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APPLICATIONS OF INFRARED SPECTROSCOPY—III*

THE SIMULTANEOUS DETERMINATION OF METHOXYL AND ETHOXYL GROUPS

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Summary—Quantitative vapour-phase infrared spectroscopy permits the simultaneous determination of methoxyl and ethoxyl groups as alkyl iodides or bromides: when the methoxyl/ethoxyl ratio exceeds 4 : 1, determinations are only possible as bromides. The reaction-time involved is 30 min. Results, correct to within ±1% for each alkoxyl group, can be obtained on the micro-scale. The presence of sulphur does not interfere.

PART II[1] of this series described a spectroscopic investigation of some of the reaction variables of the Zeisel determination, and results were reported for micro alkoxyl determinations on reference compounds. These showed that the spectroscopic method of determining the liberated alkyl iodides not only gave results comparable in accuracy and reproducibility with those obtainable by the more conventional methods, but also distinguished in the same analysis between different alkoxyl groups. On unknown compounds, this selective information cannot be obtained directly if the conventional iodometric or gravimetric finishes are used.[2,3]

Gran[2] reviewed the techniques available for the simultaneous determination of methoxyl and ethoxyl groups; the majority require time-consuming modification or extension to the standard Zeisel method. Techniques based on Martin and Vertalier's[4] use of gas chromatography were later introduced[5,6] which, although not comparable in accuracy with the more conventional methods, offered possibilities for future development. More recent publications, however, have merely reverted to modifying[7] the Willstätter and Utzinger[8] technique or to describing modifications[9,10] of the combustion method.[11]

This paper describes how the quantitative infrared technique[1,12] can be extended, without modification or loss in accuracy, to the simultaneous determination of both methoxyl and ethoxyl groups. Results, correct to within ±1% for both groups, can be obtained on the microscale. The reaction-time is 30 min, and only one weighing of the sample is involved. The presence of excess sulphur (which continues to cause difficulty[13]) in any form or quantity does not interfere.

EXPERIMENTAL

Gas-cells

Descriptions of the gas-cells used, and data giving their useful concentration range and sensitivity have been given.[1,12,14]

* Part II—see ref. 1.

Spectrometer

The spectrometer used was a Hilger H800 double-beam instrument, which has the following advantages: (*a*) accommodation of gas-cells up to 56 cm long, (*b*) linear recording of percentage absorption, with an accuracy of $\pm 0{\cdot}5\%$. This fixes the limiting accuracy of the method, and obviates the necessity of weighing 2–5 mg samples to the nearest microgram. (By adjustment of tares, all weighings were made within the range of the 0–30 mg graticule scale of an aperiodic direct-reading balance having an accuracy of $\pm 10\ \mu$g.)

Spectrometer conditions

For the calibration curve to be of maximum accuracy, the standard operating conditions (slit-width, scan speed, electronic gain etc.) must be carefully selected initially and subsequently rigorously controlled during determinations. The gas-cell carrier must be rigidly fixed, or fitted with some simple

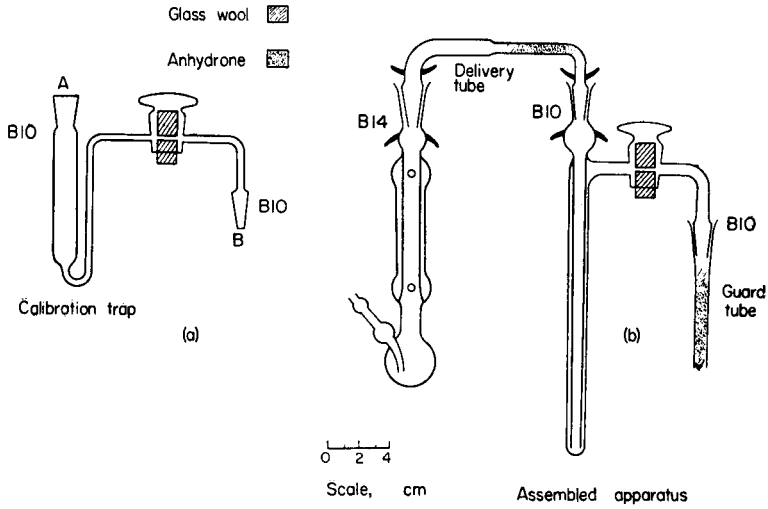

FIG. 1.—(*a*) Calibration trap. (*b*) Assembled apparatus.

locating device ensuring replacement each time in identical position with respect to the infrared beams.

Reproducibility of percentage absorption for a given concentration depends on the recorder zero-stability; any peak height must always be measured with respect to some arbitrarily fixed base-line or zero associated with the wave-length involved. All other conditions being constant, the base-line may be affected by small energy losses caused by fogged or scratched cell-windows, which must therefore be kept in good condition. Small local variations in base-line caused by such factors may, however, be satisfactorily compensated by adjustment of some auxiliary compensating device interposed in the reference beam.

Construction of calibration curves

Weigh the required amount of alkyl iodide in a micro weighing-bottle (12 × 4 mm) fitted with a leak-proof ground-glass stopper. Via *A*, place the bottle in the trap shown in Fig. 1(*a*), then immerse the limb of the trap in liquid nitrogen. Insert the requisite evacuated gas-cells at *A*, connect *B* to a suitable vacuum-line,[12] and evacuate the system with the trap still in coolant.

Vaporise the trapped alkyl iodide into the gas-cell, making the total pressure equal to atmospheric, by the technique already described.[12] Quantitative transfer, within the experimental limits of $\pm 1\%$, is easily achieved. Record the particular absorption peak selected for calibration (see below) six times, then calculate the mean peak height: this minimises any error in the peak heights drawn by the pen recorder, the reproducibility of which is $\pm 0{\cdot}25\%$.

Fundamentally, peak areas are proportional to concentration, but at the partial pressures used

peak heights are sensitive to concentration changes and are, under standard conditions, much easier to measure. "Pressure-broadening" effects do not cause complications.[12] Consequently, calibration curves can be constructed with reference to peak heights. Fig. 2 shows typical curves obtained.

Efficiency of trapping

Various weights of alkyl iodides were added to the reaction-flask and volatilised using flow-rates between 4 and 20 ml per min. At each flow-rate, recoveries ranged from 99·0–101·0% with an equal distribution of high and low results. In several experiments, two absorption traps were connected in series: in no case was alkyl iodide detectable in the second trap. These experiments led to ±1% being claimed as the accuracy of the method. In practice, results better than these limits can be expected (see Table I).

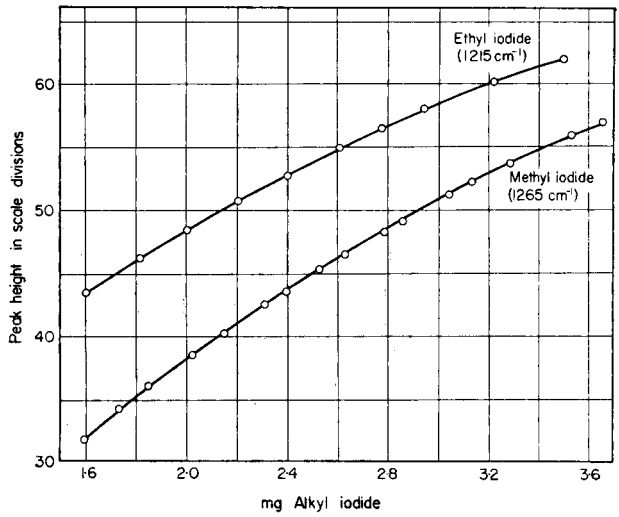

FIG. 2.—Calibration curves for methyl iodide and ethyl iodide.

Alkoxyl determinations

Details of the apparatus, reagents, flow-gas, heating, reaction-time, and weighing of samples have been described.[1] For volatile samples, the described technique obviating use of double distillation[1] is used; it may also be applied to non-volatile and solid samples. The following technique, however, has been successfully used for solids: weigh the sample in a long-handled weighing spoon.[1] Add 20–40 mg phenol to the spoon, and warm *gently* over a hot-plate to form a homogeneous melt at as low a temperature as possible. Place the spoon in a reaction-flask to which 6 ml of hydriodic acid had been added, pre-conditioned as described,[1] and cooled.

Procedure

Attach the delivery tube (Fig. 1(*b*)), packed with fresh Anhydrone, to a clean trap fitted with an Anhydrone guard-tube: immerse the trap in liquid nitrogen. (This order of assembly minimises collection of atmospheric water-vapour in the trap.) Attach the B14 cone of the delivery tube to the reaction condenser, so assembling the apparatus as shown in Fig. 1(*b*). Adjust the nitrogen flow-rate to 6–8 ml per min, and begin heating the reaction-flask.

After 30 min reflux, remove and stopper the trap, keeping it immersed in coolant. When convenient, volatilise the trapped reaction products into the appropriate gas-cell. Draw the spectrum of the products—this reveals immediately which iodides are present. Then re-draw 6 times (ensuring that the correct base-line is given) the characteristic peak on which calibration of each iodide is based. Refer the average peak height for each iodide to the appropriate calibration curve, and hence determine the weight of alkyl iodides liberated.

RESULTS

Interferences

Since iodine, hydrogen sulphide and hydrogen iodide vapours do not interfere with the spectroscopic determination, conventional Zeisel scrubbers are not necessary. Phosphine, however, does interfere; preconditioning of the hydriodic acid as described[1] is required, and subsequent addition of hypophosphites to decolourise dark reaction mixtures should be avoided. The use of colourless hydriodic acid is not necessary for quantitative results. Since water vapour must be excluded in spectroscopic determinations, the reaction products are trapped after passage through Anhydrone[1].

Choice of calibration peaks

Fig. 3 diagramatically represents the spectra given in the 800–1500 cm^{-1} region,

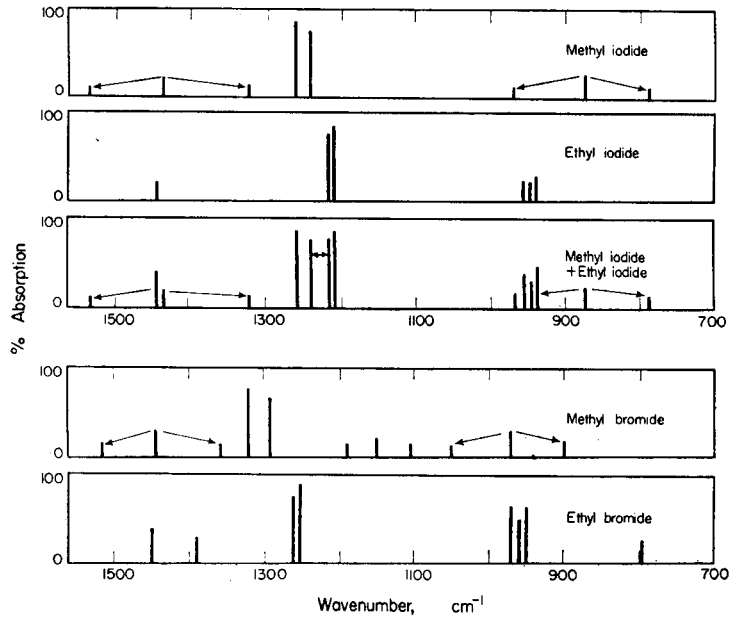

FIG. 3.—Representation of spectra given by methyl iodide, ethyl iodide, methyl bromide and ethyl bromide.

at a scan speed of 127 cm^{-1} per min, by methyl iodide, ethyl iodide, and by a mixture of the two. If a vapour contains only one component, calibration can be based on any convenient absorption peak in the spectrum, although maximum sensitivity and accuracy will clearly be obtained if calibration is based on the most intense absorption. In mixtures, however, over-lapping or coincidence of peaks can occur. Calibration for a particular component must then be based on the most intense absorption which is not masked or reinforced by peaks given by the other components present.

In the composite spectrum (Fig. 3) given by a mixture of methyl + ethyl iodides, very slight overlapping of peaks occurs at the normal scanning speed, so that the 1244 cm^{-1} peak of methyl iodide fractionally increases the height of the 1215 cm^{-1} ethyl iodide peak. The 1265 cm^{-1} methyl iodide peak is not masked, and so calibrations based on it give correct methoxyl values as shown by the typical results given in Table I.

Calibrations based on the 1215 cm^{-1} ethyl iodide peak, however, lead in this circumstance to high ethoxyl values: the more minor peaks given by ethyl iodide at 1450 cm^{-1} and 950 cm^{-1} are also subject to overlapping with minor methyl iodide peaks and so cannot be used.

Fortunately, this positive ethoxyl error was found to be a linear function of the

TABLE I. SIMULTANEOUS METHOXYL/ETHOXYL DETERMINATIONS

Compound or mixture	Weight taken, *mg*	Wt. alkyl iodide found		Corr. wt. $\overline{\text{Et}}$I found,* *mg*	Methoxyl		Ethoxyl	
		$\overline{\text{Me}}$I, *mg*	$\overline{\text{Et}}$I, *mg*		found, %	theory, %	found, %	theory, %
Vanillin	7·41	6·94			20·4	20·4		
Phenacetin	3·29		3·00	2·86			25·2	25·1
Vanillin	10·24	9·52			20·3	20·4		
Phenacetin	3·02		2·82	2·63			25·3	25·1
Vanillin	2·03	1·90			20·5	20·4		
Phenacetin	4·28		3·75	3·71			25·1	25·1
Anisic acid	9·43	8·72			20·2	20·4		
Cmpd X†	7·20		3·15	2·98			12·0	12·0
Cmpd Y†	2·60	6·26			52·7	52·3		
			2·40	2·28			25·8	25·3
Cmpd Z†	1·42	0·98			15·1	15·0		
			3·22	3·20			65·1	65·5

* Corrected weight $\overline{\text{Et}}$I = (wt. $\overline{\text{Et}}$I found) − (0·019)(wt. $\overline{\text{Me}}$I found).

† Origin of samples:
Cmpd X: 4-chloro-2-ethoxy-p-tosyl-1-naphthylamine (Prof. F. Bell)
Cmpd Y: 1:1:3-trimethoxy-3-ethoxypropane
Cmpd Z: 1:1:3-triethoxy-3-methoxypropane
} L. Light and Co. Ltd. (redistilled).

weight of methyl iodide present, and a correction factor (0·019), applicable to a particular set of standard spectrometer conditions, was calculable. When

$$(0{\cdot}019) \times (\text{weight of methyl iodide found})$$

was subtracted from the actual weight of ethyl iodide found, the results shown in Table I were obtained for methoxyl-ethoxyl compounds or for synthetic mixtures ranging in composition from methoxyl/ethoxyl = 3:1 to 1:3.

At low ethoxyl contents, the 1215 cm^{-1} ethyl iodide absorption occurs as a shoulder on the 1244 cm^{-1} methyl iodide peak and determinations become inaccurate: at methoxyl/ethoxyl ratios $> 4:1$, there is no measurable ethyl iodide peak height and the method fails. Although such combinations must be rare in actual chemical compounds, they could readily be met in determinations on mixtures of methoxyl and ethoxyl compounds. Such mixtures can be analysed by using hydrobromic acid in place of hydriodic acid during reflux.

Alkoxyl determinations using hydrobromic acid

Constant-boiling hydrobromic acid (sp. gr. 1·47) is effective in cleaving alkoxyl groups: it produces alkyl bromides quantitatively from esters and ethers almost as quickly (15–20 min for methyl and ethyl) as hydriodic acid forms the corresponding iodides. Alkyl bromides are as conveniently estimated as alkyl iodides by the infrared technique if the required calibration curves are constructed (the manometric technique[12] must be used for methyl bromide, b.p. 3·6°). Moreover, Fig. 3 shows that the 1320 cm^{-1} absorption of methyl bromide is so widely separated from the 1250 cm^{-1} peak of ethyl bromide that calibrations based on each of these are valid for the analysis of all possible methoxyl/ethoxyl percentage compositions. The only slight disadvantage in the use of the bromides is a small decrease in sensitivity. Gas-cell "B"[14] permits determination of approximately 2–6 mg of alkyl bromide as opposed to 1–4 mg of alkyl iodide; this requires that sample weights of alkoxyl compounds must be approximately doubled when determination as the bromide is used. Results equal in accuracy to those shown in Table I are, however, obtainable without the necessity of using a correction factor.

CONCLUSIONS

The method described permits satisfactory simultaneous determinations of methoxyl and ethoxyl groups on the micro scale. Although Table I shows only a few typical results, many determinations have been made during the past 18 months on a wide range of polyfunctional compounds, each of which contained, in addition to alkoxyl, one or more of the following groups: —F, —Cl, —Br, —I, —NO, —NO_2, —NH_2, =NH, —N=N—, =S, —SO_3H, ≡PO_4, —PS, =Se. Satisfactory results were obtained on pure samples; in our experience, some organic compounds are surprisingly difficult to purify sufficiently for satisfactory results to be obtained in the alkoxyl determination, which is a rigorous functional group analysis.

The accuracy obtainable, small samples required, short reaction time, elimination of conventional scrubbers, and absence of interference from sulphur combine to make this spectroscopic method undoubtedly superior to any method previously described for simultaneous determination of alkoxyl groups. At the present time, when ever-increasing numbers of chemists have access to an infrared spectrometer, this method should be of general interest.

Acknowledgements—We thank Professor E. L. Hirst, C.B.E., F.R.S., for his interest in this work, and the Carnegie Trust for the award of a Scholarship (to J. L. D.).

Zusammenfassung—Quantitative Infrarotspectroskopie in der Gasphase erlaubt die gleichzeitige Bestimmung von Methoxyl- und Äthoxylgruppen als Alkalijodide oder Bromide. Wenn das Verhältnis Methoxyl:Äthoxyl den Betrag von 4:1 überschreitet kann die Bestimmung nur über die Bromide durchgeführt werden. Die benötigte Reaktionszeit ist 30 Minuten. Die Resultate, innhalb von ±1% genau, können für Proben im Mikrobereich erhalten werden. Gegenwart von Schwefel stört nicht.

Résumé—La spectroscopie infra-rouge quantitative en phase vapeur permet le dosage simultané des groupements méthoxy et éthoxy à l'état d'iodures ou de bromures d'alkyl: quand le rapport méthoxy/éthoxy dépasse 4/1, les dosages ne sont possibles que pour les bromures. Le temps de réaction nécessaire est de 30 minutes. Les résultats, corrects dans l'intervalle de ±1 pour cent pour chaque groupement alkoxyl, peuvent être obtenus à l'échelle microscopique. La présence de soufre ne gêne pas.

REFERENCES

[1] D. M. W. Anderson and J. L. Duncan, *Talanta*, 1960, **7**, 70.
[2] G. Gran, *Svensk Papperstidn.*, 1954, **57**, 702
[3] M. Fukuda and T. Sai, *J. Pharm. Soc. Japan*, 1958, **78**, 83.
[4] F. Martin and S. Vertalier, Intl. Microchem. Symp., Lisbon, 1956,; *Chim. analyt*,, 1958, **40**, 80.
[5] J. Haslam, J. B. Hamilton and A. R. Jeffs, *Analyst*, 1958, **83**, 66.
[6] K. Kratzl and K. Gruber, *Monatsh.*, 1958, **89**, 618.
[7] R. F. Makens, R. L. Lothringer and R. A. Donia, *Analyt. Chem.*, 1959, **31**, 1265.
[8] R. Willstätter and M. Utzinger, *Ann.*, 1911, **382**, 129.
[9] M. Fukuda, *J. Pharm. Soc. Japan*, 1960, **80**, 25.
[10] K. Hozumi, *ibid.*, 1959, **79**, 237.
[11] A. Friedrich, *Mikrochem.*, 1929, **7**, 185.
[12] D. M. W. Anderson, *Analyst*, 1959, **84**, 50.
[13] H. Sobue, A. Hatano and T. Arai, *J. Soc. Text. Cellulose Ind.*, Japan, 1959, **15**, 21.
[14] D. M. W. Anderson and J. L. Duncan, *Chem. and Ind.*, 1958, 1662.

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APPLICATIONS OF COMPLEMENTARY TRI-STIMULUS COLORIMETRY—II

A LEAST SQUARE METHOD APPLIED TO MULTICOMPONENT SYSTEMS

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Summary—It is shown how the calculation of colorant concentrations in complementary tri-stimulus colorimetry can be improved by the application of the least square method, rather than by simple averaging of sets of results. In this improvement a matrix approach is especially useful, and the required equations are developed. Comparison of results obtained by the two methods shows the superiority of the matrix approach.

THE first paper in this series[1] considered the application of complementary tri-stimulus colorimetry to the photometric analysis of binary and ternary mixtures of colorants. It has been shown that more reliable results can be obtained in this manner than with the classical approach to photometric analysis. For a binary mixture, instead of two wavelengths, three "ranges" are selected, each range containing an appropriate number (5–10) of wavelengths at which absorbance readings are taken. With the use of an averaging process, the sum of the absorbance readings in each of the three ranges (denoted by U, V and W) are used to calculate the complementary colour co-ordinates u, v and w, which are defined by the following general formula

$$r_i = \frac{R_i}{\sum_{i=1}^{i=n} R_i} \tag{1}$$

where r_i is the complementary colour co-ordinate (u, v and w for $i = 1$, 2 and 3 respectively) and R_i is the sum of the absorbance readings in the ith range (U, V and W for $i = 1$, 2 and 3 respectively). The weighting factors for each range are assumed to have a value of unity. The complementary colour co-ordinates of a pure colorant are concentration-independent parameters and are characteristic of the particular colorant. The optical concentration of the solution of a colorant, J, is given by the formula

$$J \equiv \kappa \sum_{i=1}^{i=n} R_i \tag{2}$$

where κ is a constant, the numerical value of which for the present purpose can be deliberately taken to have a value of unity.

The overall absorptivity (the analogue of the extinction coefficient of the classical approach), E, is related to the analytical concentration by the formula

$$J = C \times E \times l \tag{3}$$

where C is the analytical concentration and l is the length of the light path through the solution.

Each colorant is represented by a discrete point in the complementary colour diagram (usually a u–v plot; however, if convenient, a u–w or v–w plot may be employed). Any mixture of two colorants will have complementary colour co-ordinates which define a point located on the straight line connecting the complementary colour points of the two pure colorants. (This will be true only provided that the Lambert-Beer law is valid for each of the colorants and that their absorbances in a mixture are additive.) This "system line" can be calibrated in mole fraction (or any other fraction) thus making possible direct reading of that parameter for a mixture.

A partially graphical approach was presented in the earlier paper for the calculation of the concentration of the components of a binary and also of a ternary mixture of colorants. Further, a purely algebraic approach was given to determine these concentrations, which is based on the following set of equations:

$$U_m = C_a \times u_a \times E_a + C_b \times u_b \times E_b \tag{4a}$$

$$V_m = C_a \times v_a \times E_a + C_b \times v_b \times E_b \tag{4b}$$

$$W_m = C_a \times w_a \times E_a + C_b \times w_b \times E_b \tag{4c}$$

where the subscripts m, a and b refer, respectively, to the colour parameters of the mixture and of each of the two components. Since there are three equations in the set and only two unknowns, the system is over-determined. Hence, three sets of results are obtained from the three possible pairings of the equations. The results will, of course, be identical where no erratic influences are present, or in the possible, but improbable, case that errors compensate each other. The three results may simply be averaged arithmetically in order to obtain a better result. However, when an erratic influence predominates in only one range, one result may differ markedly from the other two, and hence may be discarded in taking the average. But this is not an exact mathematical procedure.

A more reliable result will be obtained by applying the method of least squares to obtain mathematically the "best fit". This can be accomplished by applying appropriately the matrix approach developed by Bauman.[2] The treatment will be given in detail for the analysis of a binary mixture. Any number of components could be present, but then the number of ranges would have to be increased; in practice the mathematical effort would be tedious, and it might be simpler to exclude some components by separations, masking, *etc.*

In a general treatment, the sum of the absorbance readings of a mixture in any range is given by the following formula

$$R_i = \sum_{j=1}^{j=u} r_{ij} \times E_j \times C_j \tag{5}$$

where R_i is the sum of the absorbance readings in the ith range and all components present up to and including the jth and where r_{ij} is the complementary colour co-ordinate in the ith range for the jth colorant and E_j is its overall absorptivity.

For simplicity, the product $r_{ij} \times E_j$ may be denoted by K. Then in matrix notation, the equation (5) takes the form

$$R = KC \tag{6}$$

where R, K and C are the matrices of the corresponding parameters. Cramer's rule

is applicable to the solution of equation (6) if the number of equations equals the number of unknowns, as has been shown previously.[1] In order to apply the least square method effectively, more equations than unknowns are needed, but then the number of rows will not equal the number of columns and the simple determinant approach is no longer applicable. This difficulty can be overcome, as has been demonstrated by Bauman.[2]

Let d_i denote the difference between the sum of absorbance readings in the range i actually obtained in the analysis and the "true" (*i.e.*, the theoretical) value. Then the following formula is valid:

$$d_i = \sum_{j=1}^{j=n} r_{ij} \times E_{jx} \times C_j - R_i \tag{7}$$

or in matrix notation

$$D = KC - R. \tag{8}$$

To find the best set of values for C_j by the method of least squares, the values of d_i must be squared and summed, and the first derivative with respect to C must be set equal to zero. In other words $\frac{\partial}{\partial c}\sum d_i^2 = 0$. For the equation in matrix notation, the procedure may be developed stepwise as follows.

$$\Sigma d_i^2 = D^*D = (C^*K^* - R^*)(KC - R) \tag{9}$$

where the asterisks denote the transpose of the particular matrix. By multiplying out, the following is obtained:

$$D^*D = C^*K^*KC - C^*K^*R - R^*KC - R^*R. \tag{10}$$

Differentiation of this equation leads to

$$\frac{\partial D^*D}{\partial C} = \frac{\partial C^*}{\partial C} K^*KC + C^*K^*K \frac{\partial C}{\partial C} - \frac{\partial C^*}{\partial C} K^*R - R^*K \frac{\partial C}{\partial C} \tag{11}$$

and since $\frac{\partial C^*}{\partial C} = \frac{\partial C}{\partial C} = 1$ it follows that

$$\frac{\partial D^*D}{\partial C} = K^*KC + C^*K^*K - K^*R - R^*K\,. \tag{12}$$

Since the first term in (12) equals the second, and the third equals the fourth, it follows that

$$\frac{\partial D^*D}{\partial C} = 2(K^*KC - K^*R). \tag{13}$$

Setting the derivative equal to zero leads to the formula

$$K^*KC = K^*R. \tag{14}$$

Then by introducing the substitutions

$$K' = K^*K \tag{15}$$

$$R' = K^*R \tag{16}$$

the final equation is obtained which represents the condition of "best fit":

$$R' = K'C. \tag{17}$$

A mixture containing any number of components can be treated in this manner provided that the number of ranges selected exceeds by at least one the number of components, that is, $i \geqslant j + 1$.

It should be realised that the graphical treatment considered in the earlier paper[1] is no longer applicable when more than three ranges are selected, since a multi-dimensional plot would be required.

For a binary system, the extent of the calculations necessary for the matrix approach compares favourably with that using the algebraic approach, and more reliable results are obtained.

In the following paragraphs the entire matrix approach is presented in stepwise fashion for a binary system, with the general formulae paralleled by their application to the following assumed numerical results. Colorant *a* and *b* are assumed to be present in 0·100*M* solutions and to have the following complementary colorimetric parameters:

$$E_a = 1{\cdot}000 \quad u_a = 0{\cdot}100 \quad v_a = 0{\cdot}200 \quad w_a = 0{\cdot}700$$
$$E_b = 2{\cdot}000 \quad u_b = 0{\cdot}400 \quad v_b = 0{\cdot}400 \quad w_a = 0{\cdot}200.$$

From these data and the application of equations (4a)–(4c), the "theoretical" values of the complementary colorimetric parameters can be calculated for a mixture which contains 10·00 ml of each of the 0·100*M* solutions of the pure colorants in 100 ml of final solution, namely

$$U_m = 9{\cdot}000 \quad V_m = 10{\cdot}000 \quad \text{and} \quad W_m = 11{\cdot}000.$$

In order to demonstrate the improvement achieved by application of the method of least squares, the assumption is made that some erratic influence is present that causes a deviation in the *u*-range such that U_m has the "experimental" value of 9·300 rather than the "true" value of 9·000. The values of C_a and C_b can then be calculated by the algebraic approach, by inserting the numerical data into the set of equations (4):

$$9{\cdot}3 = 0{\cdot}1C_a + 0{\cdot}8C_b \tag{18}$$
$$10{\cdot}0 = 0{\cdot}2C_a + 0{\cdot}8C_b \tag{19}$$
$$11{\cdot}0 = 0{\cdot}7C_a + 0{\cdot}4C_b. \tag{20}$$

The values obtained by solving the three possible pairs of these equations are given in Table I, columns A, B and C.

It will be seen that one set of values, thus obtained, differs markedly from the other two. Hence, a better result is obtained by discarding this set of values and averaging the remaining two, rather than by averaging all three sets. Both averages are recorded in Table I.

TABLE I.—COMPARISON OF VALUES OBTAINED BY APPLYING DIFFERENT METHODS
Erratic influences operative only in the *u*-range.

	A Equations (18)–(19)	B Equations (18)–(20)	C Equations (19)–(20)	$\frac{A + B + C}{3}$	$\frac{B + C}{2}$	Least square method	True value
C_a	7·00	9·77	10·00	8·92	9·88	9·84	10·00
C_b	10·75	10·40	10·00	10·38	10·20	10·23	10·00

Since the erratic influence was assumed to be present only in the u-range, two sets of values had to be incorrect and one correct. In a practical case, the influences will most probably be operative in each of the three ranges and to different degrees. Hence, the distribution of errors and their magnitude will be more complex than in this simple demonstration example. In practical cases, it is usually not possible to discard "safely" one set of values, and all three must be averaged. In such a case the method of least squares will always yield a superior value.

The procedure takes the following form:

$$\underset{\mathrm{R}}{\begin{vmatrix} \mathrm{U}_m \\ \mathrm{V}_m \\ \mathrm{W}_m \end{vmatrix}} = \underset{\mathrm{K}}{\begin{vmatrix} u_a\mathrm{E}_a & u_b\mathrm{E}_b \\ v_a\mathrm{E}_a & v_b\mathrm{E}_b \\ w_a\mathrm{E}_a & w_a\mathrm{E}_b \end{vmatrix}} \underset{\mathrm{C}}{\begin{vmatrix} \mathrm{C}_a \\ \mathrm{C}_b \end{vmatrix}} \quad \begin{vmatrix} 9{\cdot}3 \\ 10{\cdot}0 \\ 11{\cdot}0 \end{vmatrix} = \begin{vmatrix} 0{\cdot}1 & 0{\cdot}8 \\ 0{\cdot}2 & 0{\cdot}8 \\ 0{\cdot}7 & 0{\cdot}4 \end{vmatrix} \begin{vmatrix} \mathrm{C}_a \\ \mathrm{C}_b \end{vmatrix} \tag{21}$$

$$\mathrm{K}' = \underset{\mathrm{K}^*}{\begin{vmatrix} u_a\mathrm{E}_a & v_a\mathrm{E}_a & w_a\mathrm{E}_a \\ u_b\mathrm{E}_b & v_b\mathrm{E}_b & w_b\mathrm{E}_b \end{vmatrix}} \underset{\mathrm{K}}{\begin{vmatrix} u_a\mathrm{E}_a & u_b\mathrm{E}_b \\ v_a\mathrm{E}_a & v_b\mathrm{E}_b \\ w_a\mathrm{E}_a & w_b\mathrm{E}_b \end{vmatrix}}$$

$$\mathrm{K}' = \begin{vmatrix} 0{\cdot}1 & 0{\cdot}2 & 0{\cdot}7 \\ 0{\cdot}8 & 0{\cdot}8 & 0{\cdot}2 \end{vmatrix} \begin{vmatrix} 0{\cdot}1 & 0{\cdot}8 \\ 0{\cdot}2 & 0{\cdot}8 \\ 0{\cdot}7 & 0{\cdot}7 \end{vmatrix} = \begin{vmatrix} 0{\cdot}54 & 0{\cdot}52 \\ 0{\cdot}52 & 1{\cdot}44 \end{vmatrix} \tag{22}$$

$$\mathrm{R}' = \underset{\mathrm{K}^*}{\begin{vmatrix} u_a\mathrm{E}_a & v_a\mathrm{E}_a & w_a\mathrm{E}_a \\ u_b\mathrm{E}_b & v_b\mathrm{E}_b & w_b\mathrm{E}_b \end{vmatrix}} \underset{\mathrm{R}}{\begin{vmatrix} \mathrm{U}_m \\ \mathrm{V}_m \\ \mathrm{W}_m \end{vmatrix}} \quad \mathrm{R}' = \begin{vmatrix} 0{\cdot}1 & 0{\cdot}2 & 0{\cdot}7 \\ 0{\cdot}8 & 0{\cdot}8 & 0{\cdot}4 \end{vmatrix} \begin{vmatrix} 9{\cdot}3 \\ 10{\cdot}0 \\ 11{\cdot}0 \end{vmatrix} = \begin{vmatrix} 10{\cdot}63 \\ 10{\cdot}84 \end{vmatrix} \tag{23}$$

$$\mathrm{C} = (\mathrm{K}')^{-1}\mathrm{R}' = \underbrace{\underbrace{\frac{1}{0{\cdot}54 \times 1{\cdot}44 - 0{\cdot}52 + 0{\cdot}52}}_{=\,0{\cdot}5072} \begin{vmatrix} 1{\cdot}44 & -0{\cdot}52 \\ -0{\cdot}52 & 0{\cdot}54 \end{vmatrix}}_{(\mathrm{K}')^{-1}} \underbrace{\begin{vmatrix} 10{\cdot}63 \\ 10{\cdot}84 \end{vmatrix}}_{\mathrm{R}'}$$

$$= \underset{(\mathrm{K}')^{-1}}{\begin{vmatrix} \frac{1{\cdot}44}{0{\cdot}5072} & \frac{-0{\cdot}52}{0{\cdot}5702} \\ \frac{-0{\cdot}52}{0{\cdot}5702} & \frac{0{\cdot}54}{0{\cdot}5702} \end{vmatrix}} \underset{\mathrm{R}'}{\begin{vmatrix} 10{\cdot}63 \\ 10{\cdot}84 \end{vmatrix}} = \begin{vmatrix} 2{\cdot}8391 & -1{\cdot}0252 \\ -1{\cdot}0252 & 1{\cdot}0647 \end{vmatrix} \begin{vmatrix} 10{\cdot}63 \\ 10{\cdot}84 \end{vmatrix} = \begin{vmatrix} 9{\cdot}840 \\ 10{\cdot}226 \end{vmatrix} \tag{24}$$

which is finally

$$\mathrm{C} = \begin{vmatrix} \mathrm{C}_a \\ \mathrm{C}_b \end{vmatrix} = \begin{vmatrix} 9{\cdot}84 \\ 10{\cdot}23 \end{vmatrix}$$

The final result obtained by this matrix approach is also presented in Table I. Inspection of this Table reveals that the results obtained by the matrix approach are far superior to the averages obtained by combination of the three sets of results obtained by the algebraic method. Indeed, the set of results by the least square method differs only slightly from the averages obtained in the algebraic method after rejecting the obviously erratic set of results.

The results of a further example in which the erratic influences are operative in all three ranges are presented in Table II. The "experimental" values are assumed to be $U_m = 9{\cdot}300$, $V_m = 9{\cdot}700$ and $W_m = 10{\cdot}700$ and the true values to be the same as in the first example.

TABLE II. COMPARISON OF VALUES OBTAINED BY APPLYING DIFFERENT METHODS
Erratic influences operative in all three ranges.

	A Equations (18)–(19)	B Equations (18)–(20)	C Equations (19)–(20)	$\frac{A \times B + C}{3}$	$\frac{B + C}{2}$	Least square method	True value
C_a	4·00	9·31	9·75	7·69	9·53	9·84	10·00
C_b	11·12	10·46	10·41	10·66	10·54	10·21	10·00

It will be seen from Table II that the results are "poor" when the algebraic approach is employed, especially when the most discordant set of results is retained in averaging. In contrast, the matrix approach is far less affected by the erratic influences. In this example, nearly the same result is obtained with the matrix approach as in the first one. This finding is explained when it is considered that the three parameters are close in numerical value, and that the assumed errors are equal in magnitude but opposite in sign.

The impressive improvement obtained by the matrix approach justifies the additional calculation involved. Further, when an analysis of a given system is effected repeatedly, some of the intermediate parameters of the matrix operations are independent of the concentrations and need only be calculated once. Thus, in the first illustrative sample the calculation can proceed through the inverse of K′, which is denoted in equation (24) by $(K')^{-1}$. Then only R′ need be calculated for a particular analysis according to equation (23). The combination of K′ and R′ by the last step of equation (24) then yields immediately the concentrations of the two colorants.

The matrix approach has also been applied to the ternary system described in the earlier paper[1], namely the EDTA complexes of copper, nickel and cobalt in a buffered aqueous solution. In one particular mixture, the actual concentrations of the three colorants were 10·00 ml of 0·1*M* Cu-EDTA, 5·00 ml of 0·1*M* Ni-EDTA and 5·00 ml of 0·1*M* Co-EDTA per 100 ml of the final buffered solution. By using the three ranges and the algebraic approach (which does not represent an over-determination for the three-component system), the values obtained from experiment were, respectively, 9·96, 5·28 and 4·69 ml of 0·1*M* metal-EDTA solutions per 100 ml of final solution.

To apply the matrix approach of the present paper, a fourth range was chosen; however, the wavelengths in it were selected from those in the other three ranges in

order not to introduce an unfair advantage for the matrix approach in comparing results. The results obtained were respectively, 10·15, 5·13, and 5·07.

Admittedly the matrix calculation for a three-component system is tedious, especially the calculation of the transpose $(K')^{-1}$. Of course, where the analysis is to be effected repeatedly, this matrix parameter is calculated only once, thus reducing the calculation effort in further analyses. The general scheme for the calculation of the transpose of a three-by-three matrix is described below in order to aid the reader who may be less familiar with these mathematical operations.

Let the matrix A represent the following

$$A = \begin{vmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{vmatrix}$$

Then the transpose of A, namely A^{-1}, can be calculated by the following scheme

$$A^{-1} = \frac{1}{\det |A|} \times T = \frac{1}{\det |A|} \begin{vmatrix} A_1 & A_2 & A_3 \\ B_1 & B_2 & B_3 \\ C_1 & C_2 & C_3 \end{vmatrix}$$

where T is the transpose of the matrix of co-factors, which is the adjoint of A (also called the adjugate matrix of A) and det |A| is the numerical value of the determinant A calculated in the usual way. The co-factors are calculated by applying determinant calculations to each of the two-by-two determinants separately in the following matrix

$$A^{-1} = \frac{1}{\det |A|} \begin{vmatrix} \begin{vmatrix} b_2 & c_2 \\ b_3 & c_3 \end{vmatrix} & - \begin{vmatrix} b_1 & c_1 \\ b_3 & c_3 \end{vmatrix} & \begin{vmatrix} b_1 & c_1 \\ b_2 & c_2 \end{vmatrix} \\ - \begin{vmatrix} a_2 & c_2 \\ a_3 & c_3 \end{vmatrix} & \begin{vmatrix} a_1 & c_1 \\ a_3 & c_3 \end{vmatrix} & - \begin{vmatrix} a_1 & c_1 \\ a_2 & c_2 \end{vmatrix} \\ \begin{vmatrix} a_2 & b_2 \\ a_3 & b_3 \end{vmatrix} & - \begin{vmatrix} a_1 & b_1 \\ a_3 & b_3 \end{vmatrix} & \begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix} \end{vmatrix}$$

In the application of this scheme to the problems considered in the present paper, less calculation effort is involved than the mathematical impedimenta suggest, since the original matrix possesses considerable symmetry, and therefore several terms occur repeatedly and need only be calculated once.

Zusammenfassung—Es wird gezeigt, dass die Berechnung der Konzentrationen der Komponenten von Mehrstoffsystemen in der komplementären Tristimuluskolorimetre erheblich verbessert werden kann, wenn statt einfacher Mittelung der Resultate die Methode der kleinsten Quadrate angewendet wird. Zur Durchführung der Berechnungen hat sich der Gebrauch von Determinanten und Matritzen als günstig erwiesen und die nötigen Gleichungen sind abgeleitet. Vergleich der nach beiden Methoden erhaltenen Resultate zeigt die klare Überlegenheit der neuen Methode.

Résumé—L'auteur montre que le calcul des concentrations de colorants dans la colorimétrie trichrome peut être amélioré par l'application de la méthode des moindres carrés plutôt qu'en prenant simplement la moyenne des séries de résultats. Dans cette amélioration, une approximation par matrice est spécialement utilisée, et les équations nécessaires sont développées. La comparaison des résultats obtenus par les deux méthodes montre la supériorité de l'approximation par matrice.

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REFERENCES

[1] H. Flaschka, *Talanta*, 1960, **7**, 90.
[2] R. P. Bauman, *Appl. Spectroscopy*, 1959, **13**, 156.

Talanta, 1961, Vol. 8, pp. 16 to 21. Pergamon Press Ltd. Printed in Northern Ireland

INVESTIGATIONS WITH IRIDIUM-192 OF SEPARATIONS OF PLATINUM AND RHODIUM FROM IRIDIUM—II

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Summary—^{192}Ir has been used as a tracer in a study of the separation of platinum and rhodium from iridium by the use of mercury^{I} chloride or mercury^{II} chloride and hypophosphorous acid as a selective precipitant.

It has been found that platinum may be separated satisfactorily from iridium by the use of either mercury^{I} chloride or the mercury^{II} salt and hypophosphorous acid. In the presence of bromide, rhodium may be conveniently separated from iridium by precipitation using a slurry of mercury^{I} chloride. Iridium may be precipitated quantitatively by the slurry if iodide is present.

A new rapid procedure for the separation of rhodium and iridium and subsequent determination of the two metals is proposed.

INTRODUCTION

IN 1934 Pierson[1] showed that platinum and palladium were precipitated from certain solutions by mercury^{I} chloride (calomel). More recently, Powell[2,3] has found that platinum, palladium and rhodium may be precipitated from solutions of their chlorides in dilute hydrochloric acid by the addition of mercury^{II} chloride and the subsequent addition of hypophosphorous acid and heating. The metals, precipitated in this manner, settle rapidly in a readily filtering form which yields the pure metal on ignition. The reaction is apparently due to reduction of mercury^{II} to mercury^{I} by the hypophosphorous acid, followed by the reduction of the platinum metals in solution by the mercury^{I}. Hypophosphorous acid, alone, produces no precipitate except in the case of palladium. The procedure forms a simple means of separating platinum, palladium and rhodium from iridium.

In the present study ^{192}Ir has been used as a tracer in investigations of the separation of platinum and rhodium from iridium by precipitation with calomel and also with mercury^{II} chloride and hypophosphorous acid. In addition, a new rapid procedure for the separation and determination of milligram quantities of rhodium and iridium has been developed.

Stock solutions of platinum metals and ^{192}Ir used in the work were similar to those employed in the research previously reported.[4]

OXIDATION POTENTIALS

Relevant oxidation potentials for ion-electron half-reactions of calomel and complexes of platinum, rhodium and iridium are shown in Table I. The values are those given by Latimer[5] and the conventions employed by that author have been followed.

The recorded potentials indicate that mercury^{I} chloride should serve as a precipitant for iridium metal. However, it must be remembered that oxidation potentials measure energy differences and bear no relation to reaction kinetics. Many reactions which are energetically possible are not observed because they proceed too slowly to

be followed. In addition, oxidation potential values refer only to equilibrium conditions and many reactions are encountered in which such conditions do not exist.

Reductants other than mercury^{I} chloride, *e.g.* copper powder, do not easily precipitate iridium, although oxidation potentials suggest that reduction to the metal should occur. The problem has been discussed by Tertipis and Beamish.[6]

TABLE I.—STANDARD OXIDATION POTENTIALS IN ACIDIC SOLUTION

Equation	E°_{298}, *V*
$Cl^- + \frac{1}{2}Hg_2Cl_2 \rightleftharpoons Hg\,Cl_2$ (sat. soln.) + e	−0·53
$Pt + 4Cl^- \rightleftharpoons PtCl_4^{2-} + 2e$	−0·73
$PtCl_4^{2-} + 2Cl^- \rightleftharpoons PtCl_6^{2-} + 2e$	−0·68
$Rh + 6Cl^- \rightleftharpoons RhCl_6^{3-} + 3e$	−0·44
$Ir + 6Cl^- \rightleftharpoons IrCl_6^{2-} + 4e$	−0·835

PRECIPITATION OF PLATINUM AND SEPARATION FROM IRIDIUM

Solutions containing milligram quantities of platinum and iridium labelled with ^{192}Ir were prepared in 50 ml of dil. hydrochloric acid. These were heated to boiling, and either (*a*) 5 ml of 3% (w/v) mercury^{II} chloride and 5 ml of 10% (v/v) hypophosphorous acid or (*b*) solid mercury^{I} chloride or (*c*) a slurry of mercury^{I} chloride were added. (The slurry of mercury^{I} chloride was prepared by the addition of dil. hydrochloric acid to a hot solution of mercury^{I} nitrate in dil. nitric acid; the precipitate of mercury^{I} chloride was washed by decantation with distilled water until free from acid and was used with a little water as a semi-fluid mixture).

TABLE II.—SEPARATION OF PLATINUM FROM IRIDIUM

Platinum taken, *mg*	Iridium taken, *mg*	Conditions of separation	Platinum found, *mg*	Iridium found radiometrically in recovered platinum, *mg*
10·0	10·0	10% HCl,$HgCl_2$ + H_3PO_2	10·33	0·004
10·0	10·0	10% HCl,Hg_2Cl_2 (solid)	9·94	0·052
10·0	10·0	10% HCl,Hg_2Cl_2 (slurry)	10·10	0·005

In each case the resulting solution was boiled for 10 min and the precipitate of platinum was collected on a 9-cm Whatman No. 44 filter paper. The beaker was rinsed with hot 2% hydrochloric acid. Any precipitate adhering to the walls of the beaker was removed with a small piece of filter paper, which was then placed in a porcelain crucible together with the main precipitate and ignited in the usual manner.[7] The recovered platinum was mounted on a tared aluminium counting tray, weighed, and counted with a γ-scintillation counter, type 1186A.

In each test an aliquot of the labelled iridium solution was employed for a standard, as in the studies previously described.[4]

Results of these experiments are shown in Table II. In each case a satisfactory separation of platinum from iridium was obtained.

PRECIPITATION OF RHODIUM AND SEPARATION FROM IRIDIUM

Standard solutions of rhodium with labelled iridium in dilute hydrochloric acid were treated in a similar manner to the mixtures of platinum and iridium, except that the final samples of rhodium were reduced in hydrogen before weighing and counting.

It was found that when mercury^{II} chloride and hypophosphorous acid were used as the reducing agent, the weight of rhodium precipitated decreased with an increase

in the hydrochloric acid concentration (Table III, tests 1–3). The contamination of the precipitate with iridium also decreased with an increase in the acid concentration.

In addition, it was found that either solid calomel or the freshly prepared slurry failed to precipitate rhodium quantitatively, even after re-treatment of the filtrate (Table III, tests 4–6).

TABLE III.—SEPARATION OF RHODIUM FROM IRIDIUM

Test	Rhodium taken, *mg*	Iridium taken, *mg*	Conditions of separation	Rhodium found, *mg*	Iridium found radiometrically in recovered rhodium, *mg*
1	10·0	10·0	2% $HCl,HgCl_2 + H_3PO_2$	10·14	0·082
2	10·0	10·0	10% $HCl,HgCl_2 + H_3PO_2$	9·85	0·076
3	10·0	10·0	20% $HCl,HgCl_2 + H_3PO_2$	9·76	0·050
4	10·0	10·0	10% HCl,Hg_2Cl_2 (solid)	2·74	0·016
5	10·0	10·0	10% HCl,Hg_2Cl_2 (slurry)	6·40	0·019
			Re-treatment of filtrate from test 5	2·46	0·164
6	10·0	10·0	10% HCl,Hg_2Cl_2 (slurry)	4·30	0·062

Precipitation of rhodium using calomel in the presence of bromide

The limited information available on oxidation potentials characteristic of the platinum metals[5] indicates that, in some cases, bromide complexes may be reduced more readily than the corresponding chloride complexes. It was decided, therefore, to investigate the effect of bromide on the reduction of rhodium by calomel. Separations were carried out as before, with an excess of mercury^{I} chloride slurry and varying concentrations of hydrochloric acid and of potassium bromide.

Results shown in Table IV indicate that the presence of bromide led to a better recovery of rhodium. An increase in bromide concentration gave rise to a greater contamination of the rhodium with iridium, but the contamination could be reduced to a more acceptable level by increasing the acid concentration.

Further experiments were carried out involving a double precipitation of the rhodium. The rhodium from the first precipitation was collected on a 9-cm Whatman No. 44 filter paper, washed with 2% hydrochloric acid and redissolved from the paper with hot hydrochloric acid saturated with bromine. The solution was collected in the original beaker, evaporated to *ca.* 1 ml and diluted to 50 ml with 10% (v/v) hydrochloric acid. Five g of potassium bromide were added and the rhodium was re-precipitated with mercury^{I} chloride slurry. Quantitative recoveries of rhodium were obtained in this manner and the contamination by iridium was negligible (Table IV, tests 10–12).

PRECIPITATION OF IRIDIUM BY CALOMEL IN THE PRESENCE OF IODIDE

It was found that iridium could be precipitated from the filtrates in the studies summarised in Table IV by the addition of 5 g of potassium iodide and a further quantity of mercury^{I} chloride slurry. In many cases the recovery of the metal was not quantitative, and further tests were carried out to determine the most favourable conditions for complete precipitation.

The tests were made using different concentrations of hydrochloric acid, bromide and iodide, and various volumes of solution. It was found that less iridium was

TABLE IV.—SEPARATION OF RHODIUM FROM IRIDIUM USING A SLURRY OF CALOMEL IN THE PRESENCE OF BROMIDE

Test	Rhodium taken, *mg*	Iridium taken, *mg*	Conditions of separation using mercury^{I} chloride slurry	Rhodium found, *mg*	Iridium found radiometrically in recovered rhodium, *mg*
1	10·0	10·0	50 ml 2% HCl + 1 g KBr	9·96	0·137
2	10·0	10·0	50 ml 10% HCl + 1 g KBr	9·82	0·097
3	10·0	10·0	50 ml 20% HCl + 1 g KBr	9·72	0·048
4	10·0	10·0	50 ml 2% HCl + 2·5 g KBr	10·58	0·749
5	10·0	10·0	50 ml 2% HCl + 5 g KBr	11·15	1·129
6	10·0	10·0	50 ml 2% HCl + 7·5 g KBr	11·65	1·583
7	10·0	10·0	50 ml 20% HCl + 2·5 g KBr	10·62	0·363
8	10·0	10·0	50 ml 20% HCl + 5 g KBr	10·42	0·569
9	10·0	10·0	50 ml 20% HCl + 7·5 g KBr	10·69	0·791
10	10·0	10·0	50 ml 20% HCl + 5 g KBr (double precipitation)	10·02	0·007
11	10·0	10·0	(double precipitation)	10·03	0·007
12	10·0	10·0	(double precipitation)	10·08	0·005

TABLE V.—PRECIPITATION OF IRIDIUM USING A SLURRY OF CALOMEL IN THE PRESENCE OF IODIDE

Test	Iridium taken, *mg*	Conditions of precipitation using mercury^{I} chloride slurry	Iridium found radiometrically in the precipitate, *mg*
1	10·0	100 ml 10% HCl + 5 g KBr + 5 g KI	9·53
2	10·0	200 ml 10% HCl + 5 g KBr + 5 g KI	9·00
3	10·0	300 ml 10% HCl + 5 g KBr + 5 g KI	5·37
4	10·0	200 ml 10% HCl + 5 g KI	9·72
5	10·0	200 ml 10% HCl + 5 g KI	9·71
6	10·0	200 ml 10% HCl + 10 g KI	5·92
7	10·0	200 ml 10% HCl + 15 g KI	4·23
8	10·0	200 ml 10% HCl + 20 g KI	2·82
9	10·0	200 ml 5% HCl + 10 g KBr + 10 g KI	6·57
10	10·0	200 ml 10% HCl + 10 g KBr + 10 g KI	5·52
11	10·0	200 ml 20% HCl + 10 g KBr + 10 g KI	5·68
12	10·0	200 ml 10% HCl + 10 g KBr + 1 g KI	5·27
13	10·0	200 ml 10% HCl + 10 g KBr + 3 g KI	10·11
14	10·0	200 ml 10% HCl + 10 g KBr + 5 g KI	10·17
15	10·0	200 ml 10% HCl + 10 g KBr + 5 g KI	10·09
16	10·0	200 ml 10% HCl + 5 g KBr + 5 g KI	10·07
17	10·0	200 ml 10% HCl + 5 g NaBr + 5 g KI	9·98
18	10·0	200 ml 10% HCl + 10 g NaBr + 5 g KI	10·04

recovered as the volume of the solution and the acid concentration were increased. Five g of potassium iodide appeared to be sufficient for the reaction, but the presence of bromide was found to assist in the recovery of the iridium (Table V). It was observed that in order to obtain complete recovery, it was necessary to boil the solutions until the colour changed from brown to black.

Iridium was not precipitated from solutions containing iodide by the addition of mercury^{II} chloride and hypophosphorous acid.

ANALYTICAL PROCEDURE FOR THE SEPARATION AND DETERMINATION OF MILLIGRAM QUANTITIES OF RHODIUM AND IRIDIUM

Relatively few convenient and satisfactory methods for the separation and subsequent determination of rhodium and iridium have been reported.[6,8–12] The following new procedure is proposed on the basis of the present study.

A sample solution should not contain more than 0·1 g of rhodium and iridium as chloride complexes, and oxidising acids must be absent.

TABLE VI.—SEPARATION AND GRAVIMETRIC DETERMINATION OF RHODIUM AND IRIDIUM

Test	Rhodium taken, *mg*	Iridium taken, *mg*	Conditions of separation using mercury^{I} chloride slurry	Iridium found gravimetrically *mg*	Rhodium found gravimetrically *mg*	Iridium in recovered rhodium, *mg*
1	10·0	10·0	50 ml 20% HCl + 5 g KBr, + 5 g KI (for Ir)	10·05	10·06	0·005
2	10·0	10·0	50 ml 20% HCl + 5 g KBr, + 5 g KI (for Ir)	10·02	10·19	0·005
3	30·0	30·0	100 ml 20% HCl + 10 g KBr, + 5 g KI (for Ir)	30·56	29·79	0·008
4	30·0	30·0	100 ml 20% HCl + 10 g KBr, + 5 g KI (for Ir)	30·55	29·83	0·006

Procedure

Dilute the solution in a 400-ml beaker to 100 ml with 20% (v/v) hydrochloric acid and add 10 g of potassium bromide. Boil gently, and add a slurry of mercury^{I} chloride until all of the rhodium has been precipitated (indicated by the presence of an excess of white calomel). Continue boiling, with stirring, until the rhodium coagulates and settles rapidly. Filter through a 9-cm Whatman No. 44 filter and wash the precipitate well with 2% hydrochloric acid. Retain the filtrate for the determination of iridium.

Dissolve the precipitate of rhodium on the paper with hot brominated hydrochloric acid and wash it into the original beaker. Evaporate the resulting solution to *ca.* 2 ml and dilute to 100 ml with 20% (v/v) hydrochloric acid. Add 10 g of sodium bromide and precipitate rhodium with mercury^{I} chloride slurry as before. Filter and wash the precipitate with hot 2% hydrochloric acid. Retain the filtrate for the determination of iridium.

Heat the precipitate of rhodium gently in a porcelain crucible in an efficient fume-cupboard to burn off the filter paper and volatilise mercury. Then heat for 30 min at 1000° in an electric muffle-furnace. Reduce the residue of rhodium in hydrogen, cool and weigh.

Combine the filtrates containing the iridium and evaporate to 200 ml. Add 5 g of potassium iodide, boil gently, and add an excess of mercury^{I} chloride slurry. Boil until the colour changes from brown to black. Allow the precipitate to settle. Filter, wash, ignite at 900°, reduce in hydrogen and weigh the resultant iridium as for the rhodium.

Results of tests of the procedure show that the separation and recovery of the metals is satisfactory, and that very little iridium is detectable in the recovered rhodium (Table VI).

Zusammenfassung—Iridium-192 wurde als Tracer verwendet um die Trennung von Platin und Rhodium von Iridium mittels Mercurochlorid oder Mercurichlorid und hypophosphoriger Säure als selective Fällungsmittel zu studieren. Es wurde gefunden, dass beide Reagenzien eine befriedigende Trennung von Platin und Iridium gestatten. In Gegenwart von Bromid kann Rhodium von Iridium getrennt werden durch Fällung mittels einer Aufschlämmung von Mercurochlorid. Iridium wird durch diese Aufschlämmung quantitative gefällt, wenn Iodid anwesend ist. Eine neue Schnellmethode zur Trennung von Rhodium und Iridium und anschliessenden Bestimmung der beiden Metalle wird vorgeschlagen.

Résumé—L'iridium 192 a été utilisé comme traceur dans une étude de séparation du platine et du rhodium d'une part et de l'iridium d'autre part, le chlorure mercureux ou le chlorure mercurique et l'acide hypophosphoreux étant utilisés comme précipitant sélectif. Les auteurs ont trouvé que le platine peut être séparé de l'iridium de façon satisfaisante par l'utilisation de l'un ou l'autre de ces composés. En présence de bromure, le rhodium peut être séparé convenablement de l'iridium par une précipitation utilisant une pâte de chlorure mercureux. L'iridium peut être précipité quantitativement par cette pâte si de l'iodure est présent. Une nouvelle méthode rapide de séparation du rhodium et de l'iridium et le dosage subséquent de ces deux métaux sont proposés.

REFERENCES

[1] G. Pierson, *Ind. Eng. Chem., Analyt.*, 1934, **6**, 437.
[2] W. R. Schoeller and A. R. Powell, *The analysis of minerals and ores of the rarer elements*. C. Griffin & Co. London, 3rd Ed., 1955.
[3] A. R. Powell, *Proceedings of the Congress on Modern Analytical Chemistry in Industry*. W. Heffer & Sons, Cambridge, 1957, p. 137.
[4] K. W. Lloyd and D. F. C. Morris, *Talanta* 1960, **7**, 117
[5] W. M. Latimer, *Oxidation potentials*. Prentice-Hall, New York, 2nd Ed., 1952.
[6] G. G. Tertipis and F. E. Beamish, *Analyt. Chem.*, 1960, **32**, 486.
[7] Reference 2, p. 358.
[8] R. Gilchrist, *J. Res. Nat. Bur. Stand.*, 1932, **9**, 547.
[9] A. D. Westland and F. E. Beamish, *Mikrochim. Acta*, 1956, **10**, 1474.
[10] S. S. Berman and W. A. E. McBryde, *Canad. J. Chem.*, 1958, **36**, 845.
[11] E. Jackson, *Analyst*, 1959, **84**, 106.
[12] S. T. Payne, *ibid.*, 1960, **85**, 698.

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TITRIMETRIC ANALYSIS WITH CHLORAMINE-T—II

THE CHLORAMINE-T–ARSENIC^{III} REACTION A POTENTIOMETRIC STUDY

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Summary—A potentiometric study has been made of the titration of arsenic^{III} with chloramine-T under a very wide range of conditions in order to establish the limits within which the reaction is quantitative and analytically acceptable, and also to gain an insight into the mechanism of the reaction. It has been established that, in the absence of added halide, chloramine-T oxidises arsenic^{III} either extremely slowly in strong acid solution or not at all at lower hydrogen ion concentrations. In the presence of chloride, the reaction is satisfactory with a chloride concentration greater than 0·5*M* and in hydrogen ion concentrations over the range 0·5 to 5·0*M*. In the presence of bromide at a final concentration of 0·1*M*, the reaction is quantitative over a hydrogen ion concentration range of 10^{-5}*M* to 5·0*M*; and in the presence of iodide to a final amount of 0·005*M* the results are excellent in the pH range of 4 to 9. In the presence of bromide or iodide the range can be extended to slightly higher pH limits by increasing the halide concentration. The actual oxidising species is hydrogen ion-independent, but subject to katagenic action by halide ion, and is probably free halogen. The use of diluted titrant solutions for determining small quantities of arsenic^{III} (about 0·1 mmole) at high dilution does not afford any marked improvement in accuracy.

THE chloramine-T–arsenic^{III} reaction is of fundamental importance in two ways. First, arsenious oxide is a primary, if not an ultimate, standard, and may be used for standardisation of chloramine-T solutions.[1] Upon the accuracy of this reaction, therefore, rests the accuracy of all other titrimetric determinations with chloramine-T. Second, many substances are not amenable to direct or reverse titration with chloramine-T, either because the reaction is incomplete or too slow, or because suitable indication of the end-point is lacking. In such cases it is often possible to make the reaction rapid and quantitative by using an excess of chloramine-T, followed by destruction of that excess by the addition of arsenic^{III} solution, the excess of which is finally determined by continuation of the titration with the original chloramine-T solution. This technique[2] is termed "double-excess back-titration".

Consequently, this reaction has been subjected to the closest scrutiny, and the conditions of reaction varied over a very wide range in order to define their limits, without neglecting detailed examination of conditions intermediate between the limits so that any anomalies, such as arise in the bromate–antimony^{III} reaction, may not escape detection. Since this is the most widely applicable reaction, it has been used for the development and assessment of new indicators, and of new techniques such as differential electrolytic potentiometry.[3]

Previous accounts of the reaction tend to be vague and inadequate, giving rise to ambiguity and uncertainty. Thus, arsenic^{III} has been

(a) titrated in bicarbonate solution[4] containing some potassium iodide and using

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starch as indicator. The amount of iodide has not been examined, nor has the possibility of using other buffers in place of sodium bicarbonate.

(b) titrated in "neutral" solution (*i.e.* without the addition of buffers, acids or alkalis) at an elevated, but unspecified temperature either potentiometrically[5] or using starch-iodide paper[6] as external indicator.

(c) titrated potentiometrically in hydrochloric acid.[7,8] The most suitable acid concentration is uncertain.

(d) titrated in hydrochloric acid using the visual indicators methyl red,[8] brilliant carmoisine[9] and *p*-ethoxychrysoïdine.[9] Titrations with methyl red were carried out at an elevated, but unspecified temperature in 1·0*M* acid. Titrations using brilliant carmoisine and *p*-ethoxychrysoïdine were carried out in 5% concentrated hydrochloric acid at room temperature.

Only in the case of methyl red[8] has the end-point been checked by the recognised criterion of potentiometric titration. Since most indicators incur an appreciable titration error, this is an important omission. The data presented here will be used for this purpose in a subsequent paper[13] describing work with visual indicators. In the present paper, the detailed potentiometric study of the oxidation of arsenic^{III} is described and the results are briefly discussed only as far as they affect the present determination.

EXPERIMENTAL

Apparatus and reagents

The apparatus and most of the reagents have been previously described.[1] Additional reagents are specified below. Checks on the theoretical titre were made by 50-ml titrations using the methods previously outlined[1] and confirmed by potentiometric titration under the optimum conditions.[1]

0·05*M* *arsenic^{III} solution, free from chloride:* prepared, for the titrations in sulphuric acid media, as previously described, except that sulphuric instead of hydrochloric acid was used to acidify the alkaline arsenite solution, the final acid concentration being about 0·05*M*.

Potassium bromide: AnalaR reagent, free from bromate, other oxidising agents and iodide, but containing approximately 0·15% of chloride, was used to prepare a stock 1·0*M* solution.

Stock buffer solutions: AnalaR compounds were used to prepare the stock solutions. The volume of solution or weight of solid added to the titration solution, and the pH measured with a glass electrode at the end of the titration in a volume of 200 ml are given in parentheses.

Bicarbonate—One mole of sodium bicarbonate dissolved, by prolonged stirring, in 900 ml of cold water, then diluted to 1 litre. (80 ml, pH 8·0).

Borax—Solid borax decahydrate was used. (3·8 g ≡ final concentration of 0·05*M*, pH 8·9).

Sodium carbonate—Solid anhydrous sodium carbonate was used. (2·1 g ≡ final concentration of 0·1*M*, pH 10·4).

Acetate—A solution 0·6*M* in sodium acetate and 1·4*M* in acetic acid. (50 ml, pH 4·2).

Phosphate—A solution 0·233*M* in disodium hydrogen phosphate and 0·1*M* in potassium dihydrogen phosphate. (40 ml, pH 6·2).

Phthalate—0·2*M* potassium hydrogen phthalate. (50 ml plus 15 ml of 0·5*M* hydrochloric acid, pH 2·3; 50 ml plus 10 ml of 0·5*M* hydrochloric acid, pH 2·5).

Procedure

The volume of titration solution was fixed to be 200 ml at the equivalence point, and quantities of acid, potassium halide, etc., sufficient to give the quoted concentrations at the equivalence point were initially added. In diluting the solution with halide-free distilled water to begin the titration, due allowance was made for the amount of wash water used during titration. The latter quantity was determined by averaging the amount used over a number of trial runs, and led to a final deviation in equivalence point volume of about ±2%. In passing through the end-point, increments of titrant were added split-dropwise, by allowing a drop partially to form, removing this from the burette tip with a clean, but moist glass rod, then washing into the titration beaker. Potentials were taken to be

in equilibrium when the rate of drift fell below 1 mV per min. Generally, potentials reached equilibrium through the end-point in less than 5 min, and after the end-point in less than 3 min. When equilibration was slower than this, it was usually very much slower, and in such circumstances readings were taken at 15-min intervals, except in the cases noted where the potential was rising slowly at the equivalence point, when a period up to several hr if necessary was allowed. When the potentials were "hunting", that is drifting slowly about in an aimless fashion, as happens before the equivalence point with an irreversible reductant, readings were taken at 5-min intervals. Normally

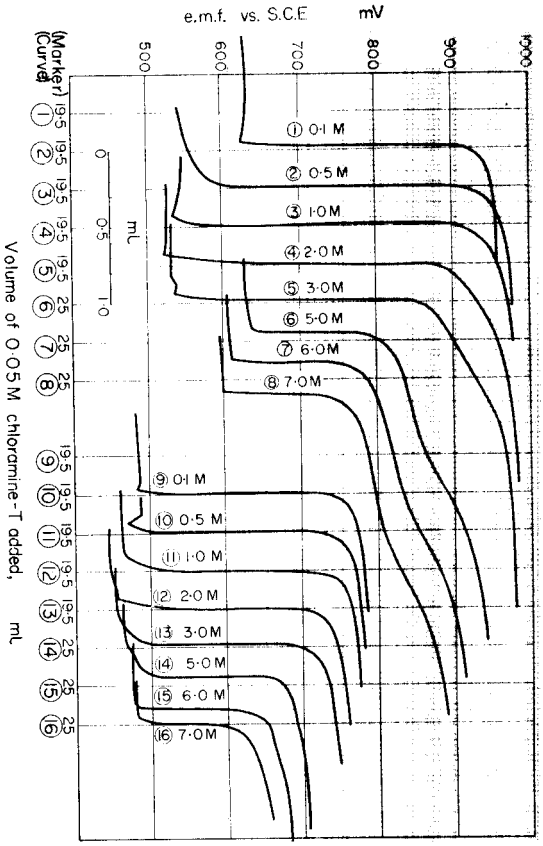

FIG. 1. Titrations in hydrochloric acid media.
Curves 1–8, HCl alone
Curves 9–16, in 0·1 *M* bromide.

the portion of the curve within ±1 ml (±4%) of the end-point was carefully studied, but where exploratory titrations indicated further features of interest, e.g. a second inflection, the range was appropriately extended. Although only one curve is illustrated under each set of conditions and the figures in the tables refer to the single result from each curve, curves and end-points were checked by replication, usually in triplicate, and all showed excellent reproducibility of potentials (within 2–5 mV) and of end-points (within a titrimetric error of ±0·016 ml or ±0·06%).

RESULTS AND DISCUSSION

Reaction in hydrochloric acid media

(a) *Alone.* Curves are shown in Fig. 1 for titrations over the range 0·1 to 7·0*M* hydrochloric acid. All gave satisfactory end-points, but in the titration at 0·1*M* hydrochloric acid, the equilibration of potential was so slow as to render the titration impracticable. At higher acid concentrations equilibration was reasonably rapid, though the potentials were unsteady before the end-point in acid concentrations below

3·0*M*, as is to be expected with an irreversible reductant. Above 3·0*M* hydrochloric acid, the pre-end-point potentials became quite steady.

The results in Table I indicate that the end- and equivalence points are in satisfactory agreement over the range of 0·5 to 5·0*M* hydrochloric acid. Below 0·5*M* acid, the end-point is premature and the reaction is incomplete and extremely slow. Above 5·0*M* acid, the end-points become progressively earlier due to a shift in the redox equilibrium at high hydrogen ion concentrations.

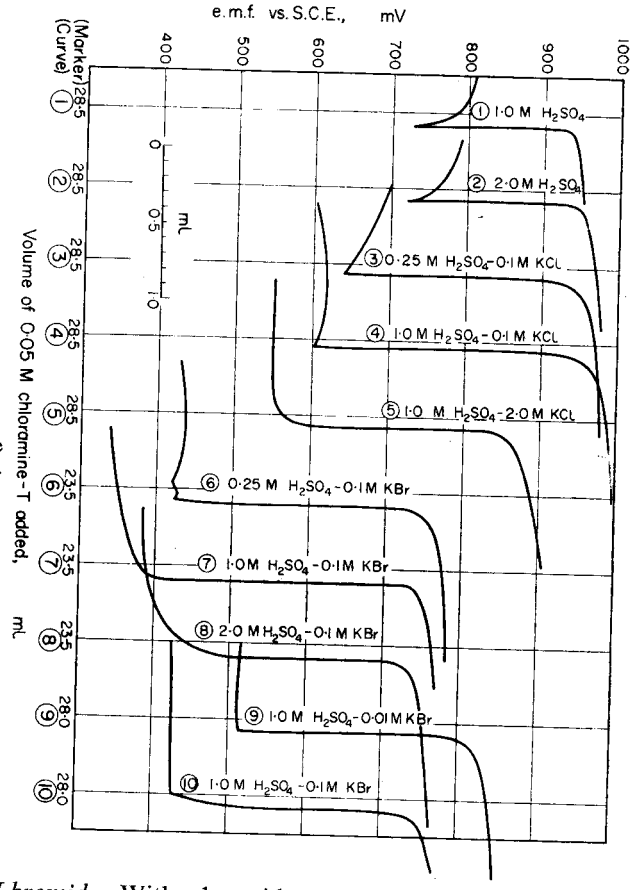

FIG. 2. Titrations in sulphuric acid media.
Curves 1–2, H_2SO_4 alone
Curves 3–5, in presence of chloride
Curves 6–10, in presence of bromide.

(b) *In the presence of* 0·1*M bromide.* With a bromide concentration of 0·1*M* at the equivalence point, excellent end-points were obtained over a range of hydrochloric acid concentrations from 0·1*M* to 7·0*M* as the curves 9 to 16 in Fig. 1 show. Equilibration of potential was rapid in all cases, and the pre-end-point potentials were steadier than in the absence of bromide, though the improvement with increasing acid concentration was not so marked. The accuracy is good from 0·1 to 5·0*M* hydrochloric acid, but at higher acid concentrations oxidation of bromide by arsenic^{V} gives rise to negative errors.

Reactions in sulphuric acid media

(a) *Alone.* Curves 1 and 2 in Fig. 2 and the results in Table 1 appear to be quite satisfactory but, in fact, the reaction was extremely slow; the points for the curves

were recorded at 15-min intervals and there was no real end-point—merely a slow increase in potential on long standing at the noted end-points. In 0·25*M* sulphuric acid the reaction, if any, was so slow that no curve could be derived. In the presence of excess chloramine-T, however, the potentials came to equilibrium quite quickly, presumably due to the formation of chloride of concentration $2 \times 10^{-3}M$ by decomposition of the chloramine-T.

(b) *In the presence of added chloride.* With a chloride concentration of 0·1*M* at the equivalence point it was possible to obtain a curve in 0·25*M* sulphuric acid, although the rate of potential rise at the end-point was still very slow. Increasing the sulphuric acid concentration to 1·0*M* gave a much more rapid, but slightly premature, rise at the end-point. By increasing the chloride concentration to 2·0*M* with the same sulphuric acid concentration satisfactory curves, equilibration speeds and end-points were produced, and the solution became green due to the liberation of chlorine after the end-point.

The presence of both hydrogen and halide ion is therefore necessary before the reaction becomes analytically useful.

(c) *In the presence of added bromide.* With a bromide concentration of 0·1*M* at the equivalence point, titration in the range of sulphuric acid concentration from 0·25*M* to 2·0*M* gave excellent end-points in close agreement with theory, and bromine was liberated immediately after the end-point. With a bromide concentration of 0·01*M* equally good results were achieved at higher potentials. Although the potentials were again unsteady on the reduced side, the equilibration rate was rapid at and beyond the end-point.

Reaction in buffer media

(a) *Alone, and in the presence of added chloride.* In 0·025*M* chloride the reaction was extremely and impracticably slow at pH 2·5, and the reaction ceased entirely at higher pH values and in the absence of added halide.

(b) *In the presence of added bromide.* With an equivalence point concentration of 0·1*M* bromide, satisfactory curves (1 and 2, Fig. 3) and results (Table I) were achieved at pH 2·5 and pH 4·2; the end-point was late at pH 6·2 and the reaction had ceased entirely at pH 8. On the grounds that the late end-point at the upper pH limit of the reaction is due to hydrolysis of the free halogen which is the active oxidant,[1] an increase in the halide concentration should afford an improvement. An increase in bromide concentration to 1·0*M* at the equivalence point does, in fact, give considerable improvement at pH 6·1 (curve 4, Fig. 3, and Table I), but at higher pH values the reaction becomes too slow to be practicable. It is also notable that the appearance of the colour of free bromine after the end-point is delayed at higher pH values, being 0·5 ml after the end-point at pH 4·2 in 0·1*M* bromide and at pH 6·1 in 1·0*M* bromide: at pH 6·2 in 0·1*M* bromide a 100% excess of oxidant was required before the colour appeared. Potential equilibration at the end-point became very slow in 0·1*M* bromide at pH 6·2, but rapid equilibration was restored on increasing the bromide concentration to 1·0*M*.

(c) *In the presence of added iodide.* Curves 5 to 10 of Fig. 3 illustrate the effects of variation of pH over the range 2·3 to 10·6 in the presence of iodide at concentrations of 0·05 to 0·0005*M* at the equivalence point. Titrations were satisfactory from pH 4 to

pH 8·9 in 0·005*M* iodide and the results (Table I) were accurate. Although the end-point appears to be satisfactory at pH 2·5, the reaction is too slow to be analytically useful, and a decrease in iodide concentration to 0·0005*M* in order to increase the redox potential did not significantly increase the rate of oxidation of the arsenic. The accuracy of the results is probably misleading, since negative errors may be expected to arise at such pH values due to the beginning of the shift in equilibrium in

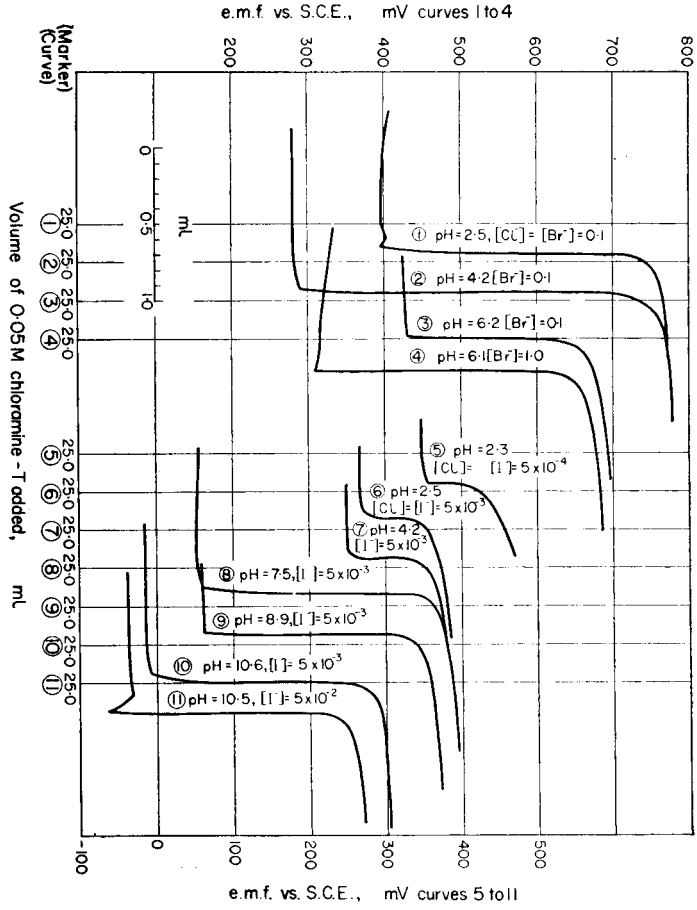

FIG. 3. Titrations in buffer media.

the iodine–arsenic^{III} reaction towards incomplete oxidation of the arsenic^{III}, but the slowness of the reaction tends to conceal this. A marked lateness in end-point appears at pH 10·6 due to hydrolysis of the iodine,[1] and the accuracy may once again be improved by increasing the iodide concentration to suppress hydrolysis. An increase of iodide concentration to 0·05*M* reduces, but does not entirely eliminate, the error. At and above pH 4, equilibration of the potentials was rapid at and beyond the end-point, but as usual the potentials were unsteady on the reduced side. At very high pH values, the reaction again ceases entirely.

It is therefore evident that the oxidising action of chloramine-T is rather specific, and is confined to restricted ranges of hydrogen ion concentration. In the absence of

TABLE I.—POTENTIOMETRIC TITRATION OF APPROXIMATELY 0·005*M* As^{III} WITH 0·05*M* CHLORAMINE-T UNDER VARIOUS CONDITIONS

Conditions									Titre		Error	
Concentrations at the equivalence point, *M*												
Fig.	Curve	HCl	H_2SO_4	Buffer pH	KCl	KBr	KI		Theory	Found	*ml*	%
1	1	0·1	—	—	—	—	—		19·75	19·72	−0·03	−0·17
	2	0·5	—	—	—	—	—		19·75	19·74	−0·01	−0·05
	3	1·0	—	—	—	—	—		19·75	19·73	−0·02	−0·10
	4	2·0	—	—	—	—	—		19·75	19·75	0	0
	5	3·0	—	—	—	—	—		19·75	19·725	−0·025	−0·13
	6	5·0	—	—	—	—	—		25·18	25·185	+0·005	+0·02
	7	6·0	—	—	—	—	—		25·18	25·125	−0·055	−0·22
	8	7·0	—	—	—	—	—		25·18	25·09	−0·09	−0·36
	9	0·1	—	—	—	0·1	—		19·75	19·74	−0·01	−0·05
	10	0·5	—	—	—	0·1	—		19·75	19·74	−0·01	−0·05
	11	1·0	—	—	—	0·1	—		19·75	19·75	0	0
	12	2·0	—	—	—	0·1	—		19·75	19·75	0	0
	13	3·0	—	—	—	0·1	—		19·75	19·725	−0·025	−0·13
	14	5·0	—	—	—	0·1	—		25·18	25·18	0	0
	15	6·0	—	—	—	0·1	—		25·18	25·15	−0·03	−0·12
	16	7·0	—	—	—	0·1	—		25·18	25·00	−0·18	−0·72
2	1	—	1·0	—	—	—	—		28·58	28·58	0	0
	2	—	2·0	—	—	—	—		28·58	28·575	−0·005	−0·02
	3	—	0·25	—	0·1	—	—		28·58	28·565	−0·015	−0·05
	4	—	1·0	—	0·1	—	—		28·58	28·55	−0·03	−0·10
	5	—	1·0	—	2·0	—	—		28·58	28·57	−0·01	−0·04
	6	—	0·25	—	—	0·1	—		23·59	23·595	+0·005	+0·02
	7	—	1·0	—	—	0·1	—		23·59	23·60	+0·01	+0·04
	10	—	1·0	—	—	0·1	—		28·08	28·085	+0·005	+0·02
	8	—	2·0	—	—	0·1	—		23·59	23·595	+0·005	+0·02
	9	—	1·0	—	—	0·01	—		28·08	28·07	−0·01	−0·04
3	1	—	—	2·5	—	0·1	—		25·18	25·19	+0·01	+0·04
	2	—	—	4·2	—	0·1	—		25·18	25·20	+0·02	+0·08
	3	—	—	6·2	—	0·1	—		25·18	25·25	+0·07	+0·28
	4	—	—	6·1	—	1·0	—		25·18	25·21	+0·03	+0·12
	5	—	—	2·3	—	—	0·0005		25·18	25·20	+0·02	+0·08
	6	—	—	2·5	—	—	0·005		25·18	25·17	−0·01	−0·04
	7	—	—	4·2	—	—	0·005		25·18	25·18	0	0
	8	—	—	7·7	—	—	0·005		25·18	25·17	−0·01	−0·04
	9	—	—	8·9	—	—	0·005		25·18	25·18	0	0
	10	—	—	10·6	—	—	0·005		25·18	25·24	+0·06	+0·24
	11	—	—	10·5	—	—	0·05		25·18	25·20	+0·02	+0·08

added halide, no reaction at all occurs at low acidities, while at high acidities the reaction is extremely slow, different in character from the normal reaction, and probably dependent on small amounts of chloride either initially present as impurity in the reagent or formed by its decomposition. In the presence of chloride ion, the reaction becomes impracticably slow and the end-point premature when the chloride ion concentration falls to 0·1*M* in strong acid solution. In the presence of hydrochloric acid the minimum practicable concentration is 0·5*M*, while the maximum concentration is 5·0*M*. In more concentrated solutions the end-points become premature due to the influence of hydrogen ion on the As^{III}/As^{V} potential. In the presence of bromide, chloramine-T is a satisfactory oxidant over the range of hydrogen ion concentration 5·0 to $10^{-5}M$ at a bromide concentration of 0·1*M*. At higher hydrogen ion concentrations the arsenic potential rises sufficiently to prevent complete reaction, and at lower concentrations the reaction becomes slow or ceases altogether. At the same time hydrolysis of bromine occurs, leading to late end-points, though this effect can be diminished by increasing the bromide concentration to 1·0*M* at a hydrogen ion concentration of $10^{-6}M$. In the presence of iodide, an upper limit is set to the permissible hydrogen ion concentration for the oxidation of arsenic^{III} by the oxidation of iodide by arsenic^{V}, which is first evidenced by a rapid decline in the speed of reaction. A lower limit is set by hydrolysis of the iodine produced as an intermediate. The practicable range is from pH 4 to pH 9 at an iodide concentration of 0·005*M*. An increase in the iodide concentration to 0·05*M* permits extension of the lower limit to pH 10.

Chloramine-T, therefore, although it has a high apparent redox potential, is incapable of effective reaction in the absence of added halide. In the presence of chloride it will react at a hydrogen ion concentration above 0·5*M*; in the presence of bromide this limit is extended to $10^{-5}M$, the upper limit of 5·0*M* being set in the titration of arsenic^{III} by partial reversal of the reaction between free halogen and arsenic^{III} at high hydrogen ion concentrations. In the presence of iodide, chloramine-T will react down to pH 9 or even pH 10, an upper limit in the case of oxidation of arsenic^{III} being set at about pH 4. It is also notable that the minimal requirement in respect to the concentration of added halide decreases with decreasing redox potential of the halide, being about 0·5*M* for chloride, 0·01*M* for bromide and 0·005*M* for iodide. Catalysts such as osmic acid, vanadates, molybdates or tungstates are without influence.

Titration at low reagent concentration

Titrations under most of the conditions described above were also made with ten-fold diluted reagents (0·0005*M* arsenic^{III} and 0·005*M* chloramine-T); the curves are shown in Fig. 4 and the results in Table II. In all cases the end-point was late, generally to the extent of about 0·4%, but at a bromide concentration of 0·1*M* the error increased to about 1·5%.

In hydrochloric acid alone, the rise in potential through the end-point at 0·5*M* was very slow, but improved at higher concentrations. The same was true in lesser degree in the presence of 0·01*M* bromide. An increase of bromide concentration to 0·1*M* gave rise to peculiar curves. At all acid concentrations the potential started to climb slowly after the equivalence point, but there was no sharp rise until the recorded end-point, some 0·4 ml after the equivalence point. At this stage the potentials

reached equilibrium quickly and the colour of free bromine became apparent. The double inflections which may be sensed in all the curves become apparent in the presence of 0·01*M* bromide, though no additional error is introduced if the first rising inflection is taken as the end-point. The most satisfactory titration is considered to be that in bicarbonate buffer with an iodide concentration of 0·005*M*. Although the end-point is still more than 0·3% late, the potentials were steady and reached

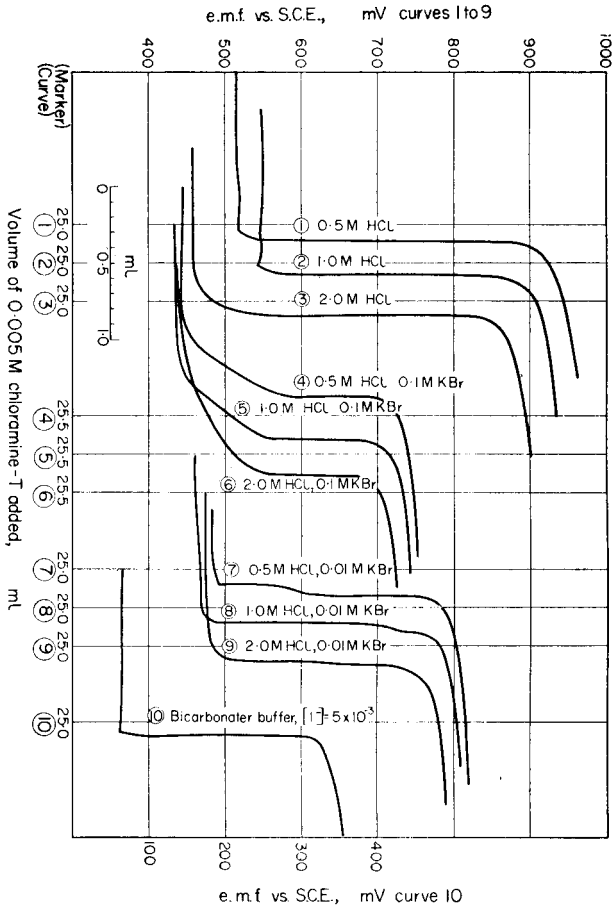

FIG. 4.—Titrations at ten-fold dilution.

equilibrium quickly. Titrations with visual indicators gave similar results, as will be shown in a subsequent paper,[13] confirming that, although there is a slight improvement in precision (replicability), there is no improvement in accuracy when using diluted titrant. The same accuracy of 0·4% is achieved in a titration requiring either 25 ml of 0·005*M* titrant or 2·5 ml of 0·05*M* titrant. Chloramine-T shares this phenomenon with many other titrimetric reagents.

Interpretation of curves

Full discussion of curve forms and potentials will be deferred until all of the data for the various reactions have been presented, but certain salient features of the curves for the arsenic^{III} reaction may be underlined at this time.

(*a*) In all cases the form of the curve and the behaviour of the potentials before the end-point is typical of an irreversible redox system. This is fully confirmed by the differential electrolytic potentiometric curves.[3]

(*b*) The form of the curves through and after the end-point indicates a high degree of reversibility in the oxidant system. Many curves (*e.g.* curves 3, 4, 5, Fig. 1) illustrate how the oxidant system picks up control of the potential just before the end-point.[11]

(*c*) The curvature on the oxidant side of the end-point under analytically useful

TABLE II.—POTENTIOMETRIC TITRATION OF APPROXIMATELY 0·0005*M* As^{III} WITH 0·005*M* CHLORAMINE-T UNDER VARIOUS CONDITIONS

Conditions	Titre,* *ml*	Error	
		ml	%
0·5*M* HCl	25·10	+0·10	+0·40
1·0*M* HCl	25·075	+0·075	+0·30
2·0*M* HCl	25·09	+0·09	+0·36
0·5*M* HCl + 0·1*M* KBr	25·38	+0·38	+1·52
1·0*M* HCl + 0·1*M* KBr	25·405	+0·40	+1·60
2·0*M* HCl + 0·1*M* KBr	25·37	+0·37	+1·48
0·5*M* HCl + 0·01*M* KBr	25·10	+0·10	+0·40
1·0*M* HCl + 0·01*M* KBr	25·10	+0·10	+0·40
2·0*M* HCl + 0·01*M* KBr	25·09	+0·09	+0·36
Bicarbonate buffer + 0·005*M* KI	25·08	+0·08	+0·32

* Theoretical titre, 25·00 ml.

conditions fits extremely well with the value n = 2 for the number of electrons transferred in the reaction

$$ox + n\varepsilon = red.$$

(*d*) The value of the potentials on the oxidant side does not rise with increasing hydrogen ion concentration. In view of the reversibility of the oxidant reaction, the potential-determining redox species cannot, therefore, involve hydrogen ion in its reaction. Chloramine-T, dichloramine-T, the free acid RNHCl, hypochlorous acid or hypochlorite ion are not, therefore, the actual reacting species.

(*e*) The potentials after the end-point fall with increasing halide concentration. A net katagenic ion is, therefore, involved in the redox reaction, and this ion must be a halide ion.

(*f*) Confirmation of the contention that hydrolysis of the free halogen supervenes at the lower useful limit of hydrogen ion concentration for each halide is given by the drop in potential which occurs in each case as well as by the slowness in equilibration of the potentials.

(*g*) In the absence of added halide (Fig. 2, curves 1 and 2), the curvature corresponds to a value of n = 4 for the number of electrons transferred, and such other deviations from n = 2 as do occur are to be found in chloride media.

(*h*) The development of a second inflection in high hydrochloric acid concentrations

is well illustrated in curves 4 to 8 in Fig. 1. These do not affect the first inflection or the analytical results, and will be shown to be due to traces of a titratable substance in the hydrochloric acid.

CONCLUSIONS

Chloramine-T, as a titrimetric reagent, reacts through reaction-intermediates which are probably free halogens, and fails to react under circumstances which preclude the generation of such intermediates, as in the absence of added halide, or when the concentration of such halide is so low that the primary redox potential of chloramine-T is not high enough to generate sufficient free halogen to afford a satisfactory reaction. It has been shown elsewhere[12] that free halogen produced slowly or in minute quantity fails as an oxidant due to hydrolysis, even in acid media. Consequently, minimal requirements in halide ion concentration have to be met. Under the appropriate conditions of hydrogen and halide ion concentrations, the oxidation of arsenic^{III} by chloramine-T is quantitative.

Zusammenfassung—Eine potentiometrische Studie wurde unternommen, um den Verlauf der Reaktion zwischen Arsen(III) und Chloramin T zu Klären und in weitem Bereich die Grenzen für die Anwendbarkeit dieser Reaktion zur Bestimmung von Arsen aufzufinden. Es wurde gefunden, dass in Abwesenheit von Halogensalzen das Arsen in stark saurer Lösung nur äusserst langsam oxydiert wird und in schwach saurer Lösung überhaupt nicht. In Gegenwart von Chloride (höher als 0·5 m) und einer H-Ionenkonzentration von 0·5–5·0 m verläuft die Reaktion zufriedenstellend. In Gegenwart von Bromid (Endkonzentration 0·1 m) ist die Reaktion quantitativ bei einer H-Ionenkonzentration 10^{-5}–5·0 m. In Anwesenheit von Jodid (Endkonzentration 0·005 m) werden ausgezeichnete Resultate erhalten im pH Bereich 4–9. Im Falle von Bromid und Jodid kann die pH-Grenze etwas nach der alkalischen Seite verschoben werden, wenn höhere Halogenkonzentration eingestellt werden. Die tatsächlich oxydierende Komponente ist ph-unabhängig, unterliegt aber katagenen Einflüssen durch die Halogenionen, und ist vermutlich freies Halogen. Die Verwendung stark verdünnter Masslösungen zur Bestimmung kleiner Arsenmengen (ca 0·1 Millimol) in hochverdünnten Lösungen ergibt keinen nennenswerten Anstieg der Genauigkeit.

Résumé—Les auteurs ont fait une étude potentiométrique du titrage de l'arsenic(III) par la chloramine T dans un très large domaine de conditions afin d'établir les limites dans lesquelles la réaction est quantitative et acceptable au point de vue analytique, et d'obtenir une connaissance du mécanisme de la réaction. Il a été établi que, en l'absence d'halogenures ajoutés, la chloramine T oxyde l'arsenic (III) soit extremement lentement en milieu acide fort, soit pas du tout pour les concentrations en ions hydrogène plus faibles. En présence de chlorure, la réaction est satisfaisante avec une concentration de chlorure supérieure à 0,5*M* et des concentrations en ion hydrogène comprises dans le domaine 0,5*M* à 5*M*. En présence de bromure, à une concentration finale 0,1*M*, la réaction est quantitative dans un domaine de concentration d'ion hydrogène de 10^{-5}*M* à 5*M*, et en présence d'iodure en concentration finale 0,005*M*, les résultats sont excellents dans le domaine de pH 4–9. En présence de bromure ou d'iodure le domaine peut être étendu à limites de pH légèrement plus élevées en augmentant la concentration d'halogénure. L'espèce oxydante réelle est indépendante de l'ion hydrogène, mais est sujette à l'action catagénique de l'ion halogénure et est probablement de l'halogène libre. L'utilisation de solutions diluées titrantes pour doser de faibles quantités d'arsenic (III) (environ 0,1 mole) à grande dilution n'apporte pas d'amélioration marquée de la précision.

REFERENCES

[1] E. Bishop and V. J. Jennings, *Talanta*, 1958, **1**, 197.
[2] V. J. Jennings, *Titrimetric Analysis with Chloramine-T*, Univ. Exon., 1957.
[3] E. Bishop, *Mikrochim. Acta*, 1956, 619; *Analyst*, 1958, **83**, 212.
[4] A. Noll, *Chem.-Ztg.* 1924, **48**, 845.
[5] B. Samek, *Chem. Zentr.*, 1942, **1**, 517.

[6] J. R. Bendall, F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1942, 157.
[7] A. McMillan and W. Easton, *J. Soc. Chem. Ind.*, 1927, **46**, 472T.
[8] O. Tomiček and B. Suchanla, *Casopis Ceskoslov Lekarnictva*, 1931, **11**, 285, 309.
[9] W. Poethke and F. Wolf, *Z. anorg. Chem.*, 1952, **268**, 244.
[10] A. J. Berry, *Analyst*, 1934, **55**, 736.
[11] E. Bishop, *Comprehensive Analytical Chemistry*, Edited by C. L. Wilson and D. W. Wilson, Elsevier Publishing Co., Amsterdam, 1960, Vol. 1B, Chapter VII, 2, p.133ff.
[12] E. Bishop, *Mikrochim. Acta*, Emich Festschrift, 1960, 803.
[13] E. Bishop and V. J. Jennings, *Talanta*, 1960, **8**, 34.

Talanta, 1961, Vol. 8, pp. 34 to 42. Pergamon Press Ltd. Printed in Northern Ireland

TITRIMETRIC ANALYSIS WITH CHLORAMINE-T—III

THE CHLORAMINE-T–ARSENIC^{III} REACTION A STUDY OF VISUAL INDICATORS

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Summary—A search has been made for visual indicators suitable for application in chloramine-T titrimetry, and ten compounds, five reversible and five irreversible, have been rigorously examined in the titration of arsenic^{III} under conditions for which the titrimetric reaction has been shown to be quantitative. Indicator errors have been checked by direct comparison with potentiometric titrations under similar conditions. Recommendations have been made as to the best media, and indicators have been arranged in order of preference under various conditions. Titrations at a ten-fold dilution of the customary concentration have been investigated and found to offer no advantage.

THE fundamental importance of the chloramine-T–arsenic^{III} reaction in respect to the standardisation[1] and analytical application[2] of chloramine-T has already been emphasised. The reaction has been subjected to a comprehensive potentiometric investigation[2] and the quantitative limits under various conditions have been defined. From the summary already made[2] of the conditions under which arsenic^{III} has previously been titrated with chloramine-T, it is evident that few good visual indicators are available for this titration. Apart from starch which, as it requires the presence of iodide, may not always be used, only methyl red,[3] methyl orange,[4] brilliant carmoisine[5] and *p*-ethoxychrysoïdine[5] have previously been recommended. Of these, only starch and *p*-ethoxychrysoïdine show reversibility, though the reversibility of the latter, which has been recognised in arsenic^{III}–bromate titrations, has not thus far been examined in the case of chloramine-T.

Of those indicators which have been used in chloramine-T titrimetry, methyl red alone[3] has been subjected to checking by the recognised criterion of potentiometric titration. This is an important omission, because visual indicators often incur an appreciable titration error. Poethke and Wolf[5] have attempted to assess the indicator errors for brilliant carmoisine and *p*-ethoxychrysoïdine, by conducting a blank titration on the pure indicator solution. Although this method has also been included in the present work, it is open to suspicion as it may not take into account such factors as the character and speed of the main and indicator reactions, induced and side reactions and concentration effects. Consequently the preferred method, used here, is direct comparison with potentiometric titrations[2] under the same conditions.

Since the chloramine-T–arsenic^{III} reaction has been so thoroughly investigated[1,2] it has been used as the test reaction for the development and examination of new indicators as well as for the critical re-assessment of those previously recommended. Substances for test as possible indicators were selected on the following grounds:

(*a*) Known reactivity to free halogen. Substances already in use as indicators in

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bromate, iodate and hypochlorite titrimetry were an obvious first choice. Other substances reported to have a poor fastness to chlorine[6] were also tried, but most proved to be unsatisfactory, either because of a poor or indistinct colour change or because they were so poorly resistant that they were prematurely destroyed.

(*b*) Known redox indicator properties. Of other known redox indicators, *o*-dianisidine[7] alone proved to have suitable characteristics.

(*c*) From a survey of several thousand dyestuffs and related materials for indicator properties,[8] those which showed the best reactivity to bromate were examined. Of these, which are mainly substitution products of pararosaniline, the best was rosaniline.

(*d*) Specific reagents for free halogen. These include rosaniline and α-naphthoflavone for bromine and starch and its derivatives for iodine.

Of the indicators finally selected for exhaustive testing, methyl orange, methyl red and *p*-ethoxychrysoïdine have previously received some attention, but the remainder, rosaniline,[1] bordeaux,[9] amaranth,[10] quinoline yellow,[11] *o*-dianisidine,[7] tartrazine,[12] and α-naphthoflavone[13] have not been applied to chloramine-T titrimetry. Of these, *p*-ethoxychrysoïdine, quinoline yellow, *o*-dianisidine, tartrazine and α-naphthoflavone show reversibility under certain conditions.

Rosaniline has already been carefully examined[1] and found to yield accurate results with a negligible ($< 0{\cdot}01$ ml) correction in media 0·5 to 2·5*M* in hydrochloric acid and 0·01 to 0·1*M* in potassium bromide. The chloramine-T–arsenic^{III} reaction has also been shown[2] to be quantitative (*a*) in the presence of a minimum chloride concentration of 0·5*M* over the range of hydrogen ion concentration of 0·5 to 5·0*M*, (*b*) in the presence of 0·01 to 0·1*M* bromide at hydrogen ion concentrations between 10^{-5} and 5·0*M*, and (*c*) in the presence of 0·005*M* iodide within the pH range 4 to 9. Errors arising in visual indicator titrations under these conditions may therefore be ascribed to the indicator.

EXPERIMENTAL

Apparatus and reagents

These have already been described.[1,2] Arsenic^{III} solutions for use in sulphuric acid media were prepared by the alternative method.[2] The source of material, strength and method of preparation of indicator solutions are shown in Table I. Normally 2 drops of the indicator solution per 100 ml of titration solution were used, except in the cases of starch and α-naphthoflavone where 1 ml was added.

Procedures

A detailed account has been given.[16] Volumetric glassware was used in the manner already described,[17] titrations were completed split-dropwise,[1,2] allowing 15–30 sec between the addition of each increment. All titrations were conducted at room temperature and the results corrected to 20°. The method given for rosaniline[1] was employed with the other irreversible indicators. Reversibility, where appropriate, was checked by adding a known amount, 5 or 10 ml, of arsenic^{III} solution, warming or allowing the mixture to stand until the original colour was fully restored, and titrating to a second end-point. The concentrations of reagents recorded refer to the equivalence point volume of the titration solution, and in diluting the mixture before starting the titration, due allowance was made for the amount of wash water used. Except for the second end-points with reversible indicators, the equivalence point volume was normally 100 ml ± 5%.

RESULTS

Indicator blanks

Table II shows the results of titrations of 1 ml of the indicator solution in various media at a dilution of 100 ml with 0·005*M* chloramine-T. These figures must be

Table I.—Indicators

Compound	Source and grade	British Colour Index number	Strength of solution	Method of preparing solution
Starch	AnalaR	—	1% aqueous solution	1 g solid to 100 ml boiling water. Solution boiled for 2 min and cooled before use. Solution prepared daily.
Rosaniline hydrochloride	Hopkin & Williams Ltd.	677	0·1% in 0·02*M* hydrochloric acid	0·1 g dissolved in 100 ml warm 0·02*M* hydrochloric acid solution, cooled and decanted.
Methyl orange	AnalaR	142	0·1% aqueous solution	0·1 g dissolved in 100 ml water.
Methyl red (sodium salt)	Hopkin & Williams Ltd. pH indicator	211	0·1% aqueous solution	0·1 g dissolved in 100 ml water.
Bordeaux	Hopkin & Williams Ltd. Revector dye	88	0·1% aqueous solution	0·1 g dissolved in 100 ml water.
Amaranth	British Drug Houses Ltd. Technical Dye	184	0·1% aqueous solution	0·1 g dissolved in 100 ml water.
p-Ethoxychrysoïdine	Hopkin & Williams Ltd. Redox Indicator	—	0·1% aqueous solution	0·1 g added to 100 ml boiling water, cooled and decanted.
Quinoline yellow	I.C.I. Ltd. Dyestuff	801	0·5% aqueous solution	0·5 g dissolved in 100 ml water.
o-Dianisidine	Hopkin & Williams Ltd.	—	0·2% in 2*M* acetic acid	0·2 g dissolved in 12 ml glacial acetic acid and diluted to 100 ml with water.
Tartrazine	Hopkin & Williams Ltd. Adsorption Indicator	640	0·1% aqueous solution	0·1 g dissolved in 100 ml water.
α-Naphthoflavone	Hopkin & Williams Ltd.	—	0·1% ethyl alcohol solution	0·1 g dissolved in 100 ml absolute ethyl alcohol.

accepted with considerable reservations as noted above, but they may serve roughly to indicate the relative blanks. Apart from α-naphthoflavone, where 1 ml is required, the amount of indicator used in normal titrations is less than 0·2 ml, so that the indicator error should be one fiftieth of the blank shown in the table. Most of the indicators should have a measurable error which is smallest in hydrochloric acid free from other halides. Induction, however, tends to reduce this error in practice, and under conditions for which the main reaction is slow, appreciable fading of the indicator colour occurs before the end-point, or else the more easily destroyed indicators yield premature end-points.

TABLE II.—TITRATION OF 1·0 ML OF INDICATOR SOLUTIONS IN 100 ML OF VARIOUS MEDIA WITH 0·005*M* CHLORAMINE-T

Indicator	Colour change	Vol. of 0·005*M* chloramine-T required to produce colour change, *ml*		
		1·0*M* HCl	1·0*M* HCl + 0·1*M* KBr	1·0*M* H_2SO_4 + 0·1*M* KBr
Rosaniline	yellow–purple	—	0·3	0·3
Methyl orange	red–pale yellow	1·0	2·0	1·5
Methyl red	crimson–pale yellow	1·0	2·7	1·8
Bordeaux	crimson–pale yellow	0·8	0·8	0·8
Amaranth	crimson–pale yellow	0·7	0·8	0·8
p-Ethoxychrysoïdine	orange–yellow	1·3	1·2	1·2
Quinoline yellow	yellow–colourless	1·2	2·0	2·0
o-Dianisidine	colourless–orange red	0·2	0·3	0·3
Tartrazine	yellow–colourless	1·3	—	—
α-Naphthoflavone	(colloidal) white–yellow	—	0·1	0·1

Indicator errors and suitability in various media

Results of titrations in equivalence point volumes of 100 ml of the various media in which the reaction is known to be quantitative[2] are shown in Table III. The indicator errors shown are the differences between replicate visual titrations and titrations conducted potentiometrically under similar conditions.[2] As previously observed,[2] 0·5*M* hydrochloric acid in the absence of bromide is a minimal condition under which the reaction between chloramine-T and arsenic^{III} is slowing down, and it is therefore not surprising that all of the indicators give positive errors of considerable magnitude.

Specific reagents for free bromine are not, of course, applicable in the absence of bromide, and quinoline yellow was prematurely decolorised under the same conditions. Tartrazine failed to show any reversibility to a further addition of 5 ml of arsenic solution after the first colour change, and *p*-ethoxychrysoïdine did not give a pleasing second end-point. *o*-Dianisidine reversed satisfactorily and gave excellent second end-points in 1·0 and 2·0*M* hydrochloric acid, and so it is recommended for use in these media. The other indicators are subject to irreversible colour changes. Methyl orange, methyl red and tartrazine show appreciable titration errors at all

hydrochloric acid concentrations, but in 1·0 and 2·0*M* hydrochloric acid the errors were negligible with bordeaux, amaranth, *p*-ethoxychrysoïdine and *o*-dianisidine, so that these indicators are recommended for this titration.

In hydrochloric acid media in the presence of bromide in a concentration of 0·1*M*, tartrazine was not oxidised by the bromine formed at the end-point. The specific reagents for free bromine gave excellent results, and α-naphthoflavone is furthermore reversible. The other indicators generally show a greater positive error in the presence of bromide and, except for *p*-ethoxychrysoïdine, the error increases with an increasing hydrochloric acid concentration. In addition to rosaniline, bordeaux, amaranth and

TABLE III.—INDICATOR ERRORS INCURRED IN THE TITRATION OF 20 OR 25 ML OF 0·05*M* ARSENIC^{III} IN VARIOUS MEDIA WITH 0·05*M* CHLORAMINE-T

Indicator	Error, *ml.* in titration in							
	0·5*M* HCl	1·0*M* HCl	2·0*M* HCl	0·5*M* HCl + 0·1*M* KBr	1·0*M* HCl + 0·1*M* KBr	2·0*M* HCl + 0·1*M* KBr	1·0*M* H_2SO_4 + 0·1*M* KBr	Acetate buffer pH = 4·1 + 0·1*M* KBr
Rosaniline	- -	- -	- -	0·00	0·00	0·00	0·00	—
Methyl orange	−0·06	−0·02	−0·02	−0·02	−0·04	+0·06	+0·04	+0·06
Methyl red	−0·05	−0·02	−0·02	−0·02	−0·04	+0·06	+0·05	+0·04
Bordeaux	−0·03	0·00	0·00	−0·02	−0·02	+0·04	0·00	+0·06
Amaranth	−0·03	0·00	0·00	0·00	+0·00	+0·02	0·00	+0·04
p-Ethoxy-chrysoïdine	−0·05	0·00	0·00	−0·05	−0·03	+0·02	+0·01	—
(2nd end-point)	- -	0·00	0·00	−0·02	−0·01	0·00	+0·02	—
Quinoline yellow	- -	- -	- -	−0·06	−0·04	+0·06	+0·03	+0·06
(2nd end-point)	- -	- -	- -	−0·02	−0·01	—	+0·06	+0·05
o-Dianisidine	−0·04	0·00	0·00	−0·02	−0·03	+0·03	0·00	—
(2nd end-point)	- -	0·00	0·00	0·00	−0·03	+0·02	—	—
Tartrazine	−0·06	−0·02	−0·02	- -	- -	—	—	+0·06
(2nd end-point)	- -	- -	- -	- -	—	—	—	+0·05
α-Naphtho-flavone	- -	- -	- -	0·00	0·00	−0·01	0·00	—
(2nd end-point)	- -	- -	- -	−0·01	−0·01	−0·01	+0·03	—

Volume of solution at the equivalence point, 100 ml. Two drops of indicator solution per 100 ml added, except for α-naphthoflavone, when 1·0 ml of indicator solution per 100 ml added. Where a second end-point is recorded, this was taken after a further addition of 5 or 10 ml of 0·05*M* arsenic^{III} solution.

α-naphthoflavone are recommended for use in these media since they give the most accurate and pleasing end-points. Although the error is rather large, and the second colour change rather poor, *p*-ethoxychrysoïdine, quinoline yellow (in 1·0*M* hydrochloric acid) and *o*-dianisidine have the advantage of being reversible.

In chloride-free sulphuric acid solution of concentrations 0·25, 0·5, 1·0, 1·5 and 2·0*M*, rosaniline in the presence of 0·1*M* bromide gave excellent end-points with no detectable indicator error. The sharpest and most pleasing colour changes occurred in 1·0 and 1·5*M* sulphuric acid; in 0·25 and 0·5*M* acid, the purple colour developed rather slowly at the end-point and in 2·0*M* acid the colour was a little pale. Decreasing the bromide concentration to 0·01*M* did not affect the quality or accuracy of the end-point. Other indicators were examined at the optimum sulphuric acid concentration and in 0·1*M* bromide. The reaction in the absence of added bromide was too slow to permit the use of visual indicators. In general, the indicator errors are smaller in sulphuric than in hydrochloric acid media. Bordeaux and amaranth gave

both accurate and pleasing results and are particularly recommended. Methyl orange and methyl red gave sharp and pleasing, though late end-points. *p*-Ethoxychrysoïdine and quinoline yellow both showed reversibility to further additions of arsenic^{III} solution, quinoline yellow being more satisfactory, but *o*-dianisidine and α-naphthoflavone, although giving very satisfactory first end-points, did not reverse well.

At a pH of 4, only in the presence of bromide is the titration analytically useful,[2] so that the indicator titrations were conducted in acetate buffer with a bromide concentration of 0·1*M*. Rosaniline, *p*-ethoxychrysoïdine, *o*-dianisidine and α-naphthoflavone changed long before the equivalence point and are therefore unsuitable.

TABLE IV.—INDICATOR ERRORS INCURRED IN THE TITRATION OF 25 ML OF 0·0005*M* ARSENIC^{III} IN VARIOUS MEDIA WITH 0·005*M* CHLORAMINE-T

Indicator	Conditions	Total error, *ml*	Error due to indicator, *ml*
Amaranth	0·5*M* HCl	+0·19	+0·09
	1·0*M* HCl	+0·11	+0·06
	2·0*M* HCl	+0·12	+0·04
Rosaniline	0·5*M* HCl + 0·1*M* KBr	—	
	1·0*M* HCl + 0·1*M* KBr	—	
	2·0*M* HCl + 0·1*M* KBr	—	
	0·5*M* HCl + 0·01*M* KBr	+0·14	−0·01
	1·0*M* HCl + 0·01*M* KBr	+0·12	+0·01
	2·0*M* HCl + 0·01*M* KBr	+0·12	+0·01
Starch	0·4*M* $NaHCO_3$ + 0·005*M* KI	+0·11	+0·03
	0·4*M* $NaHCO_3$ + 0·025*M* KI	+0·10	+0·02

Volume of solution at the equivalence point, 100 ml. 1·0 ml starch or 2 drops of amaranth or rosaniline indicator solution per 100 ml added. Results in column 4 are corrected for the inherent error in the determination.[2]

Methyl orange, methyl red, bordeaux and amaranth were subject to fading before the end-point and so gave poor—and late—colour changes. Quinoline yellow and, surprisingly, tartrazine gave sharp, though considerably late, end-points, and both showed excellent reversibility and are therefore recommended.

Titrations at low reagent concentration

Titrations at a ten-fold overall dilution are subject to a net positive error[2] of about 0·4%. With visual indicators this error is increased, and the total error is shown in Table IV. By subtracting the known titration error,[2] the net contribution of the indicator to the total error is obtained. This is greatest in 0·5*M* hydrochloric acid and decreases with rising acid concentration. The net error is least with rosaniline in the presence of 0·01*M* bromide and greatest with amaranth in hydrochloric acid alone. In hydrochloric acid, the amaranth colour change was fairly sharp in 1·0 and 2·0*M* acid, but rather slow in 0·5*M* acid. In the presence of 0·1*M* bromide, the rosaniline colour developed very slowly (compare the lower part of the potentiometric curves under these conditions[2]) and no satisfactory end-point could be discerned. A reduction of the bromide concentration to 0·01*M* effected a very considerable improvement,

but the end-points were still not quite so sharp as with amaranth in the absence of bromide. The net error with starch in bicarbonate buffer in the presence of iodide is intermediate between those of amaranth and rosaniline, and the end-points were marked by the sharp appearance of a very pale blue colour. These titrations confirm the findings by potentiometric titration[2] that no advantage pertains to the use of a diluted reagent in titrating small quantities of arsenic^{III}, since the error, of about 0·4%, is similar to the precision attained in a titration of 2·5 ml with a reagent of ordinary strength. With the aid of a microburette and potentiometric location of the end-point, indeed, the stronger reagent is the more advantageous. Where titrations with 0·005*M* chloramine-T are conducted, however, it is considered that all three indicators are suitable in their respective media, starch being the best.

Conclusions and discussion

In judging the performance of a particular indicator, three factors are relevant: (*a*) the indicator error,[14] shown in the tables, (*b*) the sharpness of the colour change, and (*c*) the quality (brightness, intensity, contrast) of the colour change. Although factor (*a*) is of prime importance, an indicator with a very sharp, highly contrasting colour change may be acceptable even if it shows a high error, provided the latter is perfectly reproducible.

Among the indicators which have proved suitable for chloramine-T titrimetry are examples of several types[15] of redox indicator:—

Reversible redox indicators: *o*-dianisidine, whose oxidation mechanism has been fully elucidated;[7,10] *p*-ethoxychrysoïdine and quinoline yellow which operate through a conjugation mechanism; the redox mechanism of tartrazine is uncertain.

Irreversible dyestuffs: methyl red, methyl orange, bordeaux and amaranth, which are irreversibly oxidised or destroyed with the formation of very weakly coloured products.

Specific sensitive reagents: starch for iodine and α-naphthoflavone for bromine, which react reversibly forming coloured addition products with free halogen in the presence of halide ion. Both are colloidal in nature, the yellow bromine addition product with α-naphthoflavone often flocculating on formation. Rosaniline reacts with free bromine[8] with the formation of deep purple polybromo compounds, the bromine atoms, in average number 4, entering the positions ortho to the nitrogen atoms. The compound is also colloidal and very sparingly soluble.

The irreversible indicators, to be satisfactory, must react more slowly than the reductant so that a local excess of titrant does not give premature end-points. For the same reason, the addition of the indicator should be delayed to as near the end-point as possible. The indicators examined, particularly amaranth and bordeaux, were reasonably satisfactory in this respect. The brilliant colour change and negligible indicator error of rosaniline make it a particularly valuable indicator despite the inconvenience of its irreversibility, and the difficulty experienced the first time the indicator is used.

The quality of the colour change is outstandingly good for rosaniline, good for amaranth and bordeaux and, where there is no fading, for methyl red and methyl orange. *o*-Dianisidine gives a good colour change and is the best of the reversible indicators, *p*-ethoxychrysoïdine, tartrazine and quinoline yellow have poor colour changes, and quinoline yellow is subject to a sudden fading of the yellow colour just

before the end-point. The colour change of α-naphthoflavone is fair in colourless solutions, but sometimes difficult to discern otherwise.

In general, only amaranth and the specific reagents for bromine stand up to the presence of bromide, the other indicators being better in hydrochloric acid alone. The substitution of sulphuric for hydrochloric acid in the presence of bromide yields a general improvement in quality and accuracy, the best end-points of all, on all counts, being with rosaniline in 1·0 to 1·5*M* sulphuric acid and 0·01 to 0·1*M* bromide.

Balancing all three factors and taking reversibility into account, the following recommendations are made:

(*a*) In hydrochloric acid at 1·0 to 2·0*M* concentration, amaranth, bordeaux and *o*-dianisidine are the best; *p*-ethoxychrysoïdine is also suitable as are methyl red and methyl orange subject to a correction of −0·02 ml.

(*b*) In hydrochloric acid at 1·0 to 2·0*M* concentration in the presence of 0·1*M* bromide, rosaniline is outstandingly good. Amaranth is also recommended, and α-naphthoflavone, though the colour change is not brilliant, is accurate and reversible. Other indicators are useful though the error is rather high.

(*c*) In 1·0*M* sulphuric acid in the presence of 0·01 to 0·1*M* bromide, rosaniline is pre-eminent, amaranth and bordeaux are excellent, and the quality of the end-point is good with both methyl red and methyl orange although the error is very high. Of the reversible indicators quinoline yellow is the most satisfactory, followed by *p*-ethoxychrysoïdine.

(*d*) In acetate buffer in the presence of 0·1*M* bromide, few indicators give satisfactory results, the best, despite high errors, being quinoline yellow and tartrazine, which have the advantage of reversibility.

(*e*) Sulphuric acid in the presence of bromide is the medium which offers the most pleasing end-points, 1·0 to 2·0*M* hydrochloric acid yields the smallest errors, and acetate buffer media are not recommended.

(*f*) A titration with 0·005*M* chloramine-T offers no advantage. At this dilution, starch in the presence of iodide in bicarbonate buffer gives the best end-points, but both amaranth in hydrochloric acid and rosaniline in hydrochloric acid media containing bromide at a concentration of 0·01*M* are acceptable.

Zusammenfassung—Es wurde nach visuellen Indicatoren für die Chloramin-T-Titration gesucht. Zehn Verbindungen, fünf reversibel und fünf irreversibel reagierend, wurden einer genauen Untersuchung unterzogen, und zwar unter Bedingungen, unter denen die Reaktion zwischen Chloaramin-T und Arsen(III) quantitativ verläuft. Indicatorfehler wurden studiert durch direkten Vergleich mit potentiometrischen Titrationen unter gleichen Bedingungen. Die bestgeeigneten Bedingungen werden beschrieben und die Indicatoren in der Reihenfolge bester Eignung aufgezählt. Titrationen mit Lösungen in zehnfacher Verdünnung der üblichen Titrationslösungen wurden durchgeführt, doch ergab sich keinerlei Vorteil.

Résumé—Les auteurs ont fait une recherche d'indicateurs visuels convenables pour l'application á la titrimétrie de la chloramine T; dix composés, cinq réversibles et cinq irréversibles, ont été examinés de manière rigoureuse dans le titrage de l'arsenic(III) dans les conditions pour lesquelles on a montré que la réaction de titrage était quantitative.

Les erreurs dues à l'indicateur ont été vérifiées par comparaison directe avec des titrages potentiométriques dans des conditions semblables. Des recommandations ont été données sur les meilleurs milieux, et les indicateurs ont été rangés par ordre de préférence dans diverses conditions. Des titrages ont été étudiés pour une dilution égale au dixième de la concentration usuelle, mais ils n'offrent aucun avantage.

REFERENCES

[1] E. Bishop and V. J. Jennings, *Talanta*, 1958, **1**, 197.
[2] *Idem, ibid.*, 1960, **8**, 22.
[3] O. Tomiček and B. Suchanla, *Casopis Ceskoslov Lekarnictva*, 1931, **11**, 285, 309.
[4] A. J. Berry, *Analyst*, 1934, **55**, 736.
[5] W. Poethke and F. Wolf, *Z. anorg. Chem.*, 1952, **268**, 244.
[6] British Colour Index.
[7] A. B. Crawford and E. Bishop, *J.R.T.C.*, 1950, **5**, 52.
[8] E. Bishop, Unpublished work, 1944–46.
[9] G. F. Smith and H. H. Bliss, *J. Amer. Chem. Soc.*, 1931, **53**, 209; G. F. Smith and R. L. May, ***Ind. Eng. Chem., Analyt.*** 1941, **13**, 460.
[10] G. F. Smith and C. S. Wilcox, *ibid.*, 1942, **14**, 49.
[11] R. Belcher, *Analyt. Chim. Acta*, 1951, **5**, 27.
[12] *Idem, ibid.* 1950, **4**, 468.
[13] E. Schulek, *Z. analyt. Chem.*, 1935, **102**, 111; G. Charlot, *Bull. Soc. chim. France*, 1941, **8**, 222; R. Belcher, *Analyt. Chim. Acta*, 1949, **3**, 578.
[14] E. Bishop, *ibid.* 1960, **22**, 205.
[15] E. Bishop, *Comprehensive Analytical Chemistry*, Edited by C. L. Wilson and D. W. Wilson, Elsevier Publishing Co., Amsterdam, 1960, Vol. 1B, Chapter VII, 2, p. 141ff
[16] V. J. Jennings, *Titrimetric Analysis with Chloramine-T*, Univ. Exon., 1957.
[17] E. Bishop, *Analyt. Chim. Acta*, 1959, **20**, 315.

Talanta, 1961, Vol. 8, pp. 43 to 51. Pergamon Press Ltd. Printed in Northern Ireland

DETERMINATION OF TUNGSTEN IN ASSOCIATION WITH IRON AND SOME OTHER ELEMENTS AS TRIS(TRI-n-BUTYLAMMONIUM)12-TUNGSTOPHOSPHATE

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Summary—Conversion of tungsten into 12-tungstophosphoric acid for determination with tri-n-butylamine requires acidification of an alkaline solution containing tungstate and phosphate. Complications associated with the presence of large amounts of iron have been resolved by adsorbing tungstophosphoric acid from 6*N* hydrochloric acid on a column of cellulose, which does not adsorb iron^{III} chloride. The conditions of formation of the heteropolyacid that lead to its quantitative retention are critical and a little iron seems to be bound with the tungsten. After the adsorbate has been removed from the column, its minor iron content can be rendered innocuous by reduction before precipitation of tris(tri-n-butylammonium)12-tungstophosphate. The effect of several other elements has been briefly studied.

TUNGSTEN in the form of 12-tungstophosphoric acid can be determined as tris(tri-n-butylammonium)12-tungstophosphate in the presence of considerable amounts of calcium, cobalt^{II}, copper, lead, manganese^{II} and nickel,[1] but iron[2] and some other elements may exert a pronounced adverse effect. The primary object of this investigation was to find a means of determining tungsten in materials containing iron and a limited number of other elements, the production of 12-tungstophosphoric acid being required in their presence.

Apparently the only satisfactory method of forming tungstophosphoric acid is to acidify alkaline solutions containing tungstate and phosphate. Moderate amounts of the specified elements, except iron, and a *small* amount of iron^{II} can then be tolerated. Ascorbic acid is a suitable reductant for iron^{III} and for subsidiary amounts of cobalt^{III} and manganese^{III} formed in alkaline solutions.

We have found that authentic 12-tungstophosphoric acid is strongly adsorbed by cellulose from 6*N* hydrochloric acid solutions and separable from iron^{III} by a column procedure. However, the heteropolyacid obtained from tungstate in the presence of phosphate and iron behaves differently and, under conditions in which the tungsten is quantitatively retained by a column of cellulose, a little iron is also held. When tungsten has been eluted from the column and tungstophosphoric acid reformed, the accompanying iron can be reduced with ascorbic acid before tributylamine is added.

Methods have been developed for determination of tungsten in a few selected materials.

EXPERIMENTAL

Reagents

Johnson, Matthey's tungsten metal powder (≥ 99·9%), spectrographically standardised tungsten^{VI} oxide (99·99%) and iron sponge, AnalaR sodium tungstate and 12-tungstophosphoric acid, and Hilger's "specpure" solutions of tantalum and niobium fluorides were used. As far as possible other reagents were analytical-reagent grade. The tungsten content of anhydrous sodium tungstate was

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checked with reference to the tungsten(VI) oxide. Tri-n-butylamine was purified as before.[1] Sodium hydroxide solutions were stored in polythene bottles. The concentrated hydrochloric acid was 12*N*.

Apparatus

6-, 10- and 25-Ml platinum crucibles with lids were used for various operations. Polytetrafluoroethylene beakers, covers and stirring rods permitted the use of hydrofluoric acid with *aqua regia*.

Notes on methods

Unless otherwise stated, all determinations of tungsten as tris(tri-n-butylammonium)12-tungstophosphate relate to precipitates formed in 1*N* hydrochloric acid solutions and left overnight before filtration.[1]

Small amounts of tungsten in effluents and filtrates were detected and estimated semi-quantitatively, essentially as described by Miller,[3] except that the zinc complex of toluene-3:4-dithiol[4] ("dithiol") was used. Portions of solutions containing tributylammonium salts were evaporated to dryness, with the aid of an air current, in a boiling water-bath, *not* on a hot-plate. Ascorbic acid did not upset the reaction.

DETERMINATION OF TUNGSTOPHORIC ACID DERIVED FROM TUNGSTEN

In the presence of just sufficient (0·6 ml) orthophosphoric acid (sp. gr. 1·75) to prevent the separation of tungstic acid at a later stage, 200-mg amounts of tungsten powder were oxidised with nitric acid along with either hydrochloric or hydrofluoric acid. The quantities of hydrochloric and nitric acids were so chosen that, after the reaction had ceased, the addition of 90 ml of water gave an approximately 1*N* hydrochloric acid solution. Hydrofluoric acid was expelled by heating the platinum crucible containing the reactants within a metal block which was heated finally at 180°. Water was used to transfer the syrupy residue to a beaker and hydrochloric acid added. Precipitation and separation of the tributylamine complex were then effected.

By the *aqua regia* method, apparent recoveries of tungsten were 99·9 and 100·1% with, however, 0·4% in the filtrates, whereas by the hydrofluoric acid method, 99·0, 99·3 and 100·4% were obtained, with 0·5, 0·8 and 0·1% in the respective filtrates. Residual fluoride was probably not responsible for the low recovery of tungsten in two precipitates since, when 160 mg of sodium fluoride were added to a solution of 12-tungstophosphoric acid, the determination of tungsten was little affected, no doubt because the glassware reacted with the fluoride. When a polythene beaker was used there was, however, a marked negative error.

In three further experiments involving the use of hydrofluoric and nitric acids, increasing amounts of sodium hydroxide solution were added to the aqueous extracts of the phosphoric acid residues in order to raise the pH to 9·6, 10 and >10. The solutions were acidified with 6*N* hydrochloric acid before the addition of the amine. The tungsten in the precipitates correspondingly increased from 99·3 to 100·0% of that originally taken and that in the filtrates decreased from 0·4 to 0·2%.

It was concluded that, for the satisfactory formation of 12-tungstophosphoric acid from materials disintegrated with acids, it would be necessary, in order to break down all tungsten complexes, to make the solutions strongly alkaline, then re-acidify them. Since precipitated tungstic acid dissolves readily in sodium hydroxide solution, it would be superfluous to add phosphoric acid initially. Instead, sulphuric acid could be used and less phosphate, if desired, added afterwards to the alkaline solution. The

influence of elements that had previously been found not to upset the determination of 12-tungstophosphoric acid, when they were added to acidified solutions, had now to be found when the solutions containing them were made alkaline, then re-acidified. A few additional elements were included in the tests.

Effect of other elements

Solutions of chlorides (nitrate for lead) of various elements were added to solutions containing 200 mg of tungsten^{VI}, which were then made strongly alkaline

TABLE I—EFFECT OF VARIOUS ELEMENTS ON THE DETERMINATION OF TUNGSTEN

Element	Amount added, *mg*	Tungsten calculated, %	Tungsten in filtrate, %
Calcium	200	99·9	0·7
	200*	100·5	<0·1
	50*	99·9	<0·4
Cobalt^{II}	200†	100·4	0
Copper^{II}	200	100·6	0
Lead	200	100·2	n.d.
Manganese^{II}	200	102·3	0·2
	200†	100·1	<0·1
Nickel	200	100·2	<0·1
Aluminium	100	98·5	1·2
Tin^{IV}	25	100·6	0·3
Titanium^{IV}	10	105·8	1·5
Tantalum^{V} + niobium^{V}	5 + 5	104·8	0·4

* Sulphate present
† Ascorbic acid added

with sodium hydroxide solution. 43 Mg of phosphate (PO_4) were added, the heated stirred solutions were gradually acidified with concentrated hydrochloric acid (nitric acid for lead) and tungsten was determined. Tantalum and niobium fluorides were added to a solution prepared by dissolving 200 mg of tungsten in hydrofluoric, nitric and sulphuric acids. The first two acids were expelled and the residue was made alkaline, *etc.* as above. A precipitate, presumably of tantalic and niobic acids, was collected in a sintered-glass filter crucible when the volume of the solution was 40 ml and the acid concentration 1*N*.

The results given in Table I show that titanium, tantalum and niobium interfere seriously. Chromium^{III}, molybdenum^{VI} and vanadium^{V} were also known to interfere.[1] Interference caused at first by manganese resulted from its oxidation in alkaline solution, but 100 mg of ascorbic acid added to the re-acidified solution eliminated the error. Such reduction was also useful for some cobalt^{III}.

Influence of iron

For the determination of 200 mg of tungsten^{VI} as above in the presence of 100 mg of iron^{III}, the re-acidified solution was reduced in a silver reductor and precipitation with tributylamine effected in 2*N* hydrochloric acid.[2] Although the apparent recovery of tungsten in the precipitate was 99·5%, 1% was found in the filtrate. Ascorbic acid,

if used in a large excess, was a suitable reductant for *small* amounts of iron^{III}. 100 Mg added to re-acidified solutions containing tungstate and iron^{III} counteracted the interference of up to 2 mg of the latter in the subsequent determination of tungsten with tributylamine in 1*N* hydrochloric acid solution. When 5-25 mg of iron were present, iron-contaminated precipitates of tributylammonium tungstophosphate were obtained.

ELIMINATION OF INTERFERENCE OF LARGER AMOUNTS OF IRON

12-Tungstophosphoric acid was found to be strongly adsorbed by filter paper from moderately concentrated hydrochloric, nitric and sulphuric acid solutions. When a

TABLE II—ADSORPTION BEHAVIOUR OF AUTHENTIC 12-TUNGSTOPHOSPHORIC ACID (200 mg of tungsten)

Hydrochloric acid present in applied solution and eluent, *N*	Other components of the applied solution, *mg*	Tungsten found in successive 50-ml portions of effluent, *mg*	
		Original solution unheated	Original solution boiled for 20 min and cooled before use
6	—	0·1, 0, 0, 0	1·1, 0·3 (25 ml tested)
6	850, PO_4 (as H_3PO_4)	0·15, 0	3·5, 0
6	200, iron	0·3, 0, 0	—
6	200, iron; 850, PO_4	0·3, 0	—
2	—	0·15, 0·1	<0·2, 0, 0·15
2	200, iron	8, 0·3, 0	—

spot of a hydrochloric acid solution, containing 25 μg of tungsten as the heteropoly-acid and 25 μg of iron^{III}, was applied near the top of a paper strip and a chromatogram developed with 6*N* hydrochloric acid as the mobile phase, iron travelled just behind the solvent front and tungsten was detected[5] at the starting position. In 3*N* acid, tungsten gave two bands, with R_F values 0 and 0·06, and iron behaved as before. These results suggested a possible means of separating tungstate from iron.

Adsorption of 12-tungstophosphoric acid by cellulose

Glass columns (15-mm internal diameter) containing cellulose, derived from a suspension of Whatman ashless, standard-grade cellulose powder (6 g) in water, were made up and the behaviour thereon of 30 ml of solutions of varied composition, prepared from solid 12-tungstophosphoric acid, was studied. Solutions were added to columns pre-treated with acid of the same strength as that of the sample and a flow-rate of 3-5 ml per min was used, suction or light pressure being applied when necessary. 17–20 Ml of liquid (the retention volume of the column) were rejected, then liquid was continuously collected as the solution passed into the cellulose and the column was washed with acid of the requisite strength. Successive portions of effluent were tested qualitatively for tungsten, with the results shown in Table II. After use, the columns were freed from tungstate by washing them with water, 0·2*N* sodium hydroxide solution and again with water.

12-Tungstophosphoric acid is obviously strongly held by cellulose. In unheated 6*N* hydrochloric acid an excess of phosphate did not influence the behaviour and the

effect of iron was slight, but in boiled solutions the initial expulsion of a significant amount of tungsten occurred. Only in acid of the higher concentration was tungsten adequately withheld in the presence of iron^{III} which was not retained by the cellulose. Chromium^{III} behaved like iron^{III}. The presence of hydrofluoric acid hindered the adsorption of tungsten. 12-Tungstosilicic, 12-tungstoboric, 18-tungsto-2-phosphoric and 12-molybdophosphoric acids were also adsorbed by cellulose from 6*N* hydrochloric acid.

Tentative experiments on the adsorption of tungstophosphoric acid prepared from tungsten

50–80-Mg amounts of tungsten, alone or in presence of 12 mg of iron, were dissolved and oxidised in the three ways outlined on p. 44, except that 0·3 ml of orthophosphoric acid was used and volumes were kept down so as to give 6–15 ml of 6*N* hydrochloric acid solutions for application to columns of cellulose. The column procedure was the same as before, 6*N* hydrochloric acid being used for elution and portions of effluent being tested for tungsten.

Generally, a sharp initial expulsion of a few mg of tungsten occurred. Thereafter, a slight continuous loss of tungsten was noted, the loss being least where *aqua regia* had been used to dissolve tungsten. When iron was present, the bulk was soon eluted but a little "tailed" on the column and could not be expelled with an amount of hydrochloric acid that did not also cause more significant loss of tungsten.

More promising results with respect to retention of tungsten were obtained when hydrofluoric and nitric acids were used and phosphoric acid was replaced by sulphuric acid, which permitted more certain removal of hydrofluoric acid and avoided possible complications arising from the formation of polyphosphoric acids. Thereafter the suspension of tungstic acid was made alkaline, then phosphate and acid were added. Further experiments with 200 mg of tungsten plus 50–200 mg of iron indicated that the quantity of sulphuric acid was not critical, but that the amount of phosphate had to be small and the rate of acidification rapid. Quantitative separation of iron from tungsten seemed to be impossible, but the small amount left with tungsten was amenable to treatment with ascorbic acid (p. 45) before determination of the tungsten.

Critical investigation of the formation and adsorption behaviour of tungstophosphoric acid

In a series of experiments, 20–25 ml of solutions, containing sodium tungstate, disodium hydrogen phosphate and sufficient sodium hydroxide to give a blue colour with thymol blue indicator, were swirled or magnetically stirred while hydrochloric acid was added fairly quickly dropwise from a burette until the indicator was red. The volumes of the cold solutions were then doubled by the rapid dropwise addition of 12*N* hydrochloric acid. The solutions were applied as before to columns containing 6 g of cellulose, equilibrated with 6*N* hydrochloric acid, and elution was effected with that acid. The results given in Table III show that the neutralisation of hot solutions with 12*N* acid almost prevented any loss of tungsten in the first fraction of effluent. The tungsten contents of subsequent fractions showed that a high concentration of phosphate and, to a much smaller extent, a high concentration of neutralising acid accelerated the travel of tungsten on the column. The use of more cellulose might have improved matters.

In further experiments, 0·3 ml of concentrated sulphuric acid, 4 ml of 12*N* sodium hydroxide solution and 43 mg of phosphate (PO_4) were added in succession to tungstate solutions, which were then heated to 80°. Thereupon 12*N* hydrochloric acid was added from a burette at a much faster rate than before to rapidly stirred solutions until the pH was 4, 2 or 1. Solutions were maintained hot for 5 min, cooled, treated with the same volume of 12*N* acid, re-cooled and transferred to columns, *etc.* 100 Ml of column effluent yielded 0·1 mg of tungsten for the first two experiments and

TABLE III—LOSS OF TUNGSTEN FROM COLUMNS TO WHICH TUNGSTOPHOSPHORIC ACID PREPARED FROM 200 mg OF TUNGSTEN^{VI} AND PHOSPHATE HAD BEEN APPLIED

(200 mg of W ≡ 8·5 mg of PO_4)

Phosphate (PO_4), *mg*	17	17	17	17	17	43	85	850	850	850
HCl for neutralisation, *N*	2	2	6	6	12	6	6	2	2	12
Approx. temp. when neutralised, °*C*	18	100	100	100	100	100	100	18	100	100
Volume applied to column, *ml*	50	50	50	30	50	50	50	60	60	60
Tungsten in successive 50-ml portions of effluent, *mg*	2 0·4 0·2	0·5 <0·1 0·2	0·2 0·1 0·3	0·2 <0·1 0·5	0 0·7 1·5	0·8 0·4 1·5	0·4 2 6	4 20 16	1 15 11	0·3 40 20

0·3 mg for the last. The difference was insignificant and it was concluded that even the very rapid addition of acid was permissible up to and beyond the point at which the formation of 12-tungstophosphoric acid might be considered complete.[6] Overnight delay before or after increasing the acidity to 6*N* did not influence the column behaviour of tungsten.

Effect of iron

The above experiments were repeated, but with iron^{III} sulphate (100 mg of iron) in sulphuric acid solution added to the tungstate just before the sodium hydroxide. The mixture was heated to 80°, then phosphate and acid were added. It was difficult to stop at exactly pH 4 or 2 and simplest to stop the addition of acid when hydrated iron^{III} oxide was significantly dissolving (pH < 1). Continued heating at this stage assisted solution. In several experiments about 0·2 mg of tungsten was collected in the first 50 ml of column effluent, but 2–6 mg in the next. The travel of tungstophosphoric acid had been accelerated in the presence of iron. A column containing 10 g of cellulose reduced the loss of tungsten in 100 ml of effluent to 0·2 mg. This loss was unchanged when 200 mg of iron^{III} and 17–43 mg of phosphate (PO_4) were used but rose to 1·2 mg with 430 mg of phosphate, thus confirming the harmful influence of a large quantity. In all experiments a minor amount of iron remained with the tungsten.

DETERMINATION OF TUNGSTEN IN ASSOCIATION WITH IRON

Preparation of columns and conditions of use

A 24-cm length of Pyrex glass tubing (about 20-mm internal diameter) was sealed close to the barrel of a capillary stopcock of which the full length of capillary below the tap was retained. The

base of the column was so constructed that a perforated disc of nearly the same diameter as the column could be readily seated, leaving minimum free space below it. On the disc a circle of Whatman No. 41 filter paper was placed. More uniform packing of the column was achieved by adding a suspension of cellulose powder (10 g) in 6*N* hydrochloric acid, instead of in water. When the cellulose had settled, a circle of filter paper was placed on top of the column, which was then washed with water, 0·2*N* sodium hydroxide solution and again water. It was essential to avoid prolonged contact of cellulose with 6*N* acid, which apparently caused slight degradation that led to cellulosic material being carried into the sodium hydroxide effluent and slowly precipitated in the re-acidified solution. If tungstophosphoric acid were determined in such a solution, the weight of precipitate obtained might be 2–3 mg too high. In practice, columns were recycled, when necessary, and equilibrated with 6*N* hydrochloric acid just before use. Tungstophosphoric acid was collected on and removed from columns without delay, a suitable flow-rate for solutions being 3–5 ml per min. The low solubility of

TABLE IV—DETERMINATION OF TUNGSTEN IN ASSOCIATION WITH 200 MG OF IRON

Phosphate (PO_4) present, *mg*	Tungsten taken, *mg*	Tungsten found, *mg*	Tungsten in first part of column effluent, *mg*
43	200·0	200·2	<0·2
17	200·0	200·2	<0·1
43	50·0	49·7	0·1
43	50·0	49·9	0·2

sodium chloride in 6*N* hydrochloric acid usually caused it to separate out. Warm solutions, applied to columns, deposited crystals within the pores of the upper disc of filter paper and clogged it. With cold solutions no clogging occurred.

Method for tungsten

To 200 or 50 mg of tungsten^{VI} in 20 ml of water 200 mg of iron^{III} (as sulphate), 0·7 ml of concentrated sulphuric acid and 6 ml of 12*N* sodium hydroxide solution were added. Phosphate was added to the hot stirred solution and then 12*N* hydrochloric acid quickly from a burette until hydrated iron^{III} oxide was dissolving. The solution was cooled, doubled in volume with 12*N* acid, recooled and applied to a column of cellulose in equilibrium with 6*N* acid. After the rejection of 30 ml of effluent the liquid was collected. In order to avoid having an excessive amount of acid afterwards in the tungstophosphate solution collected from the column, the latter was washed with 50 ml of 6*N* acid, then with 20 ml of water. Tungstophosphate was eluted by means of 30 ml of 0·2*N* sodium hydroxide solution and 30 ml of water. The solution was made strongly alkaline with 12*N* sodium hydroxide solution, 43 mg of phosphate were added, then sufficient 12*N* hydrochloric acid was run quickly dropwise into the hot stirred solution to give finally 100 ml of 1*N* acid. 100 Mg of ascorbic acid were added to the hot solution before precipitation of tris(tributylammonium) tungstophosphate, which was separated and weighed.

Behaviour of manganese, chromium, tin and tantalum plus niobium in the above procedure

When 200 mg of manganese^{II} were substituted for iron, some oxidation occurred in the alkaline solution. When the acidified solution was put on the column, a purple complex travelled slowly through the cellulose and 200 mg of tungsten yielded 0·3% to the first part of the effluent. The remaining tungsten was not determined since ascorbic acid would prevent the interference of accompanying manganese (p. 45).

Chromium^{III} could not be quantitatively separated from the heteropolyacid formed in its presence. Even 25 mg caused the loss of several mg of tungsten to the

first fraction of column effluent and some chromium remained on the cellulose. Interference was prevented by forming chromate. Several drops of bromine and then an excess of sodium hydroxide solution were added to the solution containing tungstate and 25 mg of chromium^{III}, which was afterwards treated as usual. No tungsten escaped initially from the column and the recovery was almost complete.

25 Mg of tin^{IV} with 200 mg of tungsten^{VI} caused the loss of 0·9% of tungsten from the column and an apparent recovery of 99·5% with tributylamine. In the presence of tantalum^{V} and niobium^{V} together (5 mg of each) the corresponding values were 0·1% and 102·8%. (*cf.* p. 45). Obviously, very little of these elements could be tolerated.

DETERMINATION OF TUNGSTEN IN FERROTUNGSTEN, SCHEELITE AND WOLFRAMITE

At present the proposed method could be applied only to samples containing insignificant amounts of molybdenum, vanadium, titanium, tantalum and niobium

TABLE V—RESULTS FOR THE DETERMINATION OF TUNGSTEN

Sample	Tungsten found by new method, %	Tungsten found by classical methods, %
Ferrotungsten	81·9, 81·9	81·3*
Scheelite	44·3, 44·4	44·6, 44·9
Wolframite	59·1, 59·2	60·0, 59·9

* Certificate value

and small amounts of chromium and tin. British Chemical Standard ferrotungsten No. 242 (0·1% of tin) was used. Samples of scheelite and wolframite, kindly supplied by the late Dr. A. M. Cockburn of Edinburgh University, were analysed by classical procedures,[7] quantitatively for tungsten and semiquantitatively for elements commonly present that might interfere. The scheelite contained about 25% of silica, a little iron, an amount of tin that could be ignored, $\geq$0·1% of tantalum and niobium, and no molybdenum or titanium. The wolframite contained iron and manganese, a little silica, a trace of molybdenum and about 0·1% of niobium.

It was, therefore, concluded that the new method for tungsten could be applied to all of these samples, the cellulose-column procedure being required only for ferrotungsten and wolframite.

Procedure for ferrotungsten

Use a 25-ml platinum crucible. To an amount of material containing $\geq$200 mg of tungsten add 1 ml of hydrofluoric acid (40%) and 1 ml of concentrated sulphuric acid. Add 1 drop of concentrated nitric acid, heat gently, if necessary, to initiate reaction and cautiously add more nitric acid until disintegration is complete. Expel hydrofluoric and nitric acids by heating the crucible at a controlled temperature, in a metal block or on a hot-plate, and finally heat carefully with a micro Bunsen burner until sulphuric acid is fuming strongly. Allow to cool, transfer the contents of the crucible to a beaker with a minimum amount of water and four 1-ml rinsings, alternately with 2*N* sodium hydroxide solution and 2*N* hydrochloric acid. The volume at this stage should not exceed 25 ml. Next add 12*N* sodium hydroxide solution to the magnetically stirred solution until precipitation of hydroxides is complete and a 2-ml excess is present, heat the solution to about 80° and add 160 mg of hydrated

disodium hydrogen phosphate (43 mg of PO_4). Finally, while maintaining the heating, add 12*N* hydrochloric acid rapidly dropwise until hydrated iron^{III} oxide is just dissolving (pH ~ 1) and wait until solution is nearly complete. (It is permissible to increase the acidity of the hot solution to 1*N* to assist solution.) Cool the solution, raise the acid concentration to 6*N* by adding 12*N* acid and transfer it to a suitably prepared column (p. 48). Wash the beaker and column with 50 ml of 6*N* acid, then the column with 20 ml of water. Elute tungstophosphoric acid from the column with 30 ml of 0·2*N* sodium hydroxide solution and 30 ml of water.

Neutralise the eluate with 12*N* sodium hydroxide solution and add 2 ml more, then add phosphate and 12*N* hydrochloric acid to the hot solution as above until the pH is ~1. At this point increase the volume to 90 ml with water and the acid concentration to 1*N*, add 100 mg of ascorbic acid to the hot solution, and precipitate and separate the tributylammonium complex.

Procedure for minerals

To a sample containing up to 200 mg of tungsten add 3 ml of hydrofluoric acid and, after 15 min, 1 ml of nitric acid. Heat the containing crucible gently on a temperature-controlled hot-plate, then cool and cautiously add 1 ml of concentrated sulphuric acid. Thereafter, in analysing wolframite, follow the instructions given for ferrotungsten. With scheelite omit the column treatment and instead, after forming tungstophosphoric acid in the hot solution (pH 1), make 100 ml of 1*N* acid solution add ascorbic acid and precipitate tributylammonium tungstophosphate.

Zusammenfassung—Die Überführung von Wolfram in Phosphorwolframsäure zur Bestimmung mit Tri-*n*-butylamine benötigt Ansäuern der alkalischen Lösung, die Wolfram und Phosphat enthält. Schwierigkeiten, die durch Anwesenheit von grösseren Mengen Eisen entstehen, werden vermieden, wenn man die Phosphorwolframsäure aus 6*N* Salzsäure an einer Kolonne von Cellulose adsorbiert. Die Kolonne hält Eisenchlorid nicht zurück. Die Bedingungen, unter denen die Heteropolysäure quantitativ zurückgehalten wird, sind kritisch. Nachdem das Adsorbat eluiert wurde, können kleine Mengen Eisen durch Reduktion unschädlich gemacht werden, bevor die Phosphorwolframsäure gefällt wird. Störungen durch einige andere Metalle wurden kurz studiert.

Résumé—La transformation du tungstène en acide 12-tungstophosphorique pour le dosage de la tri-*n*-butylamine nécessite l'acidification d'une solution alcaline contenant du tungstate et du phosphate. Des complications liées à la présence de grandes quantités de fer ont été résolues en faisant adsorber l'acide tungstophosphorique en solution acide chlorhydrique 6*N* sur une colonne de cellulose, qui n'adsorbe pas le chlorure ferrique. Les conditions de formation de l'hétéropolyacide qui conduisent à sa fixation quantitative sont critiques, et il semble qu'un peu de fer soit lié au tungstène. Quand le composé adsorbé a été extrait de la colonne, on peut rendre la faible quantité de fer qu'il contient inoffensive par réduction avant la précipitation du tris(tri-*n*-butylammonium)12-tungstophosphate. L'effet de différents autres éléments a été brièvement étudié.

REFERENCES

[1] C. C. Miller and D. H. Thow, *Analyst*, 1959, **84**, 440.
[2] *Idem, Talanta*, 1960, **5**, 128.
[3] C. C. Miller, *Analyst*, 1944, **69**, 109.
[4] R. E. D. Clark, *ibid.*, 1957, **82**, 182.
[5] A. de Sousa, *Mikrochem. Mikrochim. Acta*, 1952, **40**, 104.
[6] P. Souchay, *Ann. Chim.* (*France*), 1947, **2**, 203.
[7] W. R. Schoeller and A. R. Powell, *Analysis of Minerals and Ores of the Rarer Elements*. Griffin, London, 3rd Ed., 1955.

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SHORT COMMUNICATION

Contributions to the basic problems of complexometry—IV
Determination of thallium

(*Received* 1 *September* 1960)

FOR the complexometric determination of mono- and tervalent thallium, several methods have been proposed. Thallium^{III} can be reliably determined by direct titration with EDTA using Xylenol Orange[1] or PAN as indicator.[2] The indirect determination of thallium, which has also been proposed, depends on the back-titration of excess of EDTA with thorium nitrate[3] at pH 3·5 using Alizarin S. Flaschka[4] recommends the direct titration of thallium in an alkaline medium using Eriochrome Black T, after first adding Mg–EDTA complex. The conditions for the determination of thallium^{I} were studied by Foley and Pottie.[5] Titration in an ammoniacal medium was followed spectrophotometrically at 222 mμ.

TABLE I.—DETERMINATION OF THALLIUM IN THALLIUM^{I} IODIDE. EVAPORATION WITH NITRIC ACID. The residue, after evaporation, diluted to 100 ml, pH adjusted to 3·0–3·2, and titrated with 0·01*M* or 0·05*M* EDTA, with Xylenol Orange as indicator.

Tl^{I} taken, *mg*	Tl^{I} found, %	Remarks
200·8	5·87	1 × (2 ml HNO_3 – 2 ml H_2O)
99·9	16·05	1 × (2 ml HNO_3 – 2 ml H_2O)
50·8	16·11	1 × (2 ml HNO_3 – 2 ml H_2O)
200·5	27·42	1 × 10 ml HNO_3
50·3	29·28	1 × 10 ml HNO_3
200·2	24·60	20 ml HNO_3 – 10 ml H_2O
50·9	82·94	20 ml HNO_3 – 10 ml H_2O
1·80	45·45	10 ml HNO_3
1·40	89·10	20 ml HNO_3
2·50	68·70	30 ml HNO_3
4·10	13·41	10 ml HNO_3
5·70	14·70	20 ml HNO_3
5·00	51·70	30 ml HNO_3

HNO_3 1:1

The complexity constants of Tl-EDTA complexes of both valencies have not yet been measured. From the analytical results, it is assumed that thallium^{III} forms a substantially stronger complex than that of lead, cadmium or zinc (pK_{Me} 16–18), because their presence does not interfere with the determination of thallium^{III} in a weakly acidic medium. Thallium^{I} which forms a relatively weak complex in an alkaline medium behaves quite differently. The existence of Tl^{I}–EDTA complex was proved[5] from the decrease and shift of polarographic waves. Further, thallium does not precipitate in an ammoniacal medium with iodide[6] (solubility product 2·8 × 10^{-8}). In an acidic medium, on the other hand, thallium^{I} in the presence of EDTA can be separated from many elements (Cu, Fe, Pb etc.) by precipitation with iodide, or it can be determined amperometrically.[7] From the experiments outlined, it can be reasoned that the stability constant should be of the same order as that of silver (pK 7–8).

Flaschka[4] in his early work on the determination of thallium, isolated thallium from an EDTA medium as iodide,[7] which he decomposed with nitric acid. In the solution obtained he presumed the

presence of thallium^{III}. Using the same procedure he prepared his stock solutions of thallium nitrate by decomposition of thallium iodide. This is not in agreement with the early literature according to which decomposition of thallium iodide with nitric acid yields thallium^{I} nitrate only. Flaschka's method had been evolved, of course, at a time when a suitable indicator for thallium^{III} was not known. Now, when Xylenol Orange has been found to be a very suitable indicator for thallium^{III}, we are able to control very easily the content of thallium^{III} in thallium solutions. As a result of many experiments it was proved that decomposition of thallium iodide by evaporation with concentrated nitric acid yielded thallium^{III} in small amounts only (Table I). With small weighed amounts of thallium iodide, thallium^{III} is mainly formed, but never quantitatively. With Flaschka's method, even after repeated experiments with monovalent or tervalent thallium, we never obtained a sharp colour change using Eriochrome Black T. Thallium iodide could be quantitatively transformed to thallium^{III} nitrate by a careful evaporation with *aqua regia* only. In Table II some results (including experimental conditions) are given of thallium determinations in thallium iodide after its decomposition in *aqua regia*. Oxidation of thallium ions with bromine water was found not to be advantageous, because the resulting bromide ions form very stable complexes with thallium^{III} which render this determination invalid. Oxidation with potassium permanganate was likewise unsuitable.

TABLE II.—DETERMINATION OF THALLIUM IN THALLIUM^{I} IODIDE. EVAPORATION WITH *AQUA REGIA*. Procedure as in Table I.

Tl^{I} taken, *mg*	Tl^{I} found, %	Remarks
200·6	99·53	2 ml *aqua regia* + 2 ml H_2O
50·8	98·57	2 ml *aqua regia* + 2 ml H_2O
200·1	99·61	5 ml *aqua regia*
51·4	99·04	5 ml *aqua regia*
200·1	99·85	20 ml *aqua regia* + 10 ml H_2O
100·0	99·98	20 ml *aqua regia* + 10 ml H_2O
50·1	100·20	20 ml *aqua regia* + 10 ml H_2O

From the theoretical point of view the sequential determination of tervalent and monovalent thallium in the same solution is extremely interesting. It would be the first complexometric determination of the element in both valency forms. As was said above, thallium^{III} could be reliably determined in the presence of thallium^{I} by direct titration with EDTA using Xylenol Orange in a weak acid medium (Table III). Subsequent titration of thallium^{I} in an alkaline medium, however,

TABLE III.—DETERMINATION OF THALLIUM^{III} IN THE PRESENCE OF THALLIUM^{I}. The mixture of $TlCl_3$ and TlCl was diluted to 100 ml, pH adjusted to 3·0–3·2 with monochloracetic acid and titrated with 0·05*M* EDTA with Xylenol Orange as indicator.

Tl^{3+} taken, *mg*	Tl^{+} taken, *mg*	Tl^{3+} found, *mg*	Difference, *mg*
9·99	60·80	10·06	+0·07
30·25	60·80	30·35	+0·10
50·48	60·80	50·69	+0·21
201·90	60·80	202·29	+0·39
9·99	101·38	10·17	+0·18
9·99	404·70	10·06	+0·07

fails. The oxidation of thallium^{I} to thallium^{III} with potassium bromate, and its titration with EDTA following titration of the thallium^{III}, also fails (see the note on oxidation with bromine). The mixture of tervalent and monovalent thallium may, however, be analysed in the following way: In one aliquot of the solution thallium^{III} is determined by direct titration with EDTA using Xylenol Orange. In a

second aliquot of the solution the thallium^{I} is determined by potentiometric titration with potassium bromate. Another procedure depends on evaporation of the sample with *aqua regia* and on the complexometric determination of total thallium.

It has to be emphasised that all titrimetric methods for the determination of thallium are unfavourably influenced by the high atomic or equivalent weight of the element.

The results of the study of selective determination of thallium will be published later.

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Summary—It has been shown that Thallium^{I} iodide, by evaporation with nitric acid, forms mainly Thallium^{I} nitrate and not Thallium^{III} nitrate, as assumed in the recent literature[4]. Only decomposition with *aqua regia* leads to the quantitative formation of Thallium^{III} nitrate. It has further been found that titrations of Thallium^{I} and Thallium^{III}, in alkaline medium using Eriochrome Black T, do not give reliable results, since the colour change with this indicator is not sharp enough. The titration with Xylenol Orange, in acid medium, is, however, quite reliable, and permits the determination of Thallium^{III} in the presence of Thallium.^{I}

Zusammenfassung--Es wurde gezeigt, dass Thallium(I)jodid, wenn mit Salpetersäure abgeraucht, in der Hauptsache Thallium (I)nitrat und nicht Thallium(III)nitrat gibt, entgegen den Annahmen jüngster Literatur. Nur Abrauchen mit Königswasser führt zur quantitativen Bildung von Thallium (III)nitrat. Es wurde weiterhin gefunden, dass die Titration von Thallium(I) und Thallium(III) in alkalischem Medium mit Eriochromschwarz T als indicator unzuverlässige Resultate ergibt, da der Farbwechsel dieses Indicators nicht genügend scharf ist. Die Titration mit Xylenolorange in saurem Medium ist jedoch zuverlässig und gestattet die Bestimmung von Thallium(III) in Gegenwart von Thallium(I).

Résumé--Les auteurs ont montré que, per évaporation avec l'acide nitrique, l'iodure de thallium (I) forme surtout du nitrate de thallium (I) et non du nitrate de thallium (III), comme cela était supposé dans la littérature récente. Seule la décomposition avec l'eau régale conduit à la formation quantitative de nitrate de thallium (III). On a trouvé ultérieurement que la titrage du thallium (I) et du thallium (III), en milieu alcalin, en utilisant le noir ériochrome T, ne donne pas de résultats sûrs, car le changement de couleur avec cet indicateur n'est pas assez net. Le titrage avec le xylénol orange, en milieu acide, est cependant, tout à fait sûr, et permet le dosage de thallium (III) en présence de thallium (I).

REFERENCES

[1] J. Kinnunen and B. Wennestrand, *Chem. Analyst*, 1955, **46**, 92.
[2] A. I. Busev and V. G. Tipcova, *Zhur. analit. Khim*, 1958, **13**, 180.
[3] W. T. Foley and R. F. Pottie, *Analyt. Chem.*, 1956, **28**, 1101.
[4] H. Flaschka, *Mikrochem.*, 1952, **40**, 42.
[5] R. Přibil and Z. Zábranský, *Chem. Listy*, 1951, **45**, 427.; *Coll. Czech. Chem. Comm.*, 1951, **16**, 554.
[6] R. Přibil, *Chem. Listy*, 1951, **45**, 57; *Coll. Czech. Chem. Comm.*, 1951, **16**, 542; *Magyar Kém. Folyóirat*, 1952, **58**, 251.
[7] R. Přibil and Z. Zábranský, *Chem. Listy*, 1952, **46**, 16.

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NOTICE

The following meetings have been arranged:

Wednesday 1 *February* 1961: **Society for Analytical Chemistry**: *X-ray fluorescence.* Burlington House, London, W.1. 7.00 p.m.

Wednesday 15 *February* 1961: **Society for Analytical Chemistry,** Biological Methods Group: *Use of enzymes in biological assay.* Burlington House, London, W.1. 7.00 p.m.

Thursday 16 *February* 1961: **Society for Analytical Chemistry,** Midlands Section and **Association of Clinical Biochemists:** *Chromatography:* Mr. N. F. KEMBER, A.R.I.C. and Dr. H. G. SAMMONS. General Hospital, Birmingham, 6.30 p.m.

Thursday 23 *February* 1961: **Society for Analytical Chemistry,** Western Section and **Royal Institute of Chemistry,** Bristol and District Section: *Titrations in non-aqueous solvents:* MR. E. MINSHALL, M.Sc., F.R.I.C. Gloucester.

Friday 24 *February* 1961: **Society for Analytical Chemistry,** Scottish Section and **Royal Institute of Chemistry:** Joint Meeting: *Ion-exchange*: Mr. R. A. WELLS, B.Sc., A.R.I.C. and Mr. V. E. GRIPP, B.Sc., A.R.C.S., A.R.I.C. Royal College of Science and Technology, Glasgow C.1.

Friday 24 *February* 1961: **Society for Analytical Chemistry,** Microchemistry Group: Annual General Meeting followed by Retiring Chairman's Address: Mr. F. HOLMES, B.Sc., A.R.I.C. Burlington House, London, W.1. 7.00 p.m.

Tuesday 28 *February* 1961: **Society for Analytical Chemistry,** Physical Methods Group: *Physical methods of analysis in medical research.* Royal College of Surgeons, London, 6.30 p.m. Preceded by a visit to the Research Department of Anaesthetics.

B.S.I. News announces the following new British Standards:

B.S. 1792: *One-mark volumetric flasks:* 1960. This specifies ten sizes of flask, from 5-ml to 2000-ml capacity. It gives full dimensions but, in accordance with current practice in British Standards for volumetric glassware, lists only the essential ones as mandatory, the remainder being given for the guidance of manufacturers. It includes a standard method for the determination of capacity and lists two classes of tolerance for this. It specifies requirements for material, construction, stability and graduation, and includes alternative shapes of neck suitable for stoppers of ground glass or plastics materials. (Price 4s.)

B.S. 3266: *Methods for the determination of conductivity, pH, water-soluble matter, chloride and sulphate in aqueous extracts of textile materials:* 1960. This specifies associated test methods and includes two standardised procedures for extracting textile specimens with water. Methods for determining conductivity, pH value, water-soluble matter, chloride and sulphate content of the aqueous extracts are included. (Price 4s.)

B.S. 3278: *General recommendations for the sampling of imported iron ores: Part I:* 1960: *Hammer and shovel method.* These recommendations apply to the sampling of imported iron ores from ship's holds at the port of arrival immediately after arrival. Recommendations are made for the method of selection of the sub-samples and the number of increments, the method of sampling, the gross sample and the reduction of the certificated sample, and the final samples. A plan of sampling. and sampling reduction is included, as well as an appendix giving an example of the general procedure recommended. (Price 3s.)

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PAPERS RECEIVED

Gravimetric and titrimetric determination of bismuth using ammonium salts of benzene- and naphthalene-selenoyl acids: V. S. SOTNIKOV and I. P. ALIMARIN (27 *September* 1960).

Determination and separation of scandium using *N*-benzoylphenylhydroxylamine: I. P. ALIMARIN and TZE YUN'-SYAN (27 *September* 1960).

A laboratory method for the purification of commercial niobium and tantalum oxides: EDWARD C. MURRAY (14 *October* 1960).

Isotope dilution analysis by solvent extraction—I: Principle and theory of the method: JAROMIR RUZICKA and JIRI STARY (15 *October* 1960).

Isotope dilution analysis by solvent extraction—II: Highly selective determination of zinc with dithizone: JIRI STARY and JAROMIR RUZICKA (15 *October* 1960).

Analytical applications of Xylenol Orange—VI. The photometric determination of zinc: KAREL STUDLAR and IVAN JANOUSEK (16 *October* 1960).

Spectrophotometric determination of germanium with *p*-dimethylaminophenylfluorone: A. CAMPE and J. HOSTE (17 *October* 1960).

Activation-analysis of manganese in cast iron and high-alloy steels: P. BOUTEN and J. HOSTE (17 *October* 1960).

The determination of traces of iridium in samples of rhodium by neutron-activation and gamma-ray spectrometry: D. F. C. MORRIS, D. N. SLATER and R. A. KILLICK (17 *October* 1960).

The separation of sub-microgram amounts of uranium from milligram amounts of iron, aluminium and plutonium: D. G. BOASE and J. K. FOREMAN (17 *October* 1960).

Precipitation of metal 8-hydroxyquinolates from homogeneous solution, III. Aluminium: DAVID J. MAREC, EUGENE D. SALESIN and LOUIS GORDON (18 *October* 1960).

Spectrophotometric determination of palladium with nitroso-R salt: JACOB SHAMIR and ABRAHAM SCHWARTZ (19 *October* 1960).

The selective determination of active hydrogen with dispersed sodium: PATRICIA R. MOHILNER and CHARLES A. REYNOLDS (21 *October* 1960).

Separation and colorimetric determination of trace quantities of magnesium in high-purity beryllium oxide: R. F. APPLE and J. C. WHITE (24 *October* 1960).

A critical examination of the gravimetric and titrimetric methods for the determination of gold: F. E. BEAMISH (26 *October* 1960).

The analysis of beryllium and beryllium oxide—VI: The determination of tantalum and niobium: JAMES O. HIBBITS, H. OBERTHIN, R. LIU and SILVE KALLMANN (27 *October* 1960).

The determination of oxygen, hydrogen, nitrogen and carbon in metals: A review: WILLIAM G. GULDNER (1 *November* 1960).

New methods of inorganic ultramicroanalysis under the microscope: I. P. ALIMARIN, and M. N. PETRIKOVA (6 *November* 1960).

Determination of calcium in lithium salts: RODNEY L. OLSEN, HARVEY DIEHL, PETER F. COLLINS and R. B. ELLESTAD (10 *November* 1960).

Applications of complementary tri-stimulus colorimetry—IV: Investigation of a tartrate complex containing both copper and aluminium: H. FLASCHKA, J. BUTCHER and R. SPREIGHTS (10 *November* 1960).

The precipitation of niobium oxinate of definite composition: L. KOSTA and R. DULAR (13 *November* 1960).

NOTES FOR CONTRIBUTORS

1. General

Contributions may deal with any aspect of analytical chemistry, although papers exclusively concerned with limited fields already catered for by specialist journals should normally be directed to those journals, and should only be submitted to TALANTA if their analytical implications as a whole are such as to make their inclusion in a more general background desirable.

Original papers, short communications, preliminary communications and reviews will be published. Suitable books submitted to the Editor-in-Chief will be reviewed.

Since TALANTA is an international journal, contributions are expected to be of a very high standard. Research papers should make a definite contribution to the subject. Special importance will be attached to work dealing with the principles of analytical chemistry in which the experimental material is critically evaluated, and to similar fundamental studies. Reviews in rapidly expanding fields, and reviews of hitherto widely scattered material, will be considered for publication, and should be critical. The Editor will welcome correspondence on matters of interest to analytical chemists.

All papers and short communications submitted for consideration will be refereed in the normal way. Referees will be encouraged to present critical and unbiassed reports which are designed to assist the author in presenting his material in the clearest and most unequivocal way possible. To assist in achieving this completely objective approach, referees will be asked to submit signed reports. At the discretion of the Editor the names of referees may be disclosed if thereby agreement between author and referee is likely to result. Authors should appreciate that the comments of referees are presented in a constructive spirit, and that agreement between the views of author and referee must result in a higher standard of publication.

It is hoped that research and review papers will be published within approximately three to four months of acceptance, and short communications within two months.

Twenty-five free reprints of each paper will be provided (with ten further free copies for each additional author) and additional copies can be supplied at reasonable cost if ordered when proofs are returned. A reprint order form will accompany the proofs.

2. Script Requirements

1. Contributions should be submitted to the Editor-in-Chief, or to the appropriate Regional Editor, and may be written in English, German or French.

2. **Scripts should be submitted in duplicate. They must be typewritten and the lines double-spaced.** Where possible, research papers should follow the pattern: *Introduction, Discussion, Conclusion, Experimental* (or such of these headings as apply.)

3. Because the bulk of material will be set directly in page proof, every attempt should be made to ensure that before being submitted, manuscripts are essentially in the final form desired by the authors, and that no alterations of moment will be required at the proof stage. Alterations suggested by the referee will be agreed with the authors at the manuscript stage. Authors whose native language is not English are advised that in submitting papers in English they should endeavour to have the paper thoroughly corrected before submitting for publication. If the manuscript requires considerable editing, it may have to be returned to the authors for re-typing, resulting in a serious delay in publication.

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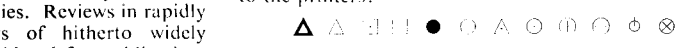

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[1] J. B. Austin and R. H. H. Pierce, *J. Amer. Chem. Soc.*, 1955, **57**, 661.
[2] S. T. Yoffe and A. N. Nesmeyanov, *Handbook of Magnesium-Organic Compounds*. Pergamon Press, London, 2nd Ed., 1956. Vol. 3, p. 214.
[3] A. B. Smith, *The Effect of Radiation on Strengths of Metals*. A.E.R.E., M/R 6329, 1962.
[4] W. Jones, *Brit. Pat.* 654321, 1959.

Footnotes, as distinct from literature references, should be indicated by the following symbols: *, †, ‡, ¶, commencing anew on each page; they should not be included in the numbered reference system.

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