperometric method can compensate for the theoretical complexity and the involved shape of the titration curves in biamperometric titrations. The coverage of the literature in this part is good and objective.

The second part is devoted to applications. The methods are first divided, according to the reaction involved, into titrations using combination reactions and those using oxidation–reduction reactions. In each group the methods, usually described in sufficient detail to be used without consulting the original paper, are classified according to the volumetric solution used. In some cases, substance X can be titrated with a solution of Y and substance Y with a solution of X; to avoid repetition such cases are discussed consecutively. This division differs from the more common classification according to the substance to be determined, and results in determinations of a given type of substance appearing in several chapters. The possibility of a direct comparison of the various methods is lost, although the extensive subject index is valuable for this purpose and can also assist in locating a particular analytical problem. Because the treatment is exhaustive rather than selective and critical, a comparison of literature coverage is perhaps allowed. When compared with the book on *Polarometric Titrations* by J. DOLEŽAL AND J. ZÝKA (1961), inspection of some randomly selected topics shows that approximately two thirds of the papers quoted by DOLEŽAL AND ZÝKA are also quoted by STOCK.

Nevertheless, this monograph, the style of which is clear and the production perfect, can be both a valuable introduction to the subject and a laboratory handbook for the practising analytical chemist. It will surely contribute to the development of this type of titration.

P. ZUMAN (Prague)

Anal. Chim. Acta, 36 (1966) 265

A. T. JAMES AND L. J. MORRIS (Editors), *New Biochemical Separations*, D. van Nostrand, London, 1964, ix+424 pp., price 84 s.

As the proliferation of the motor car threatens to bring movement on the roads to a standstill, so the inexorable increase of published scientific work makes it more and more difficult for research workers to prepare the ground adequately in their chosen subject. This problem of communication has, during the last few years, encouraged the appearance of increasing numbers of reviews, some authoritative and valuable, others of doubtful quality, that aim to relieve the research worker of much of the burden of literature search and thus allow him more time to apply his scientific skills. JAMES AND MORRIS have attempted this difficult task in the field of separative techniques for biochemical analysis. How well do they succeed?

It is not surprising that the major part of the book is devoted to selected aspects of gas–liquid and, more especially, thin-layer chromatography. The first contribution, by JAMES himself, is a first-class account of methods for the estimation of radioactive compounds by G.L.C. and the second, no less well done, is a study of the G.L.C. separation of steroids, alkaloids and sugars by HORNING AND VANDENHEUVEL. Unfortunately the contribution on steroids is strikingly similar to material that has already been published elsewhere by the same workers; for the sake of completeness, however, it could hardly have been omitted from the present volume. Other contributions on G.L.C. deal with coenzyme-A esters, bile acids and amino acids.

Thin-layer chromatography is given a much wider coverage but the material seems more variable in quality. This technique is so deceptively simple that some who come newly to it are selfstyled experts almost overnight. Such a state of affairs naturally results in a flood of papers, many of which should never have seen the light of day. The task of the reviewer must then be to separate the useful from the incompetent—admittedly a most difficult problem unless the recommendations in each paper have been put to the test. In the present volume one would have liked to have detected the personal experience of the author more frequently breaking through the crust of unsupported references. Another aspect of T.L.C. that might have received rather more attention is the problem of decomposition during chromatography. This is referred to briefly in connection with ergot alkaloids and steroids but it is considerably more of a problem than the present text would imply. Perhaps in a subsequent edition a chapter on some problems and pitfalls of T.L.C. might be included to serve as a salutary warning to the enthusiastic but unwary beginner.

Gel filtration and counter-current distribution receive limited attention but, surprisingly, there is no review of developments in electrophoretic separation nor any assessment of steady-state distribution.

Notwithstanding the unevenness that is inevitable when work is collected from many contributors there is so much of value in this book that it must command a place in every laboratory where natural products are examined.

C. A. JOHNSON (London)

J. STARY, *The Solvent Extraction of Metal Chelates*, Pergamon Press, Oxford, 1964, xiv+240 pp., price 60 s.

In recent years much attention has been given to the study of the extraction of metal ions from aqueous solution. As more precise data are obtained for the stability constants of metal chelates, so the theoretical basis for solvent extraction becomes more pronounced and the factors influencing practical extraction procedures become better understood.

In this useful monograph, Dr. STARY deals first with the theoretical aspects of solvent extraction, including his recently developed substoichiometric method, and follows this with a comprehensive account of the many chelate systems which have been studied. All the well-known chelates and many lesser-known chelates are described and classified under particular reagent types. In a final section, the author describes procedures for the selective extraction of forty-eight metal ions. A useful appendix contains tables of dissociation constants, partition coefficients and solubility data.

A valuable feature of the book is the emphasis given to reagents which form chelates suitable for spectrophotometry in the organic phase, thus avoiding tedious stripping processes and further applications of colour-forming reagents. On the whole, this book provides a relatively up-to-date picture of solvent extraction methods from both theoretical and applied points of view. As well as providing a broad view of the applications of well-known reagents, it gives some useful outlines of the rarer reagents which are as yet hardly significant analytically. The monograph represents a useful contribution on a subject of ever-increasing importance to analytical chemists.

W. I. STEPHEN (Birmingham)

ANNOUNCEMENT

COLLOQUE INTERNATIONAL SUR LES PHOSPHATES MINERAUX SOLIDES

An international Colloquium on solid inorganic phosphates will be held in Toulouse (France) on May 16–20, 1967, under the patronage of the Société Chimique de France.

Topics which will be treated include: natural phosphates, phosphate structures, ion-exchanger phosphates, phosphates as catalysts, influence of trace impurities on the structure and properties of phosphates, phosphation, phosphoric acid in manure and cements, phosphates in agriculture.

Papers will be presented in French, English or German.

Further information can be obtained from: Secrétariat du Colloque International sur les Phosphates Minéraux Solides, Département de Chimie Inorganique, Faculté des Sciences, 38 rue des Trente-Six Points, 31-Toulouse (France).

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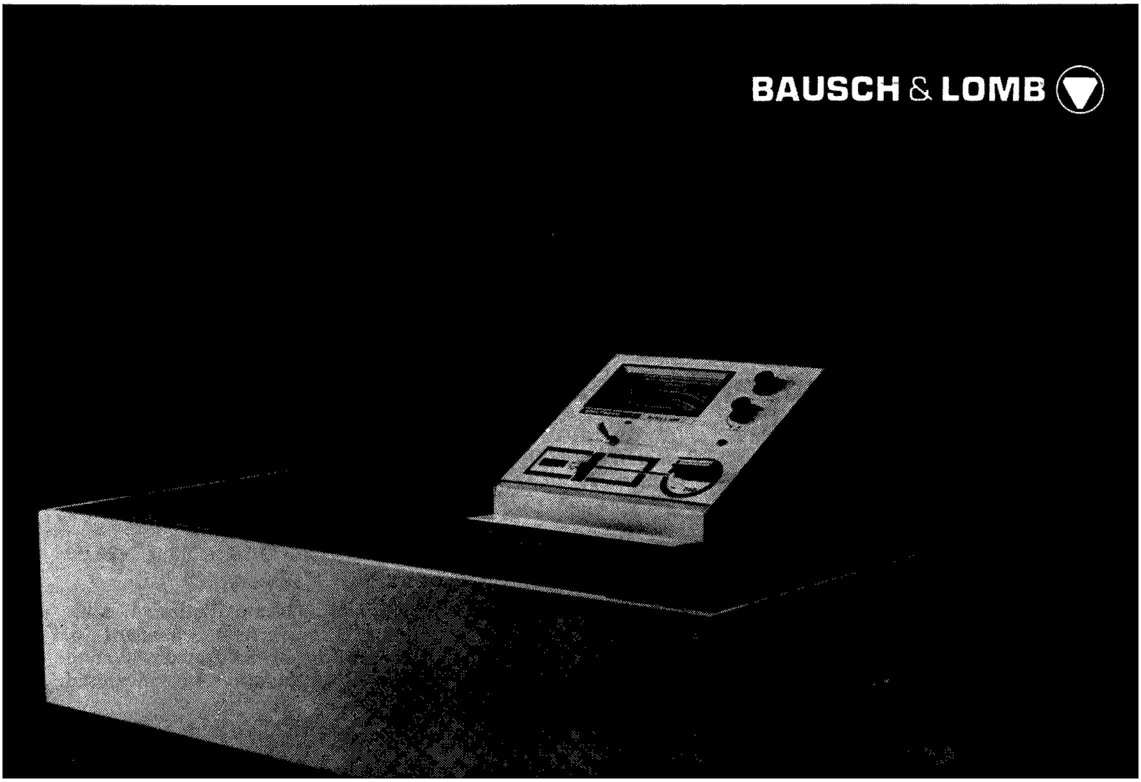
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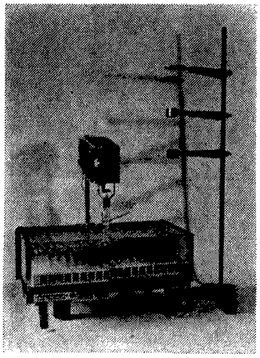

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Vol. 36 No. 2 ANALYTICA CHIMICA ACTA OCTOBER 1966

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Short communications

PRINTED IN THE NETHERLANDS

SPOT TESTS IN ORGANIC ANALYSIS

Seventh English Edition, completely revised and enlarged

by FRITZ FEIGL in collaboration with VINZENZ ANGER

6 x 9″, xxiii + 772 pages, 18 tables, over 2000 lit.refs., 1966, Dfl. 85.00, £8.10.0, $30.00

This 7th edition has involved complete revision and reorganisation of the subject in order to present a still clearer picture of the multitudinous applications open to organic spot test analysis. The amount of new work which is appearing has certainly necessitated expansion, but the author has kept this to a minimum by omitting the chapter on spot test techniques (which are covered in the companion volume *Spot Tests in Inorganic Analysis*) and by limiting the number of tables and structural formulae.
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	Number in 6th Edn.	 7th Edn.
Preliminary tests	32	45
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Individual compound tests	133	148
Detection of particular structures and types of compounds	0	74
Differentiation of isomers etc.	0	54
Applications in the testing of materials etc.	111	131

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