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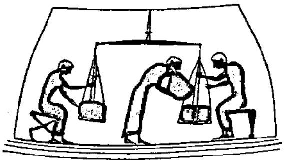

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3. R. J. Winterton in C. L. Wilson and D. W. Wilson, *Comprehensive Analytical Chemistry*, Vol. IB, p. 238. Elsevier, Amsterdam, 1960.
4. A. B. Smith, *The Effect of Radiation on Strengths of Metals.* A.E.R.E., M/R 6329, 1962.
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Talanta, 1966, Vol. 13, pp. 641 to 666. Pergamon Press Ltd. Printed in Northern Ireland

TALANTA REVIEW*

DIFFERENTIAL SPECTROPHOTOMETRY

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Department of Chemistry, University of Aberdeen, Scotland

(*Received* 21 *September* 1965. *Accepted* 29 *December* 1965)

Summary—The principles of various methods of differential spectrophotometry are briefly discussed. Practical problems connected with the measurements are presented and analytical applications so far available are reviewed.

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* For reprints of this review see Publisher's Announcement at the end of this issue.

† On leave of absence from Technical University of Budapest, Hungary.

HISTORICAL

DIFFERENTIAL spectrophotometry, often called "precision spectrophotometry", began to develop with photoelectric spectrophotometry itself. As early as 1934 Kortüm and von Halban[1] wrote about the possibilities of reducing errors of photoelectric measurements to 0·01 % by measuring relative transmittances. Kortüm[2] later described the relative transmittance measurements elsewhere, while Ringbom and coworkers,[3–5] dealing with general problems of photometry and especially with precision, pointed out the advantages of measuring the transmittance of a solution of unknown concentration against a solution containing the substance to be measured in a known amount. These considerations were, however, mainly theoretical, and ten years passed before Bastian[6] in 1949 published the first of his papers, describing the determination of high percentages of copper, using the transmittance ratio method. In the past sixteen years much work has been carried out in this field.

PREVIOUS REVIEWS

The task of the present review is to collect the material in a form which is useful from the practical point of view, *i.e.*, to help the analyst, working in the laboratory, when choosing a method for a particular task. There have been other reviews published in this field, pointing out theoretical problems. Because the most important achievement of differential spectrophotometric methods is the gain in precision, a number of papers approach the method in connection with problems of error calculation of spectrophotometric measurements. Thus, Ayres,[7] giving at the same time an excellent review of the precision of all kinds of colorimetric measurements, describes the improvement in precision both in general and particularly in the case of permanganate ions when measured by the transmittance ratio method. A similar approach was made by Gridgeman.[8,9] Svehla, Páll and Erdey[10] pointed out that apart from the

photometric error, errors due to scattering of experimental points in the calibration curve must be taken into consideration. Hiskey[11,12] in two of his papers presented a thorough theoretical and practical description of the transmittance ratio method, reviewing at the same time the few existing practical applications at that time. A more general viewpoint was expressed by Reilley and Crawford,[13] dividing all existing and possible spectrophotometric measurements into four groups, among which three may be called differential methods. Their nomenclature and grouping will be used in the present paper, symbols and expressions being changed, however, to ones more familar to practical analysts. Crawford[14] later gave a more detailed review on the subject. Snesarev,[15] Gerbaux,[16] Swietoslawska[17] and Svehla[18] published smaller reviews on differential spectrophotometry; the latter two written in Polish and Hungarian, respectively, are less accessible to most readers.

PRINCIPLES OF DIFFERENTIAL SPECTROPHOTOMETRY

Differential spectrophotometric methods were developed to improve the precision of results, and thus to enable the use of expensive, but easy-to-operate spectrophotometers for the determination of the main components of a given sample. This requirement can be fulfilled only if the coefficient of variation of the measurements decreases to a level of 0·1–0·5%. This can be achieved by the appropriate expansion of the scale used for the measurement of light intensities. Fortunately, there is no need for any mechanical or electrical changes in the internal parts of the spectrophotometers, which would require special skill and make the instrument unsuitable for ordinary spectrophotometric work. Scale expansion can be made by placing cuvettes containing solutions of suitable concentrations in the cell compartment of the instrument, and by adjusting the transmittance scale with them.

As is known in ordinary spectrophotometric work, whatever the optical or electrical layout of the instrument, two adjustments are required before the actual measurement is made. First the zero point of the transmittance scale must be adjusted. This is done by placing a shutter in the light beam (*i.e.*, the photocell is in complete darkness) and balancing the instrument with resistors (balancing the dark current of the photocell). When this is completed the instrument indicates 0% transmittance if a completely opaque species is placed in the light beam. The second manipulation brings the adjustment of the 100% transmittance on to the scale, by placing the solvent in the light beam and rebalancing the instrument with a second variable resistor. After these operations the instrument is capable of the measurement of any light intensity falling between total darkness and one equal to the light intensity passing the pure solvent. If a solution is now placed in the light beam, its transmittance can be measured, which is equal to the light intensity now falling on the photocell (relative to that passing through the solvent). Thus the transmittance scale must be adjusted (calibrated) by two different light intensities (one of them having the value zero, *i.e.*, total darkness).

Calibration of the transmittance scale, however, can also be made by two other light intensities, which differ less in value than the two described above. For example, if two reference solutions, containing the absorbing species in different concentrations, are used for scale calibration, one can adjust the zero transmittance with the more concentrated solution in the light beam and 100% with the other. After this, the transmittance of any solution with a concentration between the two calibrating solutions may be measured with an increased precision, the scale now being more sensitive. The increase of precision must, however, be expressed more quantitatively, because experimental conditions favourable for a given task can be selected with the aid of this alone.

As mentioned above, there are various possibilities for the scale calibration. To avoid further confusion we shall use different symbols for the species used for the latter: s will refer to the solvent, r to a reference solution with a lower and R to that of a higher concentration, x refers to the unknown solution and D to total darkness, *i.e.*, to an opaque species placed in the light beam, c refers to concentration (chosen for practical purposes to be mg . ml^{-1}). Note that $0 < c_r < c_x < c_R$, the concentration of the unknown being between those of the two reference solutions. I is the light intensity falling on the photocell after passing through the absorbing species. Note that in any case $I_s > I_r > I_x > I_R > 0$. Scale readings are represented by R; these may sometimes be hypothetical, falling outside the region 0–100%. In any case $R_s > R_r > R_x > R_R > R_D$. Cuvette length will be denoted by l, while specific extinction (the unit chosen for this being ml . cm^{-1} . mg^{-1}) by a. T means transmittance, values of which fall between 0 and 1 (corresponding to 0 and 100% on the scale, respectively). E is the extinction (optical density, absorbancy) of the solution. Correlation between E and T is through the well known expression:

TABLE I.—SYMBOLS USED IN THE REVIEW

Symbol	s		r		x		R		D
Species in light path	solvent		diluted reference solution		unknown sample		concentrated reference solution		opaque shutter
Concentration of absorbing solution	0	$<$	c_r	$<$	c_x	$<$	c_R		
Light intensity	I_s	$>$	I_r	$>$	I_x	$>$	I_R	$>$	0
Transmittance reading	R_s	$>$	R_r	$>$	R_x	$>$	R_R	$>$	R_D
Cell length	l		transmittance		T		standard deviation		σ
Specific extinction	a		extinction		E		coefficient of variation		V

$$E = -\log T.$$

Because these may have different meanings in different scales used, appropriate symbols will be applied in brackets after T and E in all cases. Thus, $T(x/s)$ means transmittance of the unknown measured against the solvent, *etc.* Standard deviation of a series of measurements will be denoted by σ, and the coefficient of variation (expressed as percentage) by V. The validity of Beer's law is assumed for all cases (if not stated otherwise), *i.e.*, the correlation

$$E(x/s) = a.l.c_x = -\log \frac{I_x}{I_s}$$

holds for all values of c_x. In practical cases this is sometimes not fulfilled, but these will be treated separately in the review. Table I gives a summary of symbols used in the review.

Methods of Differential Spectrophotometry

There are various possibilities for carrying out differential spectrophotometric measurements, which substantially differ from each other. These can be divided according to the methods used for scale calibration. Following the nomenclature introduced by Reilley and Crawford[13] we shall treat these briefly; first, however, a short survey must be made of ordinary spectrophotometry, to which the three possible differential methods will be added (A–D). Later, special methods, developed by alteration or combination of the previous principles will be dealt with (E–H). Omitting mathematical derivations three important characteristics of the methods will be examined:

(i) method of scale calibration,
(ii) correlation between extinction readings and concentration,
(iii) precision problems connected with the method.

These are summarised for the four principle methods in Table II.

A. Ordinary spectrophotometry

In ordinary spectrophotometric work scale calibration is made by an opaque species (shutter, 0%) and solvent (100%). Thus, $R_s = 1{\cdot}00$ and $R_D = 0{\cdot}00$. Transmittance and extinction readings can be described as

$$T(x/s) = \frac{I_x}{I_s} \quad \text{and} \quad E(x/s) = -\log T(x/s)$$

respectively. The concentration of an unknown solution can be expressed as

$$c_x = \frac{E(x/s)}{a\,.\,l} = A\,.\,E(x/s)$$

which gives a directly proportional relationship between c_x and E. The coefficient of variation of the concentration determination

$$V_{c_x} = -100\,\frac{0{\cdot}4343}{10^{-E(x/s)}\,.\,E(x/s)}\,\sigma_{T(x/s)}$$

is directly proportional to the standard deviation of transmittance readings $[\sigma_{T(x/s)}]$ and depends on the extinction values themselves. It is advisable to calculate the values of the error function

$$F(x/s) = \frac{0{\cdot}4343}{10^{-E(x/s)}\,.\,E(x/s)}$$

for various values of $E(x/s)$, and to plot these.* The result is the so called Ringbom-Ayres plot[3,7,8,10–12] shown in Fig. 1. The ordinate values give the factor by which the standard deviation values of transmittance measurements are to be multiplied to gain the coefficient of variation of concentration determinations. It can be seen that even if the extinction values fall within the favourable limits of 0·2–0·8, an average 3-fold magnification of the standard deviation must be expected. The curve has a

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* Values of error functions are plotted in this paper against extinction values (E), instead of against transmittances (T) as is frequently done in papers, because in practice extinction values are mostly determined for concentration measurements.

TABLE II.—FEATURES OF VARIOUS SPECTROPHOTOMETRIC METHODS

Group	Name of method	Scale adjustment for transmittance reading	Transmittance as function of light intensity	Extinction	Concentration of unknown as function of extinction, $c_x =$	Coefficient of variation of concentration determination, $V_{c_x} =$
A	ordinary method	$R_s = 1{\cdot}00$ $R_D = 0{\cdot}00$	$T(x/s) = \frac{I_x}{I_s}$	$E(x/s)$ $= -\log T(x/s)$	$\frac{E(x/s)}{a\,.\,l}$	$-\frac{0{\cdot}4343}{10^{-E(x/s)}E(x/s)}\sigma_{T(x/s)}\,.\,100$
B	transmittance ratio method	$R_r = 1{\cdot}00$ $R_D = 0{\cdot}00$	$T(x/r) = \frac{I_x}{I_r}$	$E(x/r)$ $= -\log T(x/r)$	$\frac{E(x/r)}{a\,.\,l} + c_r$	$-\frac{0{\cdot}4343}{10^{-E(x/r)}[E(x/r) + E(r/s)]}\sigma_{T(x/r)}\,.\,100$
C	ultimate precision method	$R_r = 1{\cdot}00$ $R_R = 0{\cdot}00$	$T\left(\frac{x - R}{r - R}\right)$ $= \frac{I_x - I_R}{I_r - I_R}$	$E\left(\frac{x - R}{r - R}\right)$ $= -\log T\left(\frac{x - R}{r - R}\right)$	$-\frac{1}{al}\log \{10^{-E(x-R)/(r-R)}$ $\times [10^{-alc_r} - 10^{-alc_R}]$ $+ 10^{-alc_R}\}$	
D	trace analysis method	$R_s = 1{\cdot}00$ $R_R = 0{\cdot}00$	$T\left(\frac{x - R}{s - R}\right)$ $= \frac{I_x - I_R}{I_s - I_R}$	$E\left(\frac{x - R}{s - R}\right)$ $= -\log T\left(\frac{x - R}{s - R}\right)$	$-\frac{1}{al}\log \{10^{-E(x-R)/(s-R)}$ $\times [1 - 10^{-alc_R}]$ $+ 10^{-alc_R}\}$	

minimum at $E(x/s) = 0{\cdot}43$, where the most precise results can be expected. This fact represents a serious limitation to the improvement of precision in ordinary spectrophotometric work.

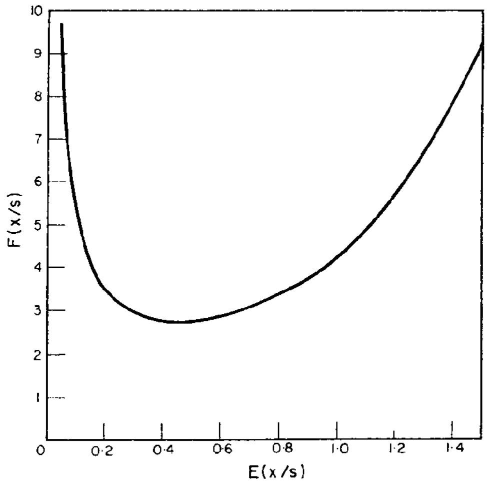

FIG. 1.—Error function of ordinary spectrophotometry.

B. Transmittance ratio method

The first method discussed is the transmittance ratio method. While the dark current in this case is measured using a shutter ($R_D = 0{\cdot}00$), 100% transmittance is given by a reference solution, containing the absorbing species to be measured in a known concentration, c_r ($R_r = 1{\cdot}00$). The concentration of the reference solution must naturally be lower than that of the unknown ($c_r < c_x$). The transmittance and extinction readings in this case are

$$T(x/r) = \frac{I_x}{I_r} \quad \text{and} \quad E(x/r) = -\log T(x/r)$$

respectively. The name of the method is derived from the fact that the transmittance read in this case can be regarded as the ratio of two transmittances:

$$T(x/r) = \frac{T(x/s)}{T(r/s)}, \quad \text{where} \quad T(x/s) = \frac{I_x}{I_s} \quad \text{and} \quad T(r/s) = \frac{I_r}{I_s}.$$

The concentration of the unknown can be expressed[11–13] as

$$c_x = \frac{E(x/r)}{a\,.\,l} + c_r = A\,.\,E(x/r) + B$$

yielding a linear (but not directly proportional) correlation between concentration and extinction. This linearity is a considerable advantage because in other methods (C–D) the relationship is not linear and calibration curves can be drawn only with difficulty.

The coefficient of variation of concentration determinations[11–13]

$$V_{c_x} = -100 \frac{0{\cdot}4343}{10^{-E(x/r)} \,.\, [E(x/r) + E(r/s)]} \sigma_{T(x/r)} \tag{1}$$

also *i.e*, depends on the value $E(r/s)$ on the "absolute" extinction of the reference

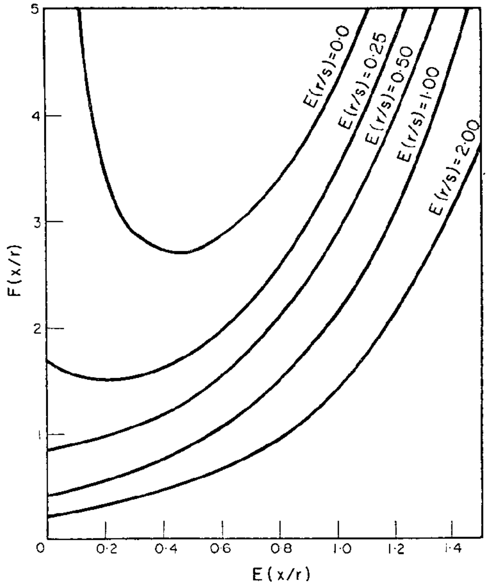

FIG. 2.—Error functions of the transmittance ratio method.

solution. Because the latter can be chosen arbitrarily within reasonable limits, when the values of the error function

$$F(x/r) = \frac{0{\cdot}4343}{10^{-E(x/r)} \,.\, [E(x/r) + E(r/s)]} \tag{2}$$

are plotted against the extinction of the unknown $[E(x/r)]$ a family of curves can be obtained, each of which corresponds to a given value of $E(r/s)$. Some of these curves are shown in Fig. 2. It is worthwhile to study these curves more closely. The top curve is identical to that shown in Fig. 1, corresponding to a reference solution with zero extinction, *i.e.*, the solvent. As the extinction of the reference solution increases, the values of $F(x/r)$ decrease, *i.e.*, the coefficients of variation themselves decrease. At the same time the minimum shifts towards lower extinction values, finally disappearing. As Páll[19] pointed out, the minimum disappears when the extinction of the reference solution against solvent $[E(r/s)]$ reaches the value 0·4343. Above these values monotonic curves appear. Because precision increases with decrease of the values $F(x/r)$, the following important conclusions can be drawn:

(a) An increase of precision can be expected if the extinction of the reference solution (measured against solvent) increases, *i.e.*, if reference solutions of higher concentration are used.

(b) Above certain values of the latter [$E(r/s) > 0{\cdot}4343$] the precision of the measurement increases with the decrease of extinction of the unknown solution (measured against the reference), gaining maximum precision if $E(x/r) = 0$, *i.e.*, if the concentration of the unknown solution is equal to that of the reference solution.

(c) There are values of $F(x/r)$ which are lower than 1. Experimental conditions corresponding to these values are especially favourable, because under these circumstances the standard deviation of the transmittance readings [$\sigma_{T(x/r)}$] is not to be magnified, but reduced to gain the coefficient of variation of concentration measurements.

It must be emphasised, however, that it is not enough to consider these values of the error function. This would lead to the absurd conclusion that the best precision can be obtained if two equally and completely opaque solutions are compared to each other. This is naturally a paradox. If the extinction of the reference solution increases above a given value, the light intensities reaching the photo-cell decrease considerably, resulting in an increase of the standard deviation of concentration readings, which, even if multiplied by favourably small values, will result in a final increase in the coefficient of variation of concentration measurements. This effect can be partly compensated by using higher slit widths than normal, but this inevitably causes deviations from Beer's law and cannot therefore be used, above a certain extent. Thus, as pointed out by Svehla, Páll and Erdey,[10] there exists an optimum concentration of reference solution for each method, which must be determined experimentally. For this reason a series of measurements must be made, using reference solutions of increasing concentrations. The standard deviations of transmittance readings [$\sigma_{T(x/r)}$] must be obtained and multiplied by appropriate values of $F(x/r)$, which can be taken from Fig. 2. These products must be examined further, the optimum reference solution being that which produces lowest values of coefficients of variation.[20]

C. Ultimate precision method

The ultimate precision (or general) method uses two reference solutions with different concentrations for the calibration of the transmittancy scale. Zero current (0%) is adjusted with the more concentrated solution in the light beam ($R_R = 0{\cdot}00$), while a less concentrated solution serves for the adjustment of 100% transmittancy ($R_r = 1{\cdot}00$). Extinctions of solutions with concentrations between those of the reference solutions ($c_r < c_x < c_R$) can be measured with a highly expanded scale. Transmittance and extinction of the unknown solution can be expressed as

$$T\left(\frac{x-R}{r-R}\right) = \frac{I_x - I_R}{I_r - I_R} \quad \text{and} \quad E\left(\frac{x-R}{r-R}\right) = -\log T\left(\frac{x-R}{r-R}\right)$$

respectively. Correlation between concentration (c_x) and extinction [$E(x-R)/(r-R)$] is not linear and follows the expression

$$c_x = -\frac{1}{a\,.\,l}\log\left\{10^{-E(x-R)/(r-R)}[10^{-alc_r} - 10^{-alc_R}] + 10^{-alc_R}\right\}.$$

The calibration curves are, therefore, exponential, and are similar to those showing "positive deviations" from Beer's law.* For further details see the paper of Reilley

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* This is only a formal statement, because absorption values are valid for these curves as well.

and Crawford.[13] Because of the non-linear relationship the expression of the coefficient of variation[13] is even more complicated and will not be quoted here. The increase of precision, however, can be shown qualitatively in Fig. 3. If a ΔE error occurs in the extinction measurement, the corresponding Δc error in the concentration determination will be smaller if positive, but higher if negative deviations from Beer's law are experienced (Δc_{I} and Δc_{III} values, respectively).

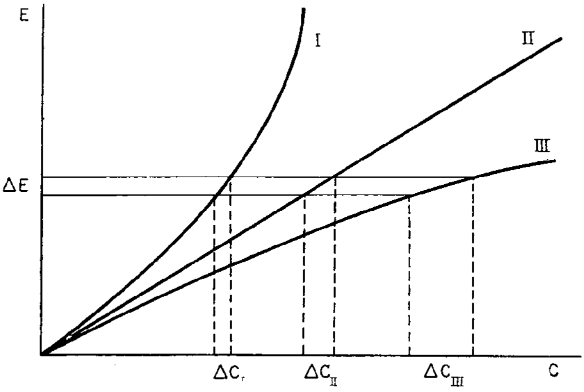

FIG. 3.—Errors in concentration determination if Beer's law is valid (II) or if positive (I) and negative (III) deviations occur.

D. Trace analysis method

The trace analysis method can be used advantageously for dilute solutions, the transmittance of which approaches 100% when compared with the solvent. Using this method, zero current is balanced with a reference solution more concentrated than the sample ($R_R = 0{\cdot}00$), while 100% transmittance is adjusted with the solvent ($R_s = 1{\cdot}00$). The transmittance and extinction of the unknown solution can be expressed as

$$T\left(\frac{x-R}{s-R}\right) = \frac{I_x - I_R}{I_s - I_R} \quad \text{and} \quad E\left(\frac{x-R}{s-R}\right) = -\log T\left(\frac{x-R}{s-R}\right)$$

respectively. The correlation between concentration and extinction is[13]

$$c_x = -\frac{1}{a\,.\,l}\log\left\{10^{-E(x-R)/(s-R)}[1 - 10^{-alc_R}] + 10^{-alc_R}\right\}.$$

The calibration curve is exponential in this case too, producing (formally) "positive deviations" from Beer's law. The precision of the method is the same as in method C. In practice, however, as pointed out by Shigematsu and Tabushi,[21] the method offers no significant improvement over ordinary spectrophotometry, and probably this is the reason why this method is only rarely used.

E. Concentration equalising methods

In connection with the transmittance ratio method (*B*) it was emphasised that most precise concentration determinations (*i.e.*, extinction measurements) can be made if the extinctions of the reference and unknown solutions are identical. This also occurs if the concentrations are equal. Starting with this principle, methods were developed based on variation of the concentration of the reference or unknown solution until these become identical, *i.e.*, until the extinction of the unknown measured against the reference solution [$E(x/r)$] becomes zero. This can be easily achieved by a procedure resembling photometric titration. The concentration is calculated from the amount of reagent added to equalise the concentrations. Although differing in technique, the same principle was used by Jones, Clark and Harrow,[22] Ringbom and Österholm,[23] Gedansky and Gordon[24] as well as by Ramaley and Enke.[25] All these methods offer a special increase in precision, and that of Ringbom and Österholm[23] can also be applied to simple instruments with filters.

F. Indirect differential spectrophotometry

The transmittance ratio method can also be applied for indirect spectrophotometric measurements, as described by Lothe.[26] In this case the substance to be determined has a bleaching effect on a component which absorbs light. First the extinction of the unbleached reagent must be measured against a solution partly bleached by a known amount of the substance to be determined. Using the symbol *o* for the unbleached reagent, the extinction measured can now be denoted as $E(o/r)$. In a second measurement the extinction of the unknown is measured against the same reference solution $E(x/r)$. From these results the concentration of the unknown can be expressed as

$$c_x = \frac{E(o/r) - E(x/r)}{a\,.\,l}$$

while the coefficient of variation of concentration determination is

$$V_{c_x} = 100\,\frac{0{\cdot}4343}{10^{-E(x/r)}[E(o/r) - E(x/r)]}\,\sigma_{T(x/r)}.$$

By closer examination of the error function, derivable from the above expression, similar conclusions can be drawn for the precision of the measurements as in the case of the transmittance ratio method.[26]

G. Differential spectrophotometry of systems deviating from the absorption law

The transmittance ratio method can be applied to solutions which show deviations from Beer's law, as described by Hiskey and Young.[27] Although considerations applied here are made for systems showing negative deviations (this is the most common case), they are valid for ones with positive deviations as well. In Fig. 4 there is a calibration curve of a system which shows negative deviation from Beer's law. This curve can be described by a function resembling the absorption law:

$$E(x/r) = E(r/s) + a'lc$$

In this expression, however, a' is not constant but varies with the concentration itself. Geometrically, a' is equal to the slope of the tangent of the extinction-concentration curve at any point.

Optimal experimental conditions for such determinations can be derived by a closer examination of the error function, valid for the transmittance ratio method. In the denominator of expression (2) the extinction of the reference solution measured against the solvent is to be found. This can also be expressed as:

$$E(r/s) = a'lc_r$$

and the original error function can be written as

$$F(x/r) = \frac{0{\cdot}4343}{10^{-E(x/r)}[E(x/r) + a'lc_r]}\,.$$

Actual values of $F(x/r)$ decrease, *i.e.*, the precision of the measurements increases if the value $a'lc_r$ increases. With increasing concentration, as is apparent from Fig. 4, the value of a' decreases, and there exists a concentration of reference solution where the product $a'lc_r$ shows a maximum. Thus, the optimal reference solution can easily be found experimentally. Hiskey and Young[27] not only derived the error function itself, but showed the application of this principle to the determination of anthracene dissolved in benzene.

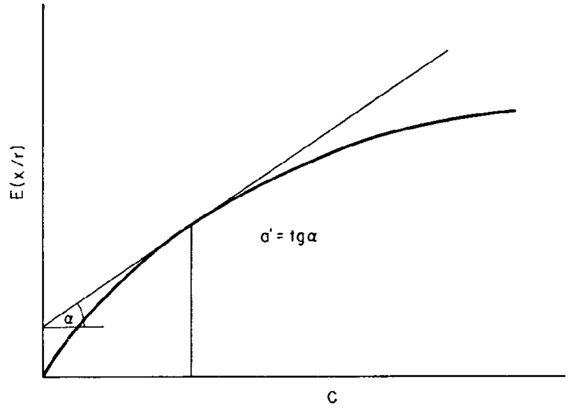

FIG. 4.—Calibration curve of a system showing negative deviations from Beer's law.

H. Differential spectrophotometry of multicomponent systems

The transmittance ratio method can also be applied to multicomponent coloured systems, as pointed out by Allen and Hammaker.[28] Later Hiskey and Firestone[29] dealt with the problem more extensively, while Ross and Wilson[30] described practical applications with two- and three component systems.

The measurement of a two component system must be carried out at two wavelengths, λ' and λ'', corresponding to the absorption maxima of substances 1 and 2, respectively. At λ' the extinction of the unknown sample is measured against a reference solution containing substance 1 $[E'(x/r_1)]$ at a known concentration (c_{r_1}), but containing no substance 2. At wavelength λ'' the extinction $E''(x/r_2)$ must be measured against a solution having a known concentration c_{r_2}. Assuming that the cuvette length chosen is 1 cm, and denoting the specific extinctions of substance 1 as a_1' and a_1'' at wavelengths λ' and λ'', respectively, while those of substance 2 are a_2' and

a_2'', the unknown concentrations c_{x_1} and c_{x_2} of substances 1 and 2, respectively, can be obtained from the following expressions:

$$c_{x_1} = \frac{c_{r_1} + \frac{1}{a_1'} E'(x/r_1) - \left[\frac{a_2'}{a_1'} c_{r_2} + \frac{a_2'}{a_1 - a_2''} E''(x/r_2)\right]}{1 - \frac{a_2'}{a_1'} \times \frac{a_1''}{a_2''}}$$

and

$$c_{x_2} = \frac{c_{r_2} + \frac{1}{a_2''} E''(x/r_2) - \left[\frac{a_1''}{a_2''} c_{r_1} + \frac{a_1''}{a_2'' - a_1'} E'(x/r_1)\right]}{1 - \frac{a_2'}{a_1'} \times \frac{a_1''}{a_2''}}$$

According to these expressions, apart from the extinction measurements the specific extinctions a_1', a_1'', a_2' and a_2'' must be known or measured. If experimental conditions are chosen so that both $E'(x/r_1)$ and $E''(x/r_2)$ are equal or close to zero, it is enough to measure the ratios of specific extinctions

$$Y' = \frac{a_2'}{a_1'} \quad \text{and} \quad Y'' = \frac{a_1''}{a_2''}$$

which can be done easily by two measurements (for particulars see the paper of Hiskey and Firestone[29]).

Error functions corresponding to this method are too complex to quote here; the practical consequences drawn from examination of these can, however, be summarised as follows:[29]

(a) The concentrations of reference standards (c_{r_1} and c_{r_2}) should be as high as possible.

(b) The measured extinctions [$E'(x/r_1)$ and $E''(x/r_2)$] should be close to zero, and in no case larger than 0·2–0·3.

(c) The determination of the ratios of specific extinctions must be made precisely.

Using this method the coefficient of variation can be reduced to 0·2–0·5 %, so that relatively high increase in precision can be expected.

PRACTICE OF DIFFERENTIAL SPECTROPHOTOMETRY

In practice, differential spectrophotometric analyses include preparation of solutions, adjustment of the spectrophotometer, checking of cuvettes, temperature control, carrying out the measurement and calculating the result.

Preparation of solutions

To gain the highest accuracy the preparation of reference and unknown solutions must be carried out with the greatest care, using calibrated volumetric apparatus. In many cases, especially if concentrated acidic solutions are to be handled, it is advisable to weigh the solutions with a precision of 0·01 g for dilution purposes. A number of determinations include evaporation with perchloric or sulphuric acid to obtain solutions with well defined composition. Perchloric acid is favoured, because it can be used as a solvent in many cases; all other anions can be removed, by fuming with perchloric acid, and it does not form complexes causing deviations from the absorption law. Evaporations with perchloric acid must be made with care; organic material, when dissolving, may cause hazardous explosions. The solutions must be brought to a predetermined constant temperature before final dilution.

Adjustment of spectrophotometer

The spectrophotometer must be switched on and left to stand until complete electronic and thermal equilibrium is reached (*ca.* 30 min). When choosing the wavelength it is essential to use an absorption band with a relatively flat maximum, enabling the use of a wider slit and obtaining higher radiation intensities at the photocell or photomultiplier. This is important, because if solutions of high (absolute) extinctions are used, only a fraction of the original radiation intensity passes through the solution and reaches the detector. With wider slits this intensity can be increased and the standard deviation of transmittance measurements [see equation (1)] reduced. The widening of the slit causes increased deviations from Beer's law. These somewhat contradictory requirements need to be examined closely before measurements are made, and an optimal set of experimental conditions must be worked out. Hiskey, Rabinowitz and Young[31] described the choice of optimal settings (including sensitivities) for various commercial instruments. Bastian, Weberling and Pallila[32] reported the same in more detail for the Beckman DU spectrophotometer, but their results can also be adapted for other instruments of similar design.

Selection of cuvettes

As derived from the absorption law, concentrations will be proportional to extinction values only if optical paths across the absorbing media are strictly identical. In practice this means that both the cuvette walls and cuvette lengths must be equal if the reference and unknown solutions are placed in the light beam. It would be best to use the same cell for measurements with the reference and unknown solutions. This involves opening the cell housing (and replacing the shutter before the photocell), rinsing and refilling the cuvette and replacing the latter in the housing. These operations require considerable time, during which the photocell response changes and other errors occur, which may offset the gain in accuracy obtained by using one cuvette. Experience has shown that it is advisable to use two cuvettes, one for the reference standard and one for the unknown, and errors due to discrepancies between cuvette lengths can be overcome by careful measurement of the relative cuvette lengths by optical methods. Details of cuvette matching and associated problems are described by Freeland and Fritz,[33] Crawford[14] and Banks, Grimes and Bystroff;[34] the latter work contains most details and deals also with differences in wall thickness.

Cuvettes must be carefully cleaned before use. Young and Hiskey[35] recommend the following procedure. Remove organic materials with appropriate solvents, rinse out the solvent with acetone and remove the latter with water. Fill and cover the cuvettes with acid permanganate-periodate solution, placed in a small beaker, and keep this at 45° for 1 hr. Then the cuvettes can be rinsed and the occasional brown film removed from the walls with acidic sodium sulphite solution. After final rinsing the cuvettes can be dried.

Temperature effects

Most authors publishing papers on differential spectrophotometry have pointed out the fact that temperature changes have more significant effects on precision in differential work than in ordinary spectrophotometry. Hiskey[11] pointed out the need of keeping temperatures constant within ±2° when obtaining the calibration curve and making the measurement of the unknown. Bastian,[36] however, made a more thorough study on the effect of temperature changes on various systems. Using two counter-switched thermocouples he measured temperature-differences between two solutions of the same concentration placed in two cuvettes, and determined the transmittance ratio of the solutions. The "reference" solution was kept at 22° while the temperature of the other solution was varied within 22° and 32°. Results for copper perchlorate, potassium permanganate and potassium dichromate are summarised in Fig. 5. It is interesting to see that systems may have both positive (copper perchlorate and potassium dichromate) and negative (potassium permanganate) temperature coefficients, their values being quite different. The temperature coefficient of a system varies considerably with the wavelength. Within the temperature range, which covers possible laboratory temperatures, measurements were made at 0·1° intervals, and the linearity of these curves (*i.e.*, constancy of temperature coefficients) was proved satisfactorily. From these curves it is apparent that a good thermostat is required for precise differential spectrophotometric work; on average the temperature must be kept constant to within ±0·2° during the measurements. This can easily be achieved by using special cell holders, now available for almost all types of spectrophotometer. These are water cooled.

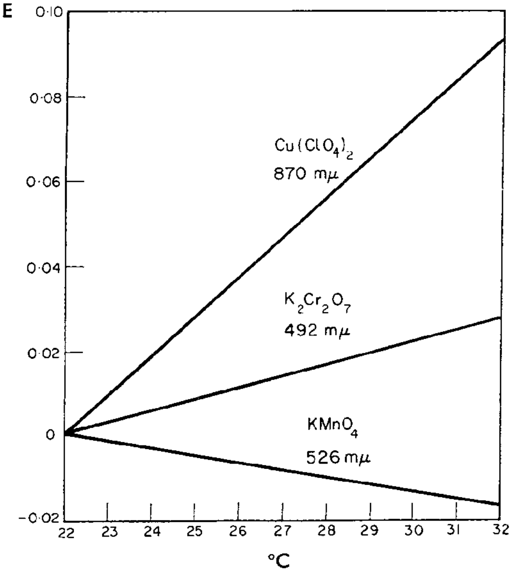

FIG. 5.—Temperature effects on extinction according to Bastian[36] (by courtesy of Analytical Chemistry).

Effect of changes of refractive index

Hiskey[11] discussed the effects of changes in refractive index of the solution measured on the values of the extinction. He found the errors to be sufficiently small in most practical cases to be generally negligible.

Extinction measurements and calculation of results

If the spectrophotometer has been switched on for at least 30 min, and instrumental settings and temperature control have been made appropriately, one can measure the extinction of unknown solutions. The cuvettes must be used consecutively and care must be taken over their precise adjustment in the cuvette holder. Zero current and 100% transmittance must be adjusted with appropriate species; this must be repeated until no further changes in galvanometer deflections occur. Then a measurement of an unknown solution can be made. The whole procedure must be repeated until the extinction values become constant (*e.g.*, differences between subsequent readings are less than 0·002 extinction unit). A similar procedure must be carried out when the calibration curve is obtained.

If linear calibration curves are to be expected, it is advisable to draw the curve according to the method of least squares. Results may be calculated with the aid of the calibration curve and known procedures. The estimation of precision (*i.e.*, determination of coefficient of variation) can be made by repeated measurements.

APPLICATIONS OF DIFFERENTIAL SPECTROPHOTOMETRY

Analytical applications of differential spectrophotometry are connected mainly with the determination of larger concentrations of metals. There are, however, methods available for the determination of anions of organic substances. Methods used in infrared analysis similar in technique to differential spectrophotometry will not be reviewed here. For the sake of uniformity, concentrations have been recalculated to units of mg/ml by the reviewer (and these are intended when equations of calibration curves are given).

Metals

Aluminium

Banerjee[37] developed a method for the determination of aluminium in titanium and its alloys. After dissolution in sulphuric acid, titanium is first precipitated with cupferron and the aluminium is determined in the filtrate. The latter must be evaporated with perchloric acid, and a reagent containing aluminon, benzoic acid, gelatin and a buffer of pH 5·30 must be added. The complex can be measured at 540 mμ, using method B, the reference solution containing 0·0005 mg of aluminium/ml. Within the range 0·0005–0·0015 mg/ml, Beer's law is obeyed and the equation $E(x/r) = -0{\cdot}85 + 1700\,c$ describes the calibration curve. Using a Beckman DU spectrophotometer with 1-cm cuvettes and 0·056-mm slit width the coefficient of variation is better than 1%. Chromium, smaller amounts of cobalt, lead and nickel do not interfere, but larger amounts of cobalt and iron cause serious interferences, which can be eliminated by adding thioglycolic acid. Titanium must be removed initially (see above).

Beryllium

White, Meyers and Manning[38] worked out a method for the determination of beryllium. The solution must be buffered with a sodium citrate-sodium tetraborate-sodium hydroxide mixture, while an alkaline solution of *p*-nitrobenzeneazo-orcinol serves as the reagent. The complex can be measured at 510 mμ, by the transmittance ratio method (B), using a reference solution containing 0·011 mg of beryllium/ml. Beer's law is valid within the concentration range 0·011–0·016 mg of beryllium/ml, and the equation of the calibration curve is $E(x/r) = -0{\cdot}72 + 76c$. Optimal slit width must be adjusted by a special procedure described in the paper, when using a Beckman DU spectrophotometer with 1-cm cuvettes. The coefficient of variation is less than 0·1 %. Uranium and aluminium cause slight interferences.

Chromium

Ross and Wilson[39] described the determination of chromium in the form of chromium(III) perchlorate. The coloured substance can be measured at two different wavelengths: 410 and 580 mμ. In practical cases a choice must be made according to the characteristics of other light-absorbing species present. Using the ultimate precision method (C) two reference solutions (0·95 and 2·21 mg of chromium/ml) serve for adjustment of 100% and 0% transmittance, respectively. Solutions within this concentration range can be measured with a coefficient of variation of 0·10%. The method can also be used in the presence of cobalt, copper and nickel; complete analysis of binary and ternary mixtures consisting of these elements can also be made.[30] These authors used the Unicam SP 500 spectrophotometer with 1-cm cuvettes.

Bastian, Weberling and Pallila[32] determined chromium in the form of dichromate ions. In aqueous or acidic solutions the compound can be measured at 350 mμ. Using the transmittance ratio method (B) a reference solution containing 0·049 mg of chromium/ml serves as a reference. Within the range 0·049–0·061 mg of chromium/ml Beer's law is valid and a calibration curve with an equation of $E(x/r) = -0{\cdot}90 + 15{\cdot}3c$ can be used for evaluation. With a Beckman DU spectrophotometer 1-cm cuvettes and 2-mm slit width can be utilised. Measurements were made at 28° and the coefficient of variation was 0·07%. The method was applied by Hiskey and Firestone[29] for chromium determinations in the presence of permanganate ions.

Ramaley and Enke[25] described an isomation technique for the determination of dichromate. The instrument is adjusted with the solution to be determined, using the dark control, then the cuvette is replaced by another containing pure solvent. The solvent is "titrated" with known amounts of dichromate until the same readings are obtained as with the unknown sample; results are calculated in a similar manner to titrimetric methods.

Cobalt

Páll, Svehla and Erdey[20] described a transmittance ratio method (B) for the determination of cobalt(II) ions. The solution must be evaporated with perchloric acid and measured at 511 mμ against a reference solution containing 12 mg of cobalt/ml. Although Beer's law is valid within a wide concentration range, the most reliable results can be expected if 12–30 mg of cobalt/ml are measured. Working at 25° with a Hilger Uvispek spectrophotometer with 1-cm cuvettes, the equation $E(x/r) = -1{\cdot}103 + 0{\cdot}0855c$ holds within the region mentioned above. The coefficient of variation is less than 1 %. Nickel, copper, manganese and iron do not interfere, but chromium(III) causes serious interference. The method can be used for the analysis of cobalt metal and cobalt-alloyed steels.

The ultimate precision method (C) was applied for the determination of cobalt in the form of perchlorate by Ross and Wilson.[39] The two solutions, used for adjustment of 100 % and 0 % transmittances, contained 0·78 and 1·09 mg of cobalt/ml, respectively. With a Unicam SP 500 spectrophotometer and 4-cm cuvettes, an error of −0·03%

and a coefficient of variation of 0·24% can be achieved. Errors are higher if binary and ternary mixtures consisting of cobalt, nickel, chromium and copper are analysed with a combination of methods (C) and (G), but coefficients of variation of cobalt determination are even lower.[30]

Copper

The first published work on the practical applications of differential spectrophotometry was Bastian's method of determination of high percentages of copper.[6] The sample (which can be pure copper metal) must be dissolved in nitric acid and evaporated with perchloric acid to fuming. Method (B) can be applied and extinction measurements must be made at 870 mμ against a reference solution containing 15·00 mg of copper/ml. Within the concentration range of 15·00–18·00 mg/ml, the calibration curve is a straight line and can be described by the equation $E(x/r) = -2{\cdot}84 + 0{\cdot}19c$. If a Beckman DU spectrophotometer is used with 1-cm cuvettes and 0·34-mm slit width, the coefficient of variation is not higher than 0·2%. Iron, nickel, chromium and cobalt do not interfere.

Ross and Wilson[39] described a procedure for much lower concentrations of copper, using the ultimate precision method (C). For the determination of 0·79–1·85 mg of copper/ml (using solutions for the adjustment of 100% and 0% transmittance with the two limiting concentrations) in the form of perchlorate, an error of −0·15% and a coefficient of variation of 0·17% is claimed. Copper can be determined in binary and ternary mixtures with nickel, cobalt and chromium with the same accuracy and precision.

Erbium

Banks, Spooner and O'Laughlin[40] used the ultimate precision method (C) for the determination of erbium. The solution must be evaporated with perchloric acid and then measured at 379 mμ. The 100% and 0% transmittances can be adjusted with solutions containing 8·35 and 14·1 mg of erbium/ml, respectively, and within these concentration limits the coefficient of variation of erbium determinations is less than 0·15%. With a Beckman DU spectrophotometer and 1-cm silica cuvettes the slit must be opened to 0·04 mm. The trace analysis method (D) can be used as well; in this case 5-cm cuvettes must be applied, while the precision of the method is much lower.

Manganese

Bastian, Weberling and Pallila[32] determined permanganate ions in aqueous solutions at 526 mμ, using the transmittance ratio method (B). The reference solution contains 0·049 mg of manganese/ml, and Beer's law is valid up to 0·061 mg/ml. The calibration curve for this concentration range can be described as $E(x/r) = -1{\cdot}50 + 30{\cdot}7c$. Working with a Beckman DU spectrophotometer at 25°, the slit width was adjusted to 0·25 mm and 1-cm cuvettes were used. The coefficient of variation is better than 0·07%.

Young and Hiskey[35] adopted the same method, but with other instrumental settings. Using a Beckman DU spectrophotometer with a slit and sensitivity which gives 1 galvanometer scale deflection if the transmittance of the solution is changed 0·1%, the calibration curve is steeper than the former one, and can be described by the equation $E(x/r) = -1{\cdot}9 + 38c$ in the concentration range of 0·05–0·06 mg of manganese/ml. The method can be used for the analysis of manganese ores. For this purpose the ore must be dissolved in concentrated hydrochloric acid, then evaporated with sulphuric acid to fumes and diluted. Phosphoric acid and potassium periodate must be added to an aliquot and the mixture boiled until permanganate is completely formed. After cooling and diluting to known volume, the spectrophotometric measurement can be made. The coefficient of variation is less than 0·1 %. Hiskey and Firestone[29] applied the method for the determination of manganese and chromium simultaneously, using method (G).

Molybdenum

Bacon and Milner[41] described a method for the determination of molybdenum in its binary alloys with uranium. The sample must be dissolved in acid, then evaporated with sulphuric acid to fuming, and finally hydrogen peroxide must be added. The solution should be 1·5*M* for sulphuric acid and 0·18*M* for hydrogen peroxide. The peroxymolybdic acid complex can be measured at 368 mμ. The transmittance ratio method (B) can be used with a reference standard containing 0·20 mg of molybdenum/ml. Beer's law is valid within a wide range, but optimal results can be gained with 0·20–0·26 mg of molybdenum/ml, when the equation of the calibration curve will be $E(x/r) = -1{\cdot}10 + 5{\cdot}50c$. The authors used a Beckman DU spectrophotometer with 1-cm cuvettes; the slit width was chosen to be 1 mm if the solution did not contain uranium, while in the presence of the latter a narrower (0·5 mm) slit was used. The coefficient of variation is less than 0·25 %, even if uranium is present.

Neodymium

For the determination of neodymium, Banks, Spooner and O'Laughlin described a method which can be used for the analysis of neodymium-yttrium,[42] neodymium-erbium and neodymium-praseodymium-samarium[40] mixtures. The ultimate precision method (C) can be applied. The sample is dissolved and evaporated with perchloric acid to fuming, then diluted appropriately. Extinction measurements must be made at 575 mμ. 100 % and 0 % transmittance can be adjusted with solutions containing 6·00 and 10·00 mg of neodymium/ml, respectively, and within this concentration range solutions can be analysed with a coefficient of variation less than 0·4 %. With a Beckman DU spectrophotometer and 1-cm cuvettes the slit must be adjusted to 0·025 mm. Yttrium, erbium, praseodymium and samarium do not interfere. The trace analysis method (D) adopted for the system gives less precise results.

Nickel

Bastian[43] described a method for the determination of high percentages of nickel in nickel alloys. The sample must be dissolved in 1 + 1 nitric acid, then evaporated with perchloric acid to fuming. The solution can be measured at 720 mμ. Using the transmittance ratio method (B) a reference solution containing 6·98 mg of nickel/ml can be applied. For the concentration region of 6·98–7·16 mg of nickel/ml, where Beer's law is valid, the equation $E(x/r) = -2{\cdot}00 + 1{\cdot}43c$ describes the calibration curve. With a Beckman DU instrument and 1-cm cuvettes a 0·63-mm slit width can be used. The extinction is sensitive to temperature changes: a 1° change within 25–35° causes a deviation of 0·004 extinction unit. The coefficient of variation is less than 0·07 %. Chromium(VI), aluminium, magnesium, lead and manganese do not interfere. The interference caused by titanium can be eliminated by previously precipitating it.

Ross and Wilson[39] applied the ultimate precision method (C) for nickel determinations. The perchlorate is to be measured at 393 mμ; the solutions used for the adjustment of 100% and 0% transmittance contain 2·40 and 2·75 mg of nickel/ml, respectively. Within this concentration range nickel can be determined with an error of −0·10% and a coefficient of variation of 0·16%. With a Unicam SP 500 spectrophotometer 4-cm cuvettes must be used. Nickel can be determined with the same accuracy and precision in binary and ternary mixtures containing nickel, chromium, cobalt and copper.[30]

Niobium

Banks, Burke, O'Laughlin and Thompson[44] used the transmittance ratio method (B) for the determination of niobium. The sample must be dissolved, evaporated with sulphuric acid and hydrogen peroxide must be added. The peroxyniobic acid, formed by the reaction, can be measured at 360 mμ against a reference standard containing 0·165 mg of niobium/ml. Within the range 0·165–0·198 mg/ml Beer's law is obeyed and the equation $E(x/r) = -1{\cdot}5 + 9{\cdot}10c$ describes the calibration curve. A Beckman DU spectrophotometer and 1-cm cuvettes were used with a slit width of 0·20 mm. The coefficient of variation is less than 1%. The method can be also used in the presence of uranium.

Pallila, Adler and Hiskey[45] used the method for the determination of niobium in the presence of tantalum. Measurements were made at 365 mμ. Although the method offers many advantages, the precision required in a special case (0·1% coefficient of variation) could not be reached.

Platinum

Ayres and Meyer[46] utilised the transmittance ratio method (B) for the yellow colour produced when tin(II) chloride and platinum(IV) chloride react in an hydrochloric acid medium. The system must contain 10 ml of concentrated hydrochloric acid and 25 ml of 20% ammonium chloride per 100 ml. Extinction measurements can be made at 403 mμ against a reference solution containing 0·05 mg of platinum/ml. Although measurements can be made within the concentration range 0·05–0·1 mg/ml, Beer's law is valid only within 0·05–0·07 mg/ml, where the calibration curve has the equation $E(x/r) = -1{\cdot}35 + 26{\cdot}9c$. A Beckman DU instrument with 1-cm cuvettes was used, while the coefficient of variation was better than 0·4%. Tellurium, rhodium, gold, ruthenium, osmium, iridium and chromium interfere and must be absent. Interference from palladium can be avoided by adding more tin(II) chloride than usual.

Plutonium

Phillips[47] used the transmittance ratio method (B) for plutonium determination. A sample is dissolved in hydrochloric acid and the plutonium reduced to the tervalent state by hydroxylamine hydrochloride. The extinction of the solution is measured at 565 mμ. The reference solution contains 8·00 mg of plutonium/ml and measurements can be made within the range 8·00–14·00 mg/ml where Beer's law is valid and the calibration curve can be described with the equation $E(x/r) = -1{\cdot}157 + 0{\cdot}14c$. Using a Beckman DU spectrophotometer with 1-cm cuvettes, the slit can be adjusted to 0·35 mm. Errors are less than +0·3%, while the coefficient of variation is about 0·4%. Tin, uranium, calcium and cerium(III) do not interfere. Interference from aluminium is slight, and that from iron(III) can be overcome by the addition of an excess of tin(II) chloride. Zirconium interferes and must be removed initially. For the elimination of interferences Atkins and Jenkins[48] recommended the use of De-Acidite FF anion-exchange resin. When a solution 7*M* in nitric acid is passed through a column filled with this resin, plutonium is retained selectively. After washing the column, the plutonium can be eluted with a 10% solution of hydroxylamine hydrochloride and determined as described above. The authors recommended 560 mμ as a wavelength for the measurement.

Praseodymium

Banks, Spooner and O'Laughlin[40] described an ultimate precision method (C) for the determination of praseodymium. The sample must be evaporated with perchloric acid to fuming and measured at 444 mμ. 100% and 0% transmittances are adjusted with solutions containing 3·96 and 6·60 mg of praseodymium/ml, respectively; unknown samples within this concentration range can be determined with a coefficient of variation of 0·2%. With a Beckman DU spectrophotometer and 1-cm cuvettes the slit must be opened to 0·03 mm. A trace analysis method (D) can also be applied; in this case the use of 5-cm cuvettes is recommended. The precision with this method is lower. Erbium, neodymium and samarium do not interfere; the complete analysis of praseodymium-erbium and neodymium-praseodymium-samarium mixtures is also described.

Samarium

An ultimate precision method (C) was described for the determination of samarium by Banks, Spooner and O'Laughlin.[40] The sample must be evaporated with perchloric acid to fuming, then measured at 401 mμ. Solutions containing 13·6 and 22·3 mg of samarium/ml can be used for the adjustment of 100% and 0% transmittances, respectively. Within this concentration range the coefficient of variation of samarium determination is less than 0·2%. With a Beckman DU spectrophotometer and 1-cm cuvettes, a slit width of 0·04 mm must be used. Neodymium and praseodymium do not interfere. The method can also be used for the complete analysis of neodymium-samarium-praseodymium mixtures. The trace analysis method (D) can also be used for lower concentrations; working with 5-cm cuvettes a loss of precision must, however, be expected,

Silver

Gedansky and Gordon[24] recommended an indirect photometric titration of milligram quantities of silver with EDTA using differential null point detection. Silver reacts with potassium tetracyanonickelate(II) to release a stoichiometric amount of nickel. The latter can be titrated with the reagent, Murexide serving as indicator. The spectrophotometer is adjusted to zero extinction for a solution containing potassium tetracyanonickelate(II) and Murexide before adding the silver solution. The unknown solution is then added and titrated with EDTA; extinction values are plotted against volumes of titrant added. The end-point is evaluated graphically by finding the intersection of the curve with the volume axis. The titration curve is a straight line. In this way 0·1–1 mg of silver can be determined.

Tantalum

Pallila, Adler and Hiskey[45] reported briefly on the differential spectrophotometric determination of tantalum using the transmittance ratio method (B). The solution to be determined must contain 96% sulphuric acid and 0·5 ml of 30% hydrogen peroxide, and the mixture must be measured at 285 mμ. A coefficient of variation of 0·42% has been obtained.

Titanium

For the differential spectrophotometric determination of titanium Neal[49] used the transmittance ratio method (B). The sample must be dissolved in the presence of ammonium sulphate by boiling with sulphuric acid, and the final solution must contain 20% of the latter and 5 ml of 20 vol. hydrogen peroxide per 100 ml. The peroxytitanic acid complex formed during the reaction is measured at 410 mμ. A solution containing 0·15 mg of titanium/ml (prepared by a similar procedure) serves as a reference. Beer's law is valid within the range 0·15–0·21 mg of titanium/ml, and the calibration curve can be described by the equation $E(x/r) = -1{\cdot}75 + 11{\cdot}7c$. When a Beckman DU spectrophotometer is used with 1-cm cuvettes the slit width must be adjusted to 0·8 mm. Temperature control is also essential for the volume measurements. Because of the concentrated sulphuric acid medium it is recommended to weigh the solutions as well. An error of 0·05% and a coefficient of variation of 0·03% are claimed for the determination. A similar method is described by Milner and Phennah[50] for the determination of titanium in titanium-uranium alloys. They recommend dissolving the metal in nitric acid in the presence of a few drops of hydrogen fluoride; after complete dissolution the mixture must be evaporated with sulphuric acid to fuming. As a reference standard a solution containing 0·12 mg of titanium/ml can be used. Beer's law is valid up to 0·19 mg/ml; the calibration curve has the equation $E(x/r) = -1{\cdot}59 + 13{\cdot}3c$, being somewhat steeper than the former one. The authors used 5-mm cuvettes and obtained a coefficient of variation lower than 0·2%.

De Carvalho[51] recommends the use of the ultimate precision method (C) for the determination of titanium in the presence of niobium and tantalum. The tantalite-columbite-ilmenite ore sample (0·25 g) must be fused with potassium pyrosulphate and dissolved in ammonium oxalate solution. Titanium, together with niobium and tantalum, must be precipitated with ammonium chloride and tannin. The precipitate, which is now free from iron which would interfere, must be washed and ignited to oxide. A second fusion must be made with potassium pyrosulphate, the resulting mass dissolved in sulphuric acid and after the addition of 30% hydrogen peroxide (0·5 ml per 50-ml final volume) measured. The concentrations of standard solutions, used for adjusting the instrument, may vary according to the expected amount of titanium. With a Beckman DU spectrophotometer and 1-cm cuvettes a coefficient of variation of 0·2% can be achieved.

Uranium

No less than eight papers deal with the determination of uranium. Silverman and Moudy[52] as well as Steele[53] described ultimate precision methods (C). The yellow coloured uranyl perchlorate can be measured at 417–420 mμ, after evaporation with concentrated perchloric acid. The concentration of uranium may vary over a wide range. To find the best reference solutions it is advisable first to make an approximate reading against water, and, in possession of the estimated concentration, to prepare two reference solutions, one being less and the other more concentrated than the unknown. Using a Beckman DU spectrophotometer with 1-cm cuvettes the attainable coefficient of variation is less than 0·5%. Chromium, vanadium, nickel, cobalt, sulphate and phosphate interfere, but no interferences were experienced with lead, thorium, zirconium and cadmium. If uranium metal fission products or uranium oxide are analysed, the sample must be dissolved in nitric acid, then evaporated with perchloric acid.

Bacon and Milner[54–56] recommend the use of the transmittance ratio method (B). Sulphuric acid is used as a reagent, after dissolving metallic or oxide samples in nitric acid. The solution to be measured must be $4M$ in sulphuric acid. Extinction measurements must be made at 430 mμ. The reference solution must contain 28 mg of uranium/ml. Within the concentration range 28–52 mg of uranium/ml Beer's law is valid and the equation $E(x/r) = -1{\cdot}67 + 0{\cdot}042c$ describes the calibration curve. Using the Beckman DU spectrophotometer with 1-cm cuvettes a 0·8-mm slit width can be used. The coefficient of variation is less than 0·05%. Susano, Menis and Talbott[57] used a similar technique, but a special method served for the optimal adjustment of the slit width. The reference solution must be chosen according to the slit width employed. The technique is very rapid and a coefficient of variation less than 1% is claimed. Banks, Burke and O'Laughlin and Thompson[44] applied the method to the determination of uranium in the presence of niobium and recommended a procedure for the simultaneous determination of the two metals.

Thiocyanate ions are used as the reagent in the method of Crouthamel and Johnson.[58] The metallic or oxide sample must be dissolved in hydrochloric acid, then evaporated with sulphuric acid to fuming. The uranium must be reduced with tin(II) chloride, and a solution, prepared by saturating acetone with potassium thiocyanate, must be added, The complex can be measured at 375 mμ. The transmittance ratio method (B) can be applied; the reference solution contains 0·108 mg of uranium/ml. Within the range 0·108–0·144 mg/ml, where Beer's law is valid, the calibration curve can be described by the equation $E(x/r) = -1{\cdot}18 + 11{\cdot}7c$. The method is more sensitive than any of those mentioned above. With a Beckman DU spectrophotometer and 1-cm cuvettes, a 1·5-mm slit width can be used. The coefficient of variation is less than 0·50%. Nitrate, sulphate, chloride, phosphate, acetate, citrate, fluoride and iodide ions do not interfere.

Zirconium

Manning and White[59] described a transmittance ratio method (B) for the determination of zirconium. The sample must be dissolved in a suitable acid, evaporated with perchloric acid to fuming, then sodium alizarin sulphonate and acetone must be added. The complex formed can be measured at 530 mμ. The reference solution contains 0·04 mg of zirconium/ml, and within the concentration range 0·04–0·06 mg/ml the calibration curve is linear with the equation $E(x/r) = -2{\cdot}4 + 60c$. With a Beckman DU spectrophotometer and 1-cm cuvettes the slit must be opened to 1·7 mm. The coefficient of variation is less than 1%. Fluoride, sulphate and phosphate interfere strongly. Freund and Holbrook[60] extended the method to higher concentrations. Instead of the reference solution they used a specially prepared cellophane to adjust 100% transmittance. For the region 1·86–6·22 mg of zirconium/ml the calibration curve can be described as $E(x/r) = -0{\cdot}014 + 0{\cdot}109c$. They claim the coefficient of variation to be better than 0·5%.

Anions

Cyanide

Ohlweiler and Meditsch[61] used a differential spectrophotometric technique for the determination of small amounts of cyanide. The method is an indirect one (F) and is based on the reaction of cyanide with the mercury(II)-*p*-dimethylaminobenzilidene-rhodanine reagent. The complex can be measured at 470 mμ. Even 0·01 μg of cyanide/ml can be determined in this way.

Fluoride

Lothe[62] used an indirect method (F) for the determination of fluoride, based on the bleaching effect of the latter on the thorium-Alizarin Red S complex. The solution must be buffered with monochloroacetic acid and sodium hydroxide to pH 2·8, then Alizarin Red S and thorium nitrate must be added. The extinction of the solution must be measured at 525 mμ against reference solutions containing 0·1, 0·2 or 0·6 mg of fluoride/ml, according to the concentration of the unknown. The calibration curve is not linear; extinctions decrease with increasing fluoride concentration. With a Beckman DU instrument and 1-cm cuvettes a coefficient of variation under 1% can be achieved.

Phosphate

The transmittance ratio method (B) has been used by Gee and Deitz[63] for the determination of phosphate. The sample is converted into a mixed vanadate-phosphate-molybdate complex in perchloric acid solution and is measured at 390 mμ. A reference solution containing 0·25 mg of phosphorus pentoxide/ml can be used for the concentration region 0·25–0·35 mg/ml. A Beckman DU spectrophotometer with a Corning 5970 filter, 1-cm cuvettes and 1-mm slit width can be applied. The coefficient of variation is better than 0·1% and the extremely good value of 0·02% is claimed in some cases by the authors. Iron, arsenic(V), phosphite, chromium and silicate ions interfere.

Organic Substances

Hiskey and Young[27] described a method for the determination of anthracene dissolved in benzene. Because the system does not obey Beer's law at all, method (G) has been used. Maximum precision is obtained if 0·03–0·04 mg of anthracene/ml is determined against a reference solution containing 0·03 mg of anthracene/ml. Extinctions are measured at 359·5 mμ, and the calibration curve (regarded as linear within the narrow concentration range) can be described with the equation $E(x/r) = -0{\cdot}99 + 33c$. With a Beckman DU spectrophotometer and 1-cm cuvettes the slit width can be adjusted to 0·24 mm.

Jones, Clark and Harrow[64] used their variable reference technique [method (E)] for the determination of various organic substances, such as fluorescein, dibromofluorescein, tetrabromofluorescein and mixtures of the three, coal-tar mixtures, benzene-toluene mixture, *o*- and *p*-aminoethylbenzene mixture, sulphadiazine and sulphathiazole. An improvement of precision was experienced in all cases over ordinary spectrophotometric methods.

Lykken and Rae[65] made colorimetric measurements when qualifying dark kerosene, light lubrication oil and other products of the oil industry against a standard coloured solution containing cobalt(II) chloride or iron(III) chloride. It seems that they found an increase in precision empirically but do not refer to the theoretical background or other literature of differential spectrophotometry at all.

Zusammenfassung—Die Grundlagen verschiedener Methoden der Differentialspektralphotometrie werden kurz diskutiert. Mit den Messungen verbundene praktische Probleme werden dargelegt und eine Übersicht über bis jetzt zugängliche analytische Anwendungen gegeben.

Résumé—On discute brièvement des principes de diverses méthodes de spectrophotométrie différentielle. On présente des problèmes pratiques liés aux mesures et passe en revue les applications analytiques existant jusqu'à présent.

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Talanta, 1966, Vol. 13, pp. 667 to 687. Pergamon Press Ltd. Printed in Northern Ireland

ÜBER DIE REAKTION VON 4-(2-THIAZOLAZO)RESORCIN MIT KUPFER(II), BLEI(II), ZINK(II), CADMIUM(II) UND WISMUT(III)

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(*Eingegangen am* 25 *Juni* 1965. *Angenommen am* 26 *September* 1965)

Zusammenfassung—Auf Grund spektralphotometrischer Untersuchungen konnte bei der Komplexbildung von 4-(2-Thiazolazo)resorcin mit Kupfer(II), Blei(II), Zink(II), Cadmium(II), Wismut(III) die Bildung überwiegend protonisierter und normaler 1:1-Chelate, zum Teil auch 1:2-Metallchelate bewiesen werden. Die vorliegenden Gleichgewichte, die Stabilität, optische Eigenschaften und die Anwendbarkeit der Chelate zur spektralphotometrischen Bestimmung dieser Metalle wurde studiert. Für die spektralphotometrische Bestimmung von Kupfer und Wismut ist das 4-(2-Thiazolazo)resorcin besonders geeignet.

Das 4-(2-Thiazolazo)resorcin (TAR) hat von den Thiazolazofarbstoffen besonderes Interesse gefunden, zum Teil wegen seiner Analogie zum oft angewandten 4-(2-Pyridinazo)resorcin (PAR), für die Anwendung als Metallindikator bei komplexometrischen Titrationen und auch als empfindliches Reagens für spektralphotometrische Metallbestimmung.[1–5] Es bilden sich rote bzw. rotviolette Chelate mit Metallen, die relativ gut in Wasser löslich sind. Da von den Chelatgleichgewichten[2,5] bisher nur jene des UO_2^{2+} und Cu^{2+} näher studiert wurden, haben wir in dieser Arbeit die Chelatbildung von Zn^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+} und Bi^{3+} in wässriger Lösung untersucht und die Möglichkeiten der Anwendung von TAR zur spektralphotometrischen Bestimmung dieser Metalle geprüft.

EXPERIMENTELLER TEIL

4-(2-Thiazolazo)resorcin, hergestellt im Institut für Reinchemikalien Brno, war die reine, in Wasser begrenzt lösliche, Base. Es wurden Lösungen in *ca.* 0,01*M* NaOH hergestellt.

Angewandte Metallsalze waren analysenreine Nitrate oder bei Zn^{2+} das Perchlorat. Die Konzentration der Lösungen wurde chelatometrisch mit dem Dinatriumsalz der EDTA ermittelt.

Für spektralphotometrische Untersuchungen wurden alkalische TAR-Lösungen nach eventueller Verdünnung mit verdünnter Perchlorsäure tropfenweise bis zum gelben Farbumschlag des Farbstoffes neutralisiert und danach die Metallsalzlösung hinzugefügt, um eine Hydrolyse zu verhindern. Der pH-Wert wurde mit verdünnter NaOH und Ammoniaklösung, die Ionenstärke $\mu = 0,1$ mit einer 1*M* Natriumperchloratlösung eingestellt.

Puffersubstanzen wie Chloracetat, Formiat, Acetat, Hexamethylentetramin wurden nur für qualitative Zwecke und bei den spektralphotometrischen Metallbestimmungen angewendet.

Die Extinktion der Lösung wurde in 10 mm-Küvetten mit einem Spektralphotometer SF-4(UdSSR) und der pH-Wert der Lösungen mit einer Glaselektrode den Instrumenten der Fa. Radiometer, Kopenhagen, mit einer Genauigkeit ±0,02 pH-Einheiten gemessen.

Die Papierelektrophorese wurde am Papier Whatman No. 1 in der Standardeinrichtung nach Jokl[6] in Lösungen mit Metallionenüberschuss ausgeführt. In Lösungen mit Ligandüberschuss störte die Eigenfarbe des Liganden erheblich. 0,1*M* $NaClO_4$-Lösung gleicher Metallionkonzentration wie in der getüpfelten Komplexlösung diente als Grundelektrolyt, $Hg(CN)_2$ indizierte die endoosmotische Bewegung des Elektrolyten, Trimethylphenyl- oder Tetramethylammoniumjodid wurden als innerer Beweglichkeitsstandard angewendet. Der pH-Wert der Lösungen wurde im Bereich von pH 4–6 mit Perchlorsäure und Lauge, aber auch mit 0,05*M*-Pufferlösungen eingestellt.

Die aktuelle Ladung des Komplexes wurde gemäss einer vereinfachten Gleichung berechnet:

$$n = d_k\sqrt{M_k}/d_s\sqrt{M_s}.$$

d_k bedeutet die Entfernung des Komplextüpfels vom Start nach der Elektrophorese, M_k-das Mol. Gew. des vorausgesetzten Komplexes, d_s und M_s analoge Angaben für das Standardkation.

Analytische Reaktionen von TAR

Eine Reihe von Metallionen geben rote bis rotviolette Farbumschläge in saurem oder neutralem Medium. In alkalischem Medium stört die eigene rote Färbung des Farbstoff-anions. Die Reaktionen hängen stark vom pH-Wert ab.

Analytisch besonders interessant sind Reaktionen mit folgenden Ionen:

$pH \leqslant 1$ Hg^{2+}, Cu^{2+}, Tl(III), Bi^{3+}, Pd^{2+}, Nb(V), Ta(V),

$2 < pH < 5$ Ga^{3+}, In^{3+}, Sc^{3+}, Y^{3+}, Ti(IV), Zr(IV), Th^{4+}, Ni^{2+}, Co^{2+}, V(V), VO^{2+}, UO_2^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Ce^{3+}, La^{3+}, und andere Lanthanide, Fe^{3+}

$pH > 5$ Mn^{2+}, Sn(IV), Al^{3+}.

Pd^{2+} gibt eine anomale grüne Färbung, ähnlich wie es auch mit 4-(2-Pyridinazo) resorcin der Fall ist.

Sn^{2+}, Cr^{2+}, Ti^{3+} reduzieren den Farbstoff.

Co^{2+} wird bei der Reaktion mit TAR leicht zu Co(III) oxydiert.

Die Reaktionen wurden ausgeführt, indem zu 1 ml Wasser 1–2 Tr. 1 M Pufferlösung, 1 Tr. 0,1 % TAR-Lösung in Äthanol und 1 Tr. der Metallionenlösung, zugefügt wurden. Die Färbung wurde mit jener der Farbstoffblindlösung bei demselben pH verglichen.

Die Empfindlichkeiten für einige Reaktionen sind in der Tabelle I zusammengestellt.

TABELLE I.—EMPFINDLICHKEITEN EINIGER REAKTIONEN MIT TAR

Ion	Pd	Bi	Cu	Pb	Zn	Cd	Mn	Co	Ni	Ga
pD	7,3	6,2	7,5	6,9	7,4	6,3	6,8	5,9	7,4	6,6
pH	2*	2*	5†	← 5–7‡ →						
Ion	Al	Sc	Y	La	Ce^{3+}	Pr	Sm	Er	Ti	Zr
pD	4,9	7,0	7,0	6,5	7,0	6,5	7,2	7,1	7,0	6,9
pH	← 6–7‡ →									
Ion	Th	UO_2^{2+}	Nb	Tl(III)						
pD	6,7	7,3	5,9¶	6,7						
pH	— 5–7‡ —			3*						

* $HClO_4$.

† Acetatpuffer.

‡ Hexamethylentetramin.

¶ In Gegenwart von 0,5 % Ammoniumoxalat.

Säure-Base-Gleichgewichte des TAR

Im pH-Bereich 0- 13 entstehen vier verschieden absorbierende Säure-Base-Formen; bei $pH < 2,5$ das orange Thiazoliumkation (RH_3^+), bei pH 2,5–4,5 die freie Base (RH_2) mit gelber Färbung. Bei $pH > 4,5$ wird das erste Hydroxylproton in 4-Stellung zur Azogruppe unter Bildung des gelborangen (RH^-) und ab $pH > 8$ das zweite Hydroxylproton in der *o*-Stellung zur Azogruppe unter Bildung des roten R^{2-}-Anions (Abb. 1 und Abb. 2) abgespalten.

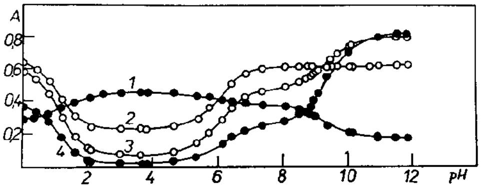


Abb. 1.—Die pH-Extinktionskurven für 4-(2-Thiazolazo)resorcin-lösungen ($c_R = 2{,}44 . 10^{-5} M$):—

1. 400 nm, 2. 480 nm, 3. 500 nm, 4. 520 nm.

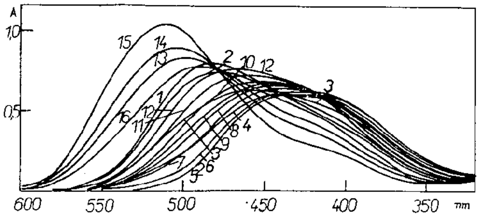
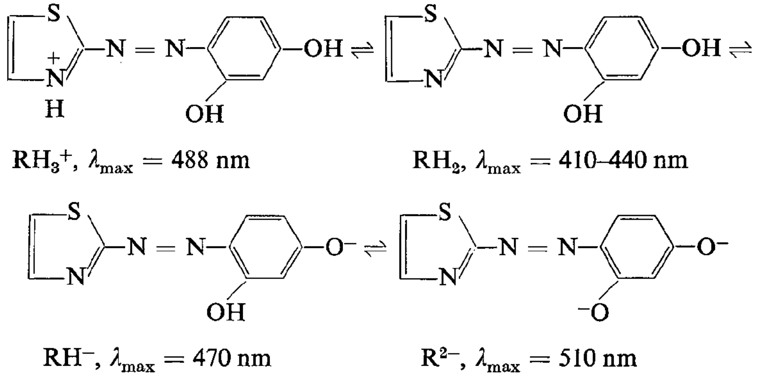


Abb. 2.—Absorptionskurven der TAR-Lösungen in Abhängigkeit von pH ($c_R = 3{,}02 . 10^{-5} M$):—

1. pH 0,11, 2. pH 0,59, 3. pH 1,04, 4. pH 1,67, 5. pH 4,00,
6. pH 5,08, 7. pH 5,76, 8. pH 6,02, 9. pH 6,17, 10. pH 6,39,
11, pH 6,81, 12. pH 7,78, 13. pH 9,66, 14. pH 9,97, 15. pH 11,96,
16. pH 9,38.



RH_3^+, $\lambda_{max} = 488$ nm

RH_2, $\lambda_{max} = 410$–440 nm

RH^-, $\lambda_{max} = 470$ nm

R^{2-}, $\lambda_{max} = 510$ nm

Den Säure-Base-Gleichgewichten entsprechen drei isosbestische Punkte der Absorptionskurven (siehe Abb. 2.).

Die entsprechenden Dissoziationskonstanten:

$$K_{a1} = [RH_2][H]/[RH_3], \; K_{a2} = [RH][H]/[H_2R], \; K_{a3} = [R][H]/[HR] \qquad (1)$$

werden gemäss (2), (3), (4) berechnet:

$$K_{a1} = \frac{(\varepsilon_{R1}c_R - A)[H]}{A - \varepsilon_{R2}c_R}; \quad K_{a2} = \frac{(A - \varepsilon_{R2}c_R)[H]}{\varepsilon_{R3}c_R - A} \qquad (2),(3)$$

$$K_{a3} = \frac{(A - \varepsilon_{R3}c_R)[H]}{\varepsilon_{R4}c_R - A} \qquad (4)$$

und zwar für Punkte der ansteigenden Äste der Extinktions-pH-Kurve des Farbstoffes im Bereiche der Absorptionskurven zwischen einzelnen isosbestischen Punkten (Siehe auch[15]).

ε_{R1}, ε_{R2}, ε_{R3}, ε_{R4} sind molare Extinktionskoeffizienten einzelner Säure-Base-Formen von TAR: H_3R^+, H_2R, HR^-, R^{2-}. ε_{R2} und ε_{R4} wurden direkt aus den Extinktionen der entsprechenden horizontalen Ästen gemäss $\varepsilon_R = A/c_R$ ermittelt. ε_{R1} und ε_{R3} wurden aus Punktpaaren in den steigenden Ästen berechnet gemäss (5), (6), (7):

$$\varepsilon_{R1} = \frac{A_1[H]_1(A_2 - \varepsilon_{R2}c_R) - A_2[H]_2(A_1 - \varepsilon_{R2}c_R)}{c_R[H]_1(A_2 - \varepsilon_{R2}c_R) - c_R[H]_2(A_1 - \varepsilon_{R2}c_R)} \qquad (5)$$

$$\varepsilon_{R3} = \frac{A_2[H]_1(A_1 - \varepsilon_{R2}c_R) - A_1[H]_2(A_2 - \varepsilon_{R2}c_R)}{c_R[H]_1(A_1 - \varepsilon_{R2}c_R) - c_R[H]_2(A_2 - \varepsilon_{R2}c_R)} \qquad (6)$$

oder

$$\varepsilon_{R3} = \frac{A_2[H]_2(\varepsilon_{R4}c_R - A_1) - A_1[H]_1(\varepsilon_{R4}c_R - A_2)}{c_R[H]_2(\varepsilon_{R4}c_R - A_1) - c_R[H]_1(\varepsilon_{R4}c_R - A_2)} \qquad (7)$$

A_1, $[H]_1$ und A_2,$[H]_2$ sind Werte für entsprechende Punktpaare. Für die Berechnung von Dissoziationskonstanten eignet sich auch eine graphische Analyse der aufsteigenden Äste der pH-Extinktionskurven.[16] Für die einzelnen Konstanten ergeben sich folgende Werte:

Tabelle II

pK_{a1}	pK_{a2}	pK_{a3}	Bemerkung
0,96	6,23	9,44	
	5,9	10,3	Nach Kaneniwa u.a.[2]
	6,40	10,52	Nach Kawase[5]

Der von uns gefundene pK_{a3}-Wert weicht ziemlich von jenem von Kaneniwa u.a.[2] und Kawase[5] in 20 Vol% Dioxan ab.

Im Vergleich mit 4-(2-Pyridynazo)resorcin[8] erscheint das Proton am Stickstoff und jenes des *o*-substituierten Hydroxyls saurer, das Proton am *p*-substituiertem Hydroxyl dagegen basischer.

Die photometrischen Konstanten von TAR und des 4-(2-Pyridinazo)resorcin-(PAR) sind in der Tabelle III zusammengestellt.

Tabelle III

Form	λ_{max}, nm		ε bei 510 nm	
	TAR	PAR	TAR	PAR
H_3R^+	488	395	$2{,}48 \cdot 10^4$	$3{,}67 \cdot 10^3$
H_2R	410–40	385	$1{,}73 \cdot 10^3$	$2{,}5 \cdot 10^3$
HR^-	470	413	$1{,}55 \cdot 10^4$	$7{,}8 \cdot 10^2$
R^{2-}	510	490	$3{,}45 \cdot 10^4$	$2{,}64 \cdot 10^4$

Bei TAR hat die Dissoziation der 4-Hydroxylgruppe im freien Liganden aber auch im Metallchelat eine grössere Änderung der optischen Eigenschaften zur Folge.

Spektralphotometrische Untersuchungen der Metallchelatgleichgewichte

Die Zusammensetzung der Metallchelate wurde durch die Variationsmethode[10] in äquimolaren Lösungen bei verschiedenem pH ermittelt.

Molare Extinktionskoeffizienten, Gleichgewichtskonstanten und die indirekten Beweise für die Komplexbildung bei gegebener Zusammensetzung folgen aus der numerischen Analyse für 2 Extinktionswerte[8] bzw., der graphischen Analyse der steigenden Äste der Extinktions-pH-Kurven der Lösungen mit Metallionenüberschuss und der äquimolaren Lösungen.[11]

Die Zahl der bei der Komplexbildung abgespaltenen Protonen und gleichzeitig der Wert der Gleichgewichtskonstante wurde durch die logarithmische Analyse der steigenden Äste der pH-Kurven ermittelt.

Für die Bildung von 1:1-Metallchelaten, die bei den Azofarbstoffen häufig auftreten, kommen folgende Gleichgewichte in Betracht (Ladungen einzelner Komplexe werden dabei zur Vereinfachung vernachlässigt):

1. Es reagiert gleichzeitig H_3R^+ und H_2R bei pH 0–1,5 in Lösungen mit Metallionüberschuss

$$M + H_3R \rightleftharpoons MRH + 2H^+ \tag{A}$$

$$M + H_2R \rightleftharpoons MRH + H^+ \tag{B}$$

mit einer Globalgleichgewichtskonstante:

$$K_{1,3} = [MRH]^2[H]^3/[M]^2[H_3R][H_2R] \tag{8}$$

Nach dem Einsetzen von $K_{a1}(1)$ und Radizieren ergeben sich die Konstanten $k_{1,2}$ und $k_{1,1}$ zu:

$$k_{1,2} = [MRH][H]^2/[M][H_3R] \tag{9}$$

$$k_{1,1} = [MRH][H]/[M][H_2R] \tag{10}$$

$$k_{1,2} = k_{1,1}K_{a1} \tag{11}$$

Beide Konstanten $k_{1,2}$ und $k_{1,1}$ können mit gleicher Berechtigung zur Charakterisierung des Systems angewendet werden, unabhängig davon, welches von den (A, B) Gleichgewichten in der Lösung überwiegt.

A. Die Unbekannten ε_1 und $k_{1,1}$ für den Fall $\varepsilon_{R2} \rightarrow 0$ ergeben sich aus den Gleichungen (10), (12)–(14) und K_{a1} für 2 Extinktionswerte:

$$c_R = [MRH] + [H_3R] + [H_2R] \tag{12}$$

$$c_M = [M] = \text{konst.} \tag{13}$$

$$A = \varepsilon_1[MRH] + \varepsilon_{R1}[H_3R] + \varepsilon_{R2}[H_2R] \tag{14}$$

$$\varepsilon_1 = \frac{a_1A_2 - a_2A_1}{c_R(a_1 - a_2)} \tag{15}$$

$$k_{1,1} = \frac{a}{c_M(\varepsilon_1 c_R - A)} \tag{16}$$

wobei $a = [H]\{A(1 + [H]/K_{a1}) - c_R\varepsilon_{R1}[H]/K_{a1}\}$ ist.

Für die graphische Interpretation wird der Ausdruck (16) in eine Gleichung für eine Gerade umgeformt:

$$c_R/A = 1/\varepsilon_1 + a/Ac_M\varepsilon_1 k_{1,1} \tag{17}$$

Der Abschnitt an der y-Koordinate entspricht $1/\varepsilon_1$. Über die Steigung der Geraden wird $k_{1,1}$ berechnet. Der ermittelte ε_1-Wert wird dann in den logarithmierten Ausdruck (16) eingesetzt und ergibt:

$$\log \frac{A(1 + [H]/K_{a1}) - c_R\varepsilon_{R1}[H]/K_{a1}}{\varepsilon_1 c_R - A} = \log k_{1,1} + \log c_M + pH. \qquad (18)$$

B. Werden unter gleichen Bedingungen das Gleichgewicht (A) mit der Gleichgewichtskonstante $k_{1,2}$ (3) gemeinsam mit den Gleichungen (12)–(14) betrachtet, so erhält man für ε_1 und $k_{1,2}$ folgende Ausdrücke:

$$\varepsilon_1 = \frac{b_1A_2 - b_2A_1}{c_R(b_1 - b_2)} \qquad (19)$$

$$k_{1,2} = \frac{b}{c_M(\varepsilon_1 c_R - A)} \qquad (20)$$

wo $b = \{A(K_{a1}/[H] + 1) - \varepsilon_{R1}c_R\}[H]^2$ ist.

Für die direkte und logarithmische Analyse werden dann folgende Umformungen durchgeführt:

$$\frac{c_R}{A} = \frac{1}{\varepsilon_1} + \frac{b}{Ac_M k_{1,2}\varepsilon_1} \qquad (21)$$

$$\log \frac{A(K_{a1}/[H] + 1) - \varepsilon_{R1}c_R}{\varepsilon_1 c_R - A} = 2pH + \log c_M + \log k_{1,2} \qquad (22)$$

C. Für den Fall der gleichzeitigen Reaktion von H_3R^+ und H_2R und Bildung von MRH in äquimolaren Lösungen geht man von den Beziehungen (10), (12), (14) und

$$c_M = [M] + [MRH] \qquad (23)$$

aus.

Es folgt für ε_1 eine komplizierte Gleichung dritten Grades für 2 Extinktionswerte der Kurve:

$$\begin{aligned} &c_R^2(a_1b_1 - a_2b_2)\varepsilon_1^3 + c_R(2a_2b_2A_1 + a_2c_2c_R - 2a_1b_1A_2 - a_1c_1c_R)\varepsilon_1^2 \\ &\quad + (a_1b_1A_2 + 2a_1c_1c_RA_2 - a_2b_2A_1 - 2a_2c_2c_RA_1)\varepsilon_1 - (a_1c_1A_2^2 - a_2c_2A_1^2) = 0 \qquad (24) \end{aligned}$$

mit bekannten Grössen:

$$a = \frac{[H]\{A(1 + [H]/K_{a1}) - c_R(\varepsilon_{R2} + \varepsilon_{R1}[H]/K_{a1})\}}{1 + [H]/K_{a1}}, \qquad b = 1 + [H]/K_{a1},$$

$$c = \varepsilon_{R2} + \varepsilon_{R1}[H]/K_{a1}.$$

(24) ist erst nach einer Vereinfachung (Beseitigung von ε_1^2) für eine Punkteschaar $\varepsilon_1 \sim 10^4$ lösbar.

$$k_{1,1} = \frac{a\{\varepsilon_1(1 + [H]/K_{a1}) - (\varepsilon_{R2} + \varepsilon_{R1}[H]/K_{a1})\}}{(\varepsilon_1 c_R - A)^2} \qquad (25)$$

Für diesen Fall ist die graphische Analyse unbrauchbar, da (25) nicht in eine Gleichung der Geraden transformiert werden kann.

2. Für pH 3–4 kommt in Lösungen mit Metallionenüberschuss in Gegenwart von TAR nur das Reaktionsgleichgewicht (B) in Frage:

Aus
$$\varepsilon_1 = \frac{A_2a_1 - A_1a_2}{c_R(a_1 - a_2)} \tag{26}$$

$$k_{1,1} = \frac{a}{c_M(\varepsilon_1 c_R - A)} \tag{27}$$

mit $a = [H](A - \varepsilon_{R2}c_R)$

folgen die Beziehungen[7]:

$$c_R/A = 1/\varepsilon_1 + a/Ac_M\varepsilon_1 k_{1,1} \tag{28}$$

$$\log \frac{(A - \varepsilon_{R2}c_R)}{(\varepsilon_1 c_R - A)} = \log c_M + pH + \log k_{1,1} \tag{29}$$

3. Bei pH 4–7 wirkt sich auch schon die Dissoziation des phenolischen Hydroxyls in der 4- Stellung zur Azogruppe aus und neben (B) bildet sich auch das normale Chelat gemäss:

$$M + HR^- \rightleftharpoons MR + H^+ \tag{C}$$

Die Berechnung wurde in diesem Fall nur für die Wellenlänge ausgeführt, bei der beide Chelate, das protonisierte und das normale, praktisch den selben molaren Extinktionskoeffizienten haben. Die Spaltung des *p*-Hydroxylprotons entfällt bei den Berechnungen.

$$k_{1,1} = \frac{a}{c_M b(\varepsilon_1 c_R - A)} \tag{30}$$

$$\varepsilon_1 = \frac{a_1b_2A_2 - a_2b_1A_1}{c_R(a_1b_2 - a_2b_1)} \tag{31}$$

mit $a = [H]\{A(1 + K_{a2}/[H]) - c_R(\varepsilon_{R2} + \varepsilon_{R3}K_{a2}/[H])\}$

und $b = 1 + K_{a2}/[H]$.

Die entsprechenden Ausdrücke für die direkte und logarithmische Analyse der Kurven sind dann:

$$c_R/A = a/bAc_M\varepsilon_1 k_{1,1} + 1/\varepsilon_1 \tag{32}$$

$$\log \frac{A(1 + K_{a2}/[H]) - c_R(\varepsilon_{R2} + \varepsilon_{R3}K_{a2}/[H])}{(1 + K_{a2}/[H])(\varepsilon_1 c_R - A)} = \log c_M + \log k_{1,1} + pH \tag{33}$$

Kupfer(II)-*Chelate mit TAR*

Mit steigenden pH-Werten bilden sich stufenweise ein violettes Chelat ab pH > 0 und ein rotes ab pH > 3 in Lösungen mit Metallionenüberschuss. In diesem Falle und auch in Lösungen mit Ligandüberschuss sind die Bildungsbereiche beider Chelate von einander gut getrennt. (Abb. 3, Kurve 2, 3.) In äquimolaren Lösungen überlagern sich die Bildungsbereiche beider Chelate (Abb. 3, Kurve 1).

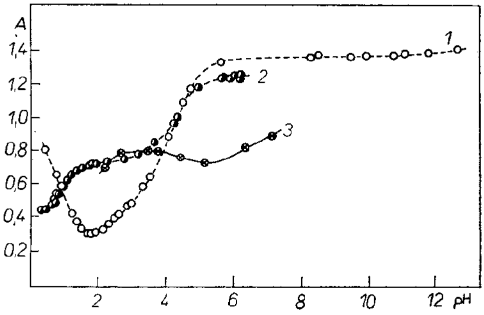


Abb. 3.—pH-Extinktionskurven der Lösungen von TAR mit Cu^{2+}-Ionen bei verschiedenen Bedingungen:—

1. $c_M = c_R = 4{,}39 . 10^{-5}M$, 510 nm;
2. $c_R = 4{,}36 . 10^{-5}M$, $c_M = 2{,}79 . 10^{-3}M$, 530 nm;
3. $c_M = 4{,}32 . 10^{-5}M$, $c_R = 2{,}62 . 10^{-4}M$, 560 nm.

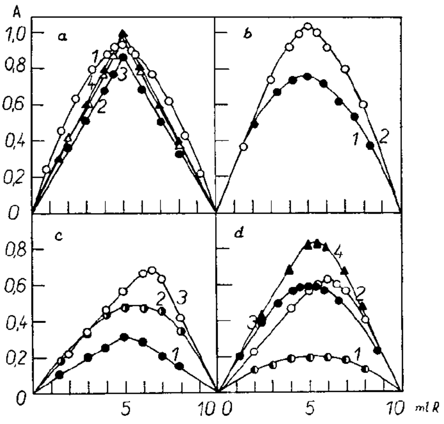


Abb. 4.—Jobkurven der Systeme TAR- Metallion:—

a. Cu^{2+}: Kurve 1. $c_0 = 1{,}86 . 10^{-4}M$, pH 2,09, 550 nm; 2. $c_0 = 8{,}24 . 10^{-5}M$, pH 4,56, 510 nm; 3. $c_0 = 8{,}24 . 10^{-4}M$, pH 4,56, 550 nm; 4. $c_0 = 6{,}48 . 10^{-5}M$, pH 7,00, 510 nm.
b. Pb^{2+}: Kurve 1. $c_0 = 1{,}38 . 10^{-4}M$, pH 5,28, 540 nm; 2. $c_0 = 8{,}28 . 10^{-5}M$, pH 6,40, 530 nm.
c. Zn^{2+}: Kurve 1. $c_0 = 8{,}30 . 10^{-5}M$, pH 5,85, 500 nm; 2. $c_0 = 5{,}96 . 10^{-5}M$, pH 6,60, 520 nm; 3. $c_0 = 5{,}96 . 10^{-5}M$, pH 8,30, 520 nm.
d. Cd^{2+}: Kurve 1. $c_0 = 9{,}96 . 10^{-5}M$, pH 6,25, 520 nm.; 2. $c_0 = 6{,}12 . 10^{-5}M$, pH 8,35, 520 nm. Bi^{3+}: Kurve 3. $c_0 = 1{,}30 . 10^{-4}M$, pH 1,12, 540 nm.; 4. $c_0 = 1{,}15 . 10^{-4}M$, pH 2,90, 540 nm.

Die Job- Kurven haben in äquimolaren Lösungen ein ausgeprägtes Maximum bei M:R = 1:1 für beide Chelate bei pH 2,1; 4,6 und 7,0 (Abb. 4a, Kurve 1–4).

Gemäss der Gleichung (18) konnte die Abspaltung überwiegend eines Protons bei pH 0,7–1,0 (n = 1,2 für 560 nm) festgestellt werden, wenn von dem Gleichgewicht (B) ausgegangen worden ist oder von 2 Protonen (n = 2,1 für 560 nm), wenn man die Reaktion der protonisierten Form des Ligandes H_3R^+ gemäss dem Gleichgewicht (A) und der Gleichung (22) voraussetzt (Abb. 5, Kurve 1, 2). Dies entspricht der Bildung eines protonisierten Chelates $CuRH^+$ gemäss:

$$Cu^{2+} + H_2R \rightleftharpoons CuRH^+ + H^+ \qquad (D)$$

$$Cu^{2+} + H_3R^+ \rightleftharpoons CuRH^+ + 2H^+ \qquad (E)$$

Die graphische logarithmische Analyse des zweiten aufsteigendes Astes der pH-Extinktionskurve für Lösungen mit Cu^{2+}-Überschuss ($c_M/c_R \sim 80$) gemäss der Gleichung:

$$\log \frac{[CuR]}{[CuRH]} = \log \frac{A - A_{01}}{A_{02} - A} = pH + \log k_{a1} \qquad (34)$$

beweist bei pH 3,8–5 und 510 nm eindeutig die Spaltung eines weiteren Protons (Abb. 6). Da das selbe Komponentenverhältnis im Chelat beibehalten wird, handelt es sich um das übrige *p*-Hydroxylproton zur Azogruppe und um die Bildung des normalen Chelates CuR.

In Übereinstimmung mit der früheren Bemerkung von Kawase[5] konnte in der Lösung ein 1:2-Kupfer(II)chelat nicht nachgewiesen werden. Die Bildungsbereiche

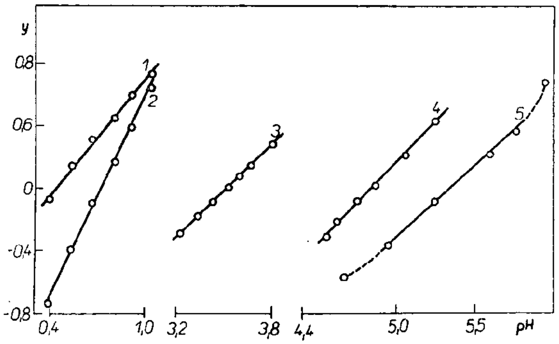


Abb. 5.—Die logarithmische Analyse der pH-Kurven der Lösungen mit TAR und Metallionüberschuss:—
1. und 2. : Cu^{2+}: $c_R = 4{,}37 \cdot 10^{-5}M$, $c_M = 2{,}79 \cdot 10^{-3}M$, 560 nm; 3. Pb^{2+}: $c_R = 4{,}19 \cdot 10^{-5}M$, $c_M = 3{,}18 \cdot 10^{-3}M$, 540 nm; 4 . Zn^{2+}: $c_R = 4{,}12 \cdot 10^{-5}M$, $c_M = 2{,}63 \cdot 10^{-3}M$, 510 nm; 5 . Cd^{2+}: $c_R = 4{,}19 \cdot 10^{-5}M$, $c_M = 4{,}33 \cdot 10^{-3}M$, 500 nm.

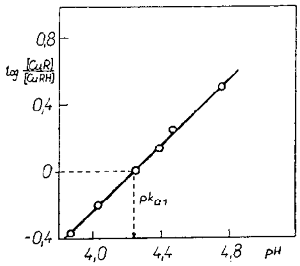


Abb. 6.—Die logarithmische Analyse des zweiten ansteigenden Astes der pH-Extinktionskurve der Lösungen mit TAR und Cu^{2+} im Überschuss ($c_R = 3{,}71 \cdot 10^{-5}M$, $c_M = 2{,}94 \cdot 10^{-3}M$, 560 nm).

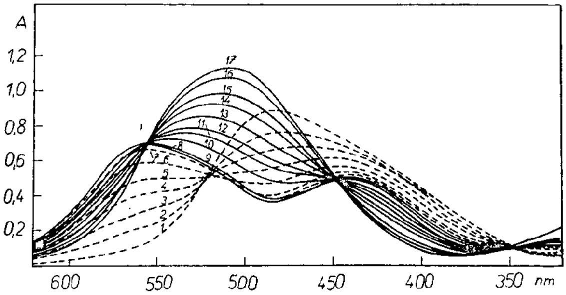


ABB. 7.—Absorptionskurven der Lösungen von TAR mit Cu^{2+}-Überschuss bei verschiedenem pH ($c_R = 3{,}71 . 10^{-5}M$, $c_M = 2{,}94 . 10^{-3}M$):—

1. pH 0,36, 2. pH 0.58, 3. pH 0.70, 4. pH 0,86, 5. pH 1,02, 6. pH 1,24, 7. pH 1,52, 8. pH 2,06, 9. pH 2,83, 10. pH 3,60, 11, pH 3,87, 12. pH 4,03, 13. pH 4,25, 14. pH 4,46, 15. pH 4,75, 16. pH 5,15, 17. pH 6,11.

beider Chelate wirken sich auch in den Absorptionskurven für Lösungen mit Cu^{2+}-Überschuss in Abhängigkeit von pH (Abb. 7) deutlich aus.

Im Bereich von pH 0,4–2,0 durchlaufen die Absorptionskurven einen isosbestischen Punkt bei 520 nm, der den Gleichgewichten (D), (E) entspricht. Die etwas verwischte Lage wird durch die gleichzeitige Anwesenheit von absorbierenden H_2R, H_3R^+-Formen des Liganden hervorgerufen.

Bei pH 2–6 durchlaufen die Kurven zwei ausgeprägte isosbestische Punkte bei 448 nm und 555 nm für den Übergang:

$$CuRH \rightleftharpoons CuR + H^+ \tag{F}$$

Die graphische Analyse der pH-Extinktionskurve der Lösungen mit Cu^{2+} bestätigt, dass man über beide Gleichgewichte (D) und (E) zu den richtigen Werten von ε_1 und der Gleichgewichtskonstante gelangen kann (Abb. 8, Kurve 7, 8), sodass beide Gleichgewichte bei der Komplexbildung massgebend sein sollten. Die Werte von ε_1 berechnet nach (17) oder (21) stimmen überein, die Gleichgewichtskonstanten $k_{1,1}$ und $k_{1,2}$ erfüllen die Bedingung $k_{1,2} = k_{1,1}K_{a1}$.

Die Werte der photometrischen Konstanten sind in der Tabelle IV zusammengestellt.

TABELLE IV

	λ_{max}, nm	ε_1	
$CuRH^+$	560; 440*	23100‡, 19000††	21500¶, 22200**, für 560 nm
CuR	505–510†	31100‡‡	(für 510 nm)

* pH 2,1.
† pH 6,1.
‡ Gemäss Gl.(15).
¶ Gl.(17).
** Gl.(21).
†† Von A/c_R für Lsg. mit Metallionüberschuss, von A/c_M für Lsg. mit Reagensüberschuss.
‡‡ Von A/c_R für Lsg. mit Metallionüberschuss bei pH > 6.

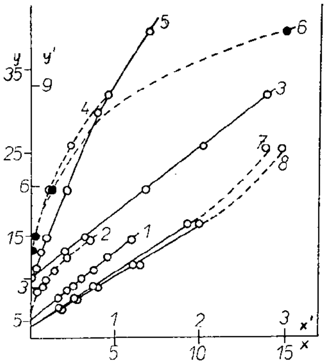


Abb. 8.—Die graphische Analyse der pH-Extinktionskurven der Lösungen mit TAR und Metallionüberschuss. (Die Konzentrationen gleichen jenen in Abb. 5.)

Pb^{2+}, 540m.:

$$\text{Kurve 1. } x = \frac{A - c_R\varepsilon_{R2}}{A}[H]\,.\,10^4,\ y = \frac{c_R}{A}\,.\,10^5;$$

$$\text{Kurve 2. } x = \frac{A - c_R\varepsilon_{R2}}{A}[H]^2\,.\,10^7,\ y = \frac{c_R}{A}\,.\,10^5.$$

Zn^{2+}, 510 nm.:

$$\text{Kurve 3. } x' = z[H]\,.\,10^5,\ y' = \frac{c_R}{A}\,.\,10^5;$$

$$\text{Kurve 4. } x' = z[H]^2\,.\,10^9,\ y' = \frac{c_R}{A}\,.\,10^5.$$

Cd^{2+}, 500 nm.:

$$\text{Kurve 5. } x' = z[H]\,.\,10^5,\ y' = \frac{c_R}{A}\,.\,10^5;$$

$$\text{Kurve 6. } x' = z[H]^2\,.\,10^{10},\ y' = \frac{c_R}{A}\,.\,10^5.\quad z = \frac{A\,(1 + K_{a2}/[H]) - c_R\,(\varepsilon_{R2} + \varepsilon_{R3}\,K_{2a}/[H])}{(1 + K_{a2}/[H])\,A}$$

Cu^{2+}, 560 nm.:

$$\text{Kurve 7. } x = \frac{A\,(K_{a1}/[H] + 1) - c_R\varepsilon_{R1}}{A}\,.\,[H]^2\,.\,10^2,\ y = \frac{c_R}{A}\,.\,10^5;$$

$$\text{Kurve 8. } x = \frac{A\,(1 + [H]/K_{a1}) - c_R\varepsilon_{R1}}{A}\,[H]\,.\,10,\ y = \frac{c_R}{A}\,.\,10^5.$$

Wismut(III)-*Chelate mit TAR*

Aus den pH-Extinktionskurven der äquimolaren Bi^{3+} und TAR-Lösungen ist ebenfalls die Bildung zweier Chelate (Abb. 9, Kurve 1) in Abhängigkeit von pH der Lösung nachweisbar. Das erste bildet sich schon ab pH $\geqslant$ 0, bei Metallionüberschuss in der Lösung auch bei pH $<$ 0, (Abb. 10, Kurve 9), das zweite ab pH $>$ 3 mit einem höheren mol. Extinktionskoeffizienten. Bei pH 1,1 haben die Job-Kurven ein Maximum für M:R = 1:1 (Abb. 4d, Kurve 3). Dieses Maximum verschiebt sich bei pH 2,9 zum Verhältnis M:R = 1:1,2 (Abb. 4d, Kurve 4). Man kann nicht unterscheiden, ob diese Verschiebung durch gleichzeitige Bi^{3+}-Hydrolyse oder Bildung eines höheren Chelates verursacht ist.

Es konnte hier nur die Bildung von $BiRH^{2+}$ eindeutig nachgewiesen werden, gemäss:

$$Bi^{3+} + H_3R^+ \rightleftharpoons BiRH^{+2} + 2H^+ \qquad (G)$$

$$Bi^{3+} + H_2R \rightleftharpoons BiRH^{+2} + H^+ \qquad (H)$$

Der höhere molare Extinktionskoeffizient bei $pH > 3$ und 540 nm scheint dem normalen Chelat zu gehören. Die photometrischen Konstanten sind in der Tabelle V angeführt.

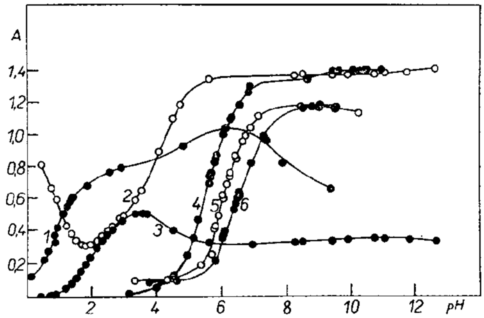


ABB. 9.—pH-Extinktionskurven äquimolarer Lösungen von TAR und Metallionen:—
1. Bi^{3+}: $4{,}77 . 10^{-5}M$, 550 nm; 2. Cu^{2+}: $4{,}39 . 10^{-5}M$, 510 nm;
3. Cu^{2+}: $4{,}39 . 10^{-5}M$, 580 nm; 4. Pb^{2+}: $4{,}28 . 10^{-5}M$, 530 nm;
5. Zn^{2+}: $3{,}19 . 10^{-5}M$, 500 nm; 6. Cd^{2+}: $3{,}19 . 10^{-5}M$, 500 nm.

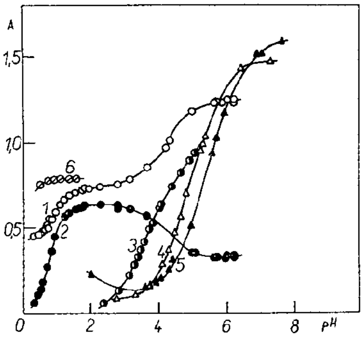


ABB. 10.—pH-Extinktionskurven der Lösungen von TAR mit Metallionüberschuss:—
1. Cu^{2+}: $c_R = 4{,}36 . 10^{-5}M$, $c_M = 2{,}79 . 10^{-3}M$, 530 nm; 2. $c_R = 4{,}36 . 10^{-5}M$, $c_M = 2{,}79 . 10^{-3}M$, 580 nm; 3. Pb^{2+}: $c_R = 4{,}19 . 10^{-5}M$, $c_M = 3.18 . 10^{-3}M$, 540 nm;
4. Zn^{2+}: $c_R = 4{,}12 . 10^{-5}M$, $c_M = 2{,}63 . 10^{-3}M$, 510 nm; 5. Cd^{2+}: $c_R = 4{,}19 . 10^{-5}M$, $c_M = 4{,}34 . 10^{-3}M$, 500 nm; 6. Bi^{3+}: $c_R = 4{,}27 . 10^{-5}M$, $c_M = 4{,}00 . 10^{-3}M$, 540 nm.

Blei(II)*-Chelate mit TAR*

Absorptionskurven und die pH-Extinktionskurven der Lösungen mit Metallionüberschuss und der äquimolaren Lösungen beweisen in schwach saurem Medium die stufenweise Bildung von zwei Chelaten, deren optische Eigenschaften sich weniger deutlich unterscheiden als bei den Cu^{2+}-Chelaten. Die Pb^{2+}-Chelate haben im ganzen pH Bereich 2,3—6,4 das Komponentenverhältnis Pb : R = 1 : 1 (Abb. 4b). Die direkte und logarithmische Analyse der pH-Extinktionskurve der Lösungen mit Metallionenüberschuss (Abb. 10, Kurve 3) beweisen bei pH 3–4 die Abspaltung eines Protons und die Bildung von $PbRH^+$ gemäss:

$$Pb^{2+} + H_2R \rightleftharpoons PbRH^+ + H^+ \qquad (I)$$

(Abb. 8, Kurve 1, 2; Abb. 5, Kurve 3). In äquimolaren Lösungen von $c_M = c_R = 4{,}3.10^{-5}$ M (Kurve 4 in Abb.10) überwiegt bei pH 4–6 bereits die Bildung eines normalen PbR-Chelates gemäss:

$$Pb^{2+} + HR^- \rightleftharpoons PbR + H^+ \qquad (J)$$

1 : 2-Chelate mit TAR konnten unter unseren Bedingungen in der Lösung bei pH < 7 nicht nachgewiesen werden. Die photometrischen Konstanten sind in der Tabelle VI zusammengestellt.

TABELLE V

	λ_{max}, nm	ε_1(540 nm)
$BiRH^{2+}$	540; 455* 540–5; 455†	22400‡, 18500¶
BiR^+	530–5**	30800††

* pH 1,71.
† pH 3,3.
‡ Gemäss Gl.(24).
Lsg. mit Metallionüberschuss.
¶ Von A/c_R im horizontalen Ast der pH-Kurve von Lsg. mit Metallionüberschuss.
** Bei pH 6,35.
†† Von A/c_M der Lsg. mit Ligandüberschuss.

TABELLE VI

	λ_{max}, nm	λ_{iso}, nm	ε_1(540 nm)
$PbRH^+$	540†	480	19700‡; 20000¶
PbR	530*	467	30400**

* Bei pH 6,1–8,1 von äquimol. Lsg.
† Bei pH 3,6–4,1 für Lsg. mit Metallionüberschuss.
‡ Gemäss Gl.(26).
¶ Gemäss Gl.(28).
** Von A/c_R der Lsg. mit Cd^{2+}-Überchuss bei pH 8.

Zink(II)-*Chelate mit TAR*

Ab pH > 5 in äquimolaren Lösungen (Abb. 9, Kurve 5), in Lösungen mit Metallionenüberschuss schon ab pH > 3 (Abb. 10, Kurve 4) bildet sich ein Chelatgemisch. Der horizontale Ast der pH-Extinktionskurve ist von der Wellenlänge abhängig und tritt für 550 nm schon ab pH 5,7 auf. Bis pH 5,85 wurde die Zusammensetzung der 1 : 1 Chelate auch durch die Variationsmethode bestätigt (Abb. 4c, Kurve 1). Mit steigendem pH-Wert verschiebt sich aber das Maximum der Job-Kurven zu höheren Verhältnissen $x = c_R/(c_M + c_R)$ und erreicht bei pH = 8 praktisch den Wert Zn : R = 1 : 2 (Abb. 4c, Kurve 2,3). Die direkte und logarithmische Analyse der pH-Extinktionskurve gemäss (32), (33) beweist bei pH 4,5–5,4 wieder die Abspaltung eines Protons bei der Komplexbildung (Abb. 8, Kurve 3,4; Abb. 5, Kurve 4), was der Bildung von $ZnRH^+$ mit H_2R entspricht. In äquimolaren Lösungen bei pH = 6 überwiegt schon die Bildung von ZnR (Siehe Abb. 9, Kurve 5) mit dem Farbstoffanion RH^-, die durch die gleichzeitige Bildung eines höheren Chelates kompliziert wird. Photometrische Konstanten sind in der Tabelle VII angeführt.

TABELLE VII

	λ_{max}, nm	ε_1(510 nm)
$ZnRH^+$,(ZnR)	510* 500††	30500†, 32900†; 30300,32000‡; 35400¶; 35700**.

* pH 4,8, Zn^{2+}-Überschuss.
† Gemäss der Gl.(31).
‡ Gl.(32).
¶ Bei pH 8, äquimol. pH-Kurve im horizont. Ast.
** pH 8 von A/c_R in Lsg. mit Metallionüberschuss.
†† pH 7, äquimol. Lsg. u. Lsg. mit Zn^{2+}-Überschuss.

Bei λ 540 nm sind die Werte der mol. Extinktionskoeffizienten beider Chelate praktisch identisch. Der Anstieg bei pH 8 im horizontalen Ast der pH-Extinktionskurve sollte früher der gleichzeitigen Bildung eines 1:2-Chelates zugeschrieben werden.

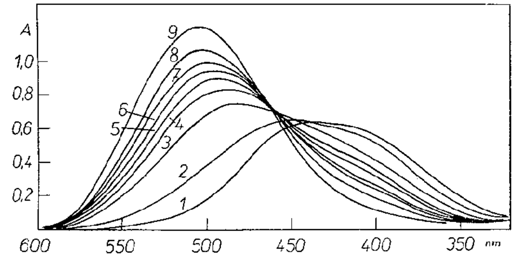


ABB. 11.—Absorptionskurven äquimolarer Lösungen von TAR und Cd^{2+}-Ionen in Abhängigkeit vom pH ($c_M = c_R = 3,19 . 10^{-5}M$):—
1. pH 5,51, 2. pH 6,39, 3. pH 6,66, 4, pH 6,94, 5. pH 7,09, 6. pH 7,21, 7. pH 7,36, 8. pH 7,44, 9. pH 8,59.

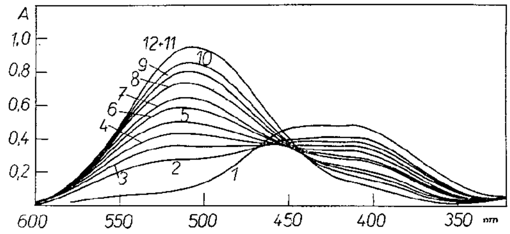


ABB. 12.—Absorptionskurven der Lösungen mit TAR und Cd^{2+}-Überschuss (c_R = 2,70 . $10^{-5}M$, c_M = 2,71 . $10^{-3}M$):—
1. pH 4,40, 2. pH 4,99, 3. pH 5,11, 4. pH 5,23, 5. pH 5,37, 6. pH 5,52, 7. pH 5,62, 8. pH 5,84, 9. pH 5,91 10. pH 6,19, 11. pH 6,57, 12. pH 6,69.

Cadmium(II)-*Chelate mit TAR*

Äquimolare Lösungen von Cd^{2+} mit TAR bei pH 7,4–8,6 und auch Lösungen mit Cd^{2+}-Überschuss bei pH 7,6 (Abb. 11, 12) haben ein einheitliches Absorptionsmaximum bei 505 nm.

Die Komplexbildungsgleichgewichte in äquimolaren Lösungen mit $c_R = c_M = 3{,}19 \,.\, 10^{-5}$ M vom pH = 5,5 (Abb. 9, Kurve 6) und auch in Lösungen mit Metallionüberschuss $c_M/c_R = 100$ für pH > 3,5 (Abb. 10, Kurve 5) sind jenen von Zink völlig analog. Die Job-Kurven haben ein Maximum für M:R = 1:1 bei pH = 6,25 (Abb. 4d, Kurve 1), bei pH = 8,35 für M:R = 1:1,5 (Kurve 2). Bei pH 4,7–6,7 wurde in Lösungen mit Metallionüberschuss die Abspaltung eines Protons bei der Komplexbildung und somit die Gleichgewichte:

$$Cd^{2+} + H_2R \rightleftharpoons CdRH^+ + H^+ \qquad (K)$$

$$Cd^{2+} + HR^- \rightleftharpoons CdR + H^+ \qquad (L)$$

bestätigt (Berechnung gemäss (32), (33) und Abb. 8, Kurve 5,6 und Abb. 5, Kurve 5).

Beim $CdRH^+$-Chelat ergeben sich die Werte des mol. Extinktionskoeffizienten für 500 nm zu:

ε_1	Bemerkung
30600	bei pH 4,7–6,1, gemäss der Gl.(31)
32300	gemäss der Gl.(32)
37100	bei pH 9 für äquimol. Lsg. aus dem horizontalen Ast der pH-Extinktionskurve.

Der Anstieg des mol. Extinktionskoeffizientenwertes bei pH = 9 und die Verschiebung des Maximums der Job-Kurven zu höheren Verhältnissen $x = c_R/(c_M + c_R)$ kann auch hier durch die gleichzeitige 1:2-Chelatbildung erklärt werden.

Die TAR-Chelate in festem Zustand

In den Lösungen von Cadmium, Zink und Blei scheiden sich in schwach saurem Medium (pH ~ 3) bei höheren Konzentrationen schwarzviolette kristalline Produkte aus. Die Analysenwerte entsprechen allgemein der Bildung eines ladungsfreien Chelates mit der Zusammensetzung $M(RH)_2 \,.\, H_2O$. Aus Lösungen von Kupfer(II)salzen scheidet sich mit TAR auch bei grossen Komponentenkonzentrationen kein Niederschlag aus.

Herstellung: Alkalische 0,001*M* Lösungen von TAR wurden mit verdünnter Perchlorsäure auf pH = 8 gebracht, filtriert und äquimolare Metallnitratlösungen zugegeben. Dabei sinkt der pH-Wert der Lösungen infolge Abspaltung von Protonen auf pH = 3. Die Lösungen wurden mit dem Niederschlag *ca.* 1 Std. auf dem Wasserbade erhitzt, die feinen Kristalle nach mehrtägigem Stehen abgesaugt und das mitgerissene Reagens sorgfältig mit Wasser und Äthanol ausgewaschen. Die Komplexe wurden zum Teil an der Luft, zum Teil über Calciumchlorid, Silikagel und Phosphorpentoxid getrocknet. Beim Trocknen an der Luft behalten sie *ca.* 1 Mol. Wasser, in zweitem Falle liegen die Wassergehalte niedriger und die Präparate sind etwas hygroskopisch. Besonders das Pb-Chelat kristallisiert in gut entwickelten Kristallen.

Die Analysenwerte der Tabelle VIII sind der Mittelwert von 2 Bestimmungen an Produkten aus äquimolaren Lösungen und aus Lösungen mit zweifachem Reagensüberschuss.

Absorptionsspektren der MRH-Chelate

Die Absorptionsspektren der MRH-Chelate haben 2 Maxima, wovon das erste bei 500–550 nm liegt und sich dem Maximum (510 nm) der völlig deprotonisierten Ligandform R^{2-} nähert. Eine anomale bathochrome Verschiebung des λ_{max} wurde bei dem Cd RH^+-Chelat beobachtet. Das kleinere kurzwellige Maximum bei 450 nm nähert sich jenem der nicht dissoziierten Form H_2R des Liganden (410–440 nm). Das kurzwellige Maximum verschwindet beim Übergang zum normalen Chelat MR infolge der Dissoziation des Hydroxylprotons in 4-Stellung, das langwellige Maximum verschiebt sich dabei nur wenig zu kürzeren Wellenlängen.

TABELLE VIII

	$Cd(RH)_2 . H_2O$ (Mol. Gew. 570, 88)			
Berechnet	19,69% Cd	14,72% N	37,87% C	2,12% H
Gefunden	20,37% Cd	14,69% N	38,07% C	2,57% H
	$Zn(RH)_2 . H_2O$ (Mol. Gew. 523,85)			
Berechnet	12,48% Zn	16,04% N	41,27% C	2,81% H
Gefunden	13,09% Zn	16,15% N	42,27% C	2,71% H
	$Pb(RH)_2 . H_2O$ (Mol. Gew. 665,68)			
Berechnet	31,13% Pb	12,63% N	32,47% C	1,82% H
Gefunden	36,15% Pb	11,74% N	30,39% C	2,01% H

In den Absorptionsspektren der Cadmium, Zink und Bleichelate in sauren Lösungen wird das kurzwellige Maximum durch Überlagerung der Absorption des freien Ligandes undeutlich.

DISKUSSION

In wässrigen Lösungen bildet 4-(2-Thiazolazo)resorcin mit Bi^{3+} Cu^{2+}, Pb^{2+}, Zn^{2+} und Cd^{2+} 1:1-Chelate bei $pH \leqslant 3$ unter Abspaltung des o-Hydroxylprotons zur Azogruppe. In Abhängigkeit vom pH Wert der Lösung bildet sich ein protonisiertes Chelat gemäss den Gleichgewichten (A) und (B) (Siehe S. 5):

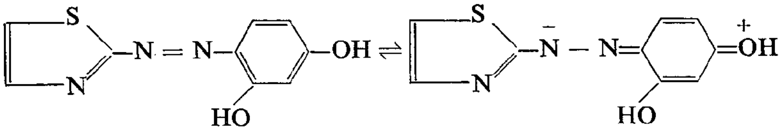
Bei $pH = 3$–$7{,}5$ dissoziiert das p-Hydroxylproton oder es reagiert ab $pH = 6$ bereits das Farbstoffanion HR^- gemäss:

$$MRH \rightleftharpoons MR + H^+ \tag{M}$$

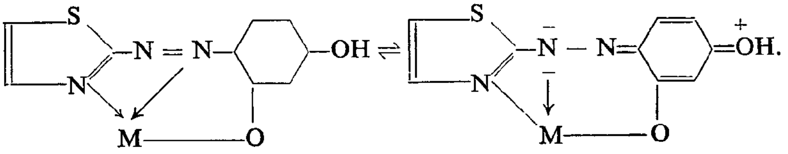
und (C) (Siehe S. 7).

Das Proton des *p*-substituierten Hydroxyls ist nach der Bindung des Liganden an das Metallion beweglicher und die erhöhte Acidität dieser protonisierten MRH-Chelate ist der Chelatstabilität proportional, wie schon früher Freiser u.a.[9] bei den PAR-Chelaten bewiesen haben. Am deutlichsten wirkt sich daher der Säurecharakter von MRH-Chelaten bei den stabilen Cu^{2+}- und Bi^{3+}-Chelaten aus.

Ähnlich wie bei PAR kann die erhöhte Acidität des *p*-Hydroxylprotons im Metallchelat auf die Verschiebung des Mesomeriegleichgewichtes



zur chinoiden Grenzstruktur, die durch die Chelatbildung stabilisiert wird zurückgeführt werden. Dies könnte jedoch die Struktur der Metallchelate in Frage stellen:



(I) (II)

In Vergleich mit 4-(2-Pyridinazo)resorcin halten wir auch bei TAR die Struktur (I) für wahrscheinlicher.

Die Bildung eines MR-Chelates, das als Zwitterion auftreten muss, bzw. eines MR(OH)-Chelates bei Bi(III) wurde auch mittels Papierelektrophorese in pufferfreien und gepufferten Lösungen mit $c_R = 1{,}76.\ 10^{-4}M$ und 50–100 fachen Metallion–überschuss, bei Cu^{2+} für pH 4–6, Bi^{3+} für pH 1,9, Pb^{2+} für pH 4–5, Zn^{2+} für pH 4–6 und Cd^{2+} ebenfalls für pH 4–6 bestätigt.

Im Vergleich mit PAR ist die Tendenz 1:2-Metallchelate bei pH = 3,5 zu bilden bei TAR stark herabgedrückt, insbesondere in äquimolaren Lösungen und in jenen mit Metallionenüberschuss. Die Tendenz zur Dreizähligkeit ist bei TAR stark angewachsen.

In Lösungen mit Ligandenüberschuss werden die Bereiche der MR-Chelatbildung bei pH > 5 durch die Gleichgewichte:

$$M + 2H_2R \rightleftharpoons M(RH)_2 + 2H^+ \qquad (N)$$

$$M(RH) + H_2R \rightleftharpoons M(HR)_2 + H^+ \qquad (O)$$

überlappt, jedoch in vernachlässigbarem Ausmasse bei Blei, und wenig bei Zink und Cadmium.

Die Gleichgewichte (N), (O) erhalten Bedeutung, wenn sich die Chelate $M(RH)_2$ dieser Metallionen in festem Zustand ausscheiden oder auch in nichtwässrige Lösungsmitteln extrahiert werden.

Die Zinkchelate mit TAR und seiner 5-Alkylderivate sind bei pH > 5 als ladungsfreie $M(RH)_2$-Chelate mit Methylcyklohexanon extrahierbar. Ab pH > 7,5 wird das *p*-Hydroxylproton abgespalten und das MR_2^{2-}-Chelat geht in die wässrige Phase.[13]

Kupfer(II) bildet mit TAR infolge der verstärkten Dreizähligkeit dieses Liganden und der Verzögerung des Kupfers die Koordinationszahl 4 in den Komplexen zu überschreiten kein 1:2-Chelat in weitem pH-Bereich. Auch das neutrale CuR^0 Chelat wird infolge des starken Dipolcharakters dieses Chelates (Zwitterion) nicht extrahiert.

Gleichgewichts- und Stabilitätskonstanten der Metallchelate

Aus den Gleichgewichtskonstanten $k_{1,1}$ und $k_{1,2}$ (siehe S. 5) wurde direkt die Stabilitätskonstante der protonisierten Chelate berechnet:

$$K_{1H} = [MRH_{(p)}]/[M][H_{(p)}R] \qquad (35)$$

$$K_{1H} = k_{1,2}/K_{a1} \cdot K_{a3} = k_{1,1}/K_{a3} \qquad (36)$$

Im Chelat liegt ausschliesslich das Anion $H_{(p)}R^-$ vor und die Berechnung der Konstanten erfolgt wieder unter der Voraussetzung[14]

$$[H_{(p)}R][H]/[H_2R] = [R][H]/[HR] = K_{a3}.$$

Bei pH < 4,5 geht es unter weiterer Bindung eines Protons in die nicht disoziierte Form H_2R über.

Der Logarithmns der Gleichgewichtskonstanten $k_{1,1}$, $k_{1,2}$ und der Stabilitätskonstante K_{1H} der untersuchten protonisierten Chelate sind in der Tabelle IX zusammengestellt und mit den Werten der analogen PAR-Chelate[8] verglichen.

Tabelle IX.—Gleichgewichts- und Stabilitätskonstanten der TAR und PAR-Chelaten.

	TAR			PAR		
	log $k_{1,1}$	log $k_{1,2}$	log K_{1H}	log $k_{1,1}$§§	log $k_{1,2}$	log K_{1H}
$CuRH^+$	2,11*; 2,09†; 2,18†	−1,11‡	11,56	4,6	1,5	16,5
$BiRH^{2+}$	3,7§	2,7	13,11	5,3	2,2	17,2
$PbRH^+$	−1,01‖; −1,02‖‖; −1,03¶	−1,98	8,34	0,0	−3,1	11,9
$ZnRH^+$	−2,20*** −2,19**; −2,36** −2,2††	−3,21	7,19	−0,3	−3,4	11,6
$CdRH^+$	−2,44**‡‡	−3,40	6,96	−1,4	−4,5	10,5

* Gemäss Gl.(16).
† Gl.(17).
‡ Gl.(21).
§ Gl.(25).
‖ Gl.(27).
¶ Gl.(28).
** Gl.(32).
†† Für 540 nm (die mol. Extinktionskoeffizienten des protonisierten und normalen Chelates haben ähnliche Werte) von dem Halbstufenwert der pH-Kurve.
‡‡ Für 560 nm.
§§ Das Gleichgewicht ist praktisch vernachlässigbar.
‖‖ Gl.(29).
*** Gl.(30).

Die Säure-Base-Konstante der MRH-Chelate:

$$k_{a1} = [MR][H]/[MRH] \qquad (37)$$

kann nur für das Kupferchelat aus dem Halbstufenwert des zweiten aufsteigenden Astes der Extinktion-pH-Kurve oder deren logarithmischer Analyse für Lösungen mit Metallionüberschuss direkt ermittelt werden (Abb. 6), da in diesem Falle die Bildungsbereiche beider Chelate gut getrennt sind.

Der Wert log $k_{a1} = -4{,}24$ liegt in guter Übereinstimmung mit jenem von Kolařík (log $k_{a1} = -4{,}15$).[12]

Die Konstante $K_1 = [MR]/[M][R]$ für das normale Chelat kann aus den entsprechenden K_{1H}, k_{a1} und K_{b2}-Werten abgeleitet werden.

$$K_1 = K_{1H} \cdot k_{a1} \cdot K_{b2} \qquad (38)$$

Für das Kupferchelat ergibt sich mit log $k_{a1} = -4{,}24$, log $K_{1H} = 11{,}56$ und log $K_{b2} = 6{,}23$ der Wert log $K_1 = 13{,}55$.

Die Stabilitätskonstanten für beide Ligandensysteme fallen in der selben Reihefolge ab. Die Stabilität der TAR-Metallchelate ist wesentlich geringer als die der analogen PAR-Chelate. Die Tendenz zur MRH-Bildung ($k_{1,2}$) von H_3R^+ in saurem Medium ist mit Ausnahme von Cu^{2+} bei TAR grösser. Dies beweist eine direkte Proportionalität zwischen der Tendenz der Komplexbildung und dem Säuregrad des Thiazoliumkation im Gegensatz zu der umgekehrten Proportionalität des Säuregrades der 2-Hydroxylgruppe. Dies kann so gedeutet werden, dass bei der TAR und PAR-Chelatbildung im ersten Schritt die Bindung Metall-Stickstoff eintritt und erst in der Folge der Chelatring über die 2-Hydroxylgruppe geschlossen wird.

Hierauf weist auch die Tatsache hin, dass sich bei Kupfer(II) kein 1:2-Chelat mit TAR bildet oder ausscheidet, weil es in Chelaten die Koordinationszahl 4 bevorzugt.

Gemäss diesen Tatsachen besitzt TAR im Vergleich mit PAR bei seiner Anwendung in der analytischen Praxis keinen Nachteil mit Ausnahme der begrenzten Löslichkeit der H_2R-Form in Wasser. Vorteilhaft kann TAR für die spektralphotometrische Bestimmung von Metallen eingesetzt werden, die schon in saurem Medium mit der H_3R^+-Form des Reagenses stabile Chelate bilden.

Spektralphotometrische Bestimmung von Kupfer

Als Grundlage wurde das Chelat $CuRH^+$ (λ_{max} 560 nm, $\varepsilon_1 = 1{,}94 \,.\, 10^4$) ausgewählt, dass sich bei pH = 2,7 — 3,4 bereits bei einem Ligandenüberschuss $p = c_R/c_M \geqslant 4$ quantitativ bildet. In diesem pH Bereich ist der optische Einfluss des überschüssigen Ligandes, der als H_2R in der Lösung vorliegt, klein.

Bei pH $\sim$ 6 im Bildungsbereich des CuR-Chelates ist zwar die Extinkion der Lösungen grösser ($\varepsilon_1 = 3{,}1 \,.\, 10^4$ bei 510 nm), doch sinkt die Selektivität und auch die Extinktion des überschüssigen Reagenses stört erheblich. Die Gegenwart von 30 Vol% Äthanol vermeidet die eventuelle Ausscheidung des überschüssigen Reagenses während der Bestimmung. Die optischen Eigenschaften des Chelates werden dadurch nicht beeinflusst.

Die Ionenstärke der Lösung ist bis zu Werten $\mu = 1{,}9$ ohne Einfluss. Auch eine 0,1*M* Natriumformiat-Konzentration als Pufferlösung beeinflusst die Extinktion der Lösung nicht.

Ausführung:

In einem 50-ml Messkolben werden 15 ml 0,02%-ige Lösung von TAR in Äthanol, 5 ml 1*M* Formiatpuffer (pH = 3,1) und die schwach saure oder neutrale Probelösung zugegeben, der pH-Wert eventuell mit verdünntem Ammoniak auf pH 3,4 korrigiert und die Lösung zur Marke aufgefüllt.

Formiatpuffer:

38 ml HCOOH 98–100% und 8 g NaOH in 1000 ml Lösung.

Das Lambert-Beersche-Gesetz ist bis 5,2 μg Cu/ml streng erfüllt. Die Empfindlichkeit ist 0,034 μg Cu/cm^2 für A = 0,01 und 555–560 mm. Die Reproduzierbarkeit der Messwerte ist ±0,7% für 1,4–2,7 μg Cu/ml. Die Extinktion ist auch nach 24 Stunden unverändert.

Einfluss fremder Ionen:

ClO_4^-, NO_3^-, Cl^-, Br^-, PO_4^{3-} stören auch bei grossem Überschuss nicht. Störend wirken sich Schwermetallspuren als Verunreinigungen der Analysenreagenzien aus. Der Einfluss einiger anderer Ionen ist in der Tabelle X zusammengefasst.

TABELLE X.—EINFLUSS EINIGER FREMDER IONEN AUF DIE SPEKTRALPHOTOMETRISCHE BESTIMMUNG VON KUPFER (2,62 μg Cu/ml bzw. 2,07 μg Cu/ml)

Ion	μg/ml	Δrel. % der Cu-Bestimmung
SO_4^{2-}	2980	−4,6
Al^{3+}	270	0
Cd^{2+}	335	+5
Zn^{2+}	52	+3,4
Pb^{2+}	21	+4,7
Co^{2+}	0,7	+5
Fe^{3+}	0,6	+5,3
Ni^{2+}	0,4	+0,7
Bi^{3+}	0,2	+3,4

Spektralphotometrische Bestimmung von Wismut

Für die Bestimmung eignet sich pH = 2,8–4 in Gegenwart eines Reagensüberschusses $p = c_R/c_M \geqslant 7$ und 30 Vol% Äthanol in Lösungen mit einer Ionenstärke $\mu = 0{,}1$. In diesem pH-Bereich bildet sich das BiR^+-Chelat (λ_{max} 540–545 nm, $\varepsilon = 3{,}1 \,.\, 10^4$ bei 540 nm) quantitativ. Puffer aller Art vermindern bei 540 nm die Extinktion der Lösung, 0,1*M* Formiat bei pH = 3,1 um 26%, 0,1*M* Chloracetat bei pH = 2,6 um 34% und 0,075*M* Glykokol mit pH = 2,7 um 26%. Man kann jedoch bei konstanter Pufferkonzentration arbeiten, wenn entsprechende Eichkurven für Standardlösungen mit gleichen Pufferkonzentrationen vorliegen, da die Befolgung des Lambert-Beerschen-Gesetzes in Gegenwart von Puffern dieser Konzentration unbeeinflusst bleibt.

Ausführung

In 50-ml Messkolben werden nachträglich 15 ml 0,03% Lösung von TAR in Äthanol und einige Tropfen verdünnter Perchlorsäure bis zur rein gelben Farbtönung der Reagenslösung und schliesslich die Probelösung zugegeben, die bis 0,4 mg Wismut als Nitrat oder Perchlorat enthält. Der resultierende pH-Wert von 2,8–4 wird mit verdünntem Ammoniak unter kräftigen Rühren eingestellt und die Lösung zur Marke aufgefüllt. Das Lambert-Beersche Gesetz für 530 oder 540 nm wird bis zu 8,3 μg Bi/ml streng befolgt. Die Empfindlichkeit ist 0,064 μg Bi/cm² für A = 0,01. Die Reproduzierbarkeit der Messungen für 3,8–5,0 μg Bi/ml ist ±1% rel. Der Einfluss einer Reihe von Ionen auf die Bestimmung von Bi^{3+} ist in der Tabelle XI zusammengefasst.

TABELLE XI.—EINFLUSS FREMDER IONEN AUF DIE SPEKTRALPHOTOMETRISCHE BESTIMMUNG VON WISMUT (4,4 μg Bi/ml)

Ion	μg/ml	Δrel. % der Bi-Bestimmung
NO_3^-	55200	−7,5
Cl^-	91	−4,3
Br^-	134	−4,5
SO_4^{2-}	119	−7,5
Mn^{2+}	1620	+5,2
Cd^{2+}	586	+2,4
Zn^{2+}	196	+5,1
Al^{3+}	216	+2,6
Pb^{2+}	53	+5,9
Fe^{3+}	0,22	+7,4
Cu^{2+}	0,19	+6,1

Die Elementaranalyse der Präparate wurde unter der Leitung von Ing. Synek im Forschungsinstitut für organische Synthesen in Pardubice-Rybitví ausgeführt.

Das 4-(2-Thiazolazo)resorcin wird bei der Fa. "Lachema" (Ing. V. Svoboda), Brno hergestellt.

Summary—A spectrophotometric investigation of the complex formation of 4-(2-thiazolylazo)resorcinol with copper(II), lead(II), zinc(II), cadmium(II) and bismuth(III) shows that protonated and normal 1:1 chelates predominate, although 1:2 chelates are also formed in part. The equilibria which are present and the stability, optical properties and applicability of the chelates in the spectrophotometric determination of these metals have been studied. The reagent is particularly suitable for the determination of copper and bismuth.

Résumé—Une étude spectrophotométrique de la formation de complexes entre le 4-(2-thiazolylazo)résorcinol et le cuivre(II), le plomb (II), le zinc(II), le cadmium(II) et le bismuth(III) montre que les chélates protonés et normaux 1:1 prédominent, bien que des chélates 1:2 se forment aussi en partie. On a étudié les équilibres en présence, ainsi que la stabilité, les propriétés optiques et les possibilités d'application des chélates au dosage spectrophotométrique de ces métaux. Le réactif convient particulièrement aux dosages du cuivre et du bismuth.

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Talanta, 1966, Vol. 13, pp. 689 to 700. Pergamon Press Ltd. Printed in Northern Ireland

PHOTOMETRIC DETERMINATION OF NIOBIUM WITH AZO-DYESTUFFS

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(*Received* 7 *October* 1965. *Accepted* 16 *November* 1965)

Summary—The azo-dyestuffs, which contain the analytically functional *O,O'*-dioxyazo group and are widely employed as photometric reagents for niobium, are reviewed. Two new groups of reagents are described: mono-azo-dyestuffs based on R-salt and 2,7-bisazo dyestuffs based on chromotropic acid. The reaction with niobium is sensitive ($\varepsilon = 20{,}000$ to 40,000), selective and takes place in strongly acidic solution (0·5–6*M* hydrochloric or nitric acid). It is possible to extract with butanol the diphenylguanidine salt of the corresponding niobium complex and to measure the absorbance of the extract.

INTRODUCTION

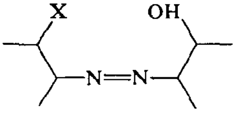
NIOBIUM is an element whose analytical chemistry is complex; methods for its colorimetric determination, in particular, have always presented difficulties. It is sufficient to record that until recently, the number of known inorganic and organic reagents, giving with niobium characteristic and specific colour reactions, were few (potassium thiocyanate, hydrogen peroxide, Pyrocatechin).[1] Latterly, with the general rapid increase in photometric analytical methods and the advent of new reagents, some rather interesting colour reactions of niobium have been described, *e.g.*, with such reagents as Xylenol Orange, Phenylfluorone, Bromopyrogallol Red, quercetinsulphonic acid, *etc.* A very promising class of reagents for the photometric determination of niobium is the azo-dyestuffs, which embody in their structure characteristic analytically functional groupings for niobium.

A study of azo-compounds as analytical reagents has always interested many investigators. This is possibly explained by the large variety of standard azo-dyestuffs available to analysts and also by the ease of synthesis of new compounds by well tried methods. Other equally important factors are their valuable analytical properties: highly sensitive colour reactions, good solubility, stability, widely favourable conditions for determining elements, *e.g.*, at low pH values, and moreover, high selectivity.

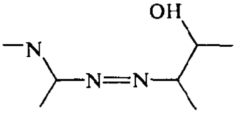
New azo-dyestuff reagents, synthesised during the last few years, have proved especially valuable for rare elements and actinides.[2] A series of compounds is suggested for niobium; so far, they do not exceed ten in number. On the whole, it is a group of reagents described earlier for other elements, but certain new compounds are also of value. Below, on the basis of original work,[3–16] a very short review is given of azo-compounds, described as photometric reagents for niobium.

Azo-Compounds with O,O′-Substituents

The most interesting reagents for niobium are azo-compounds containing two salt-producing groups in the *ortho*-position to the azo-group; one of these groups is usually hydroxyl:



$X = AsO_3H_2$, COOH, OH
(Arsenazo I, Lumogallion, *etc.*)



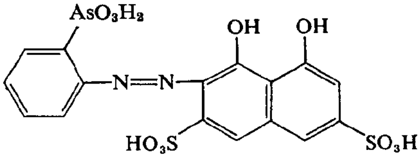
pyridylazoresorcinol and other
pyridine azo compounds

Colour reactions with niobium are possible with other substituents at X and other radicals to the left of the azo group (diazo components); but, in the absence of an oxy-grouping, a colour reaction with niobium is not observed. In general, the nature of the azo-reagent determines whether the colour reaction is positive or negative, and the nature of the diazo-component whether the reagent is analytically useful.

The nature of the reaction is incompletely understood, but the colour is probably due to the formation of reagent chelate salts with incompletely hydrolysed niobium ions. During complex formation, deep colours are generally observed: from yellow and red (the reagent) to crimson, violet and deep blue. A sharp colour change observed visually with $10^{-5}M$ reagent solution during the addition of equal amounts of niobium, indicates that the reaction has a certain practical interest. The observed colour change of more concentrated solutions of many azo-dyestuffs on the addition of niobium salts is often caused by secondary effects, *e.g.*, separation of precipitates, *etc.* Such reactions are of less practical interest.

Arsenazo I

The well-known reagent Arsenazo I, previously successfully used to determine many elements, has been used as a reagent for the photometric determination of niobium.[4,5] The reaction is a low contrast one (colour change from red to violet-red), carried out at pH 2, with a sensitivity of about 5 μg/ml.

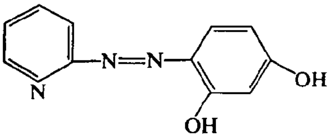


Arsenazo I

The presence of the general purpose *O*-arsono-*O′*-oxyazo-grouping, characteristic for many elements, and of low acidity, produces low specificity in the method for determining niobium. A review of the properties and specificity of other known reagents containing the same functional grouping,[6] shows that although colour reactions are observed with niobium in certain cases, they possess insufficient contrast and so are analytically of little interest.

2-(2-*Pyridylazo*)*resorcinol* (*PAR*)

A comparatively new class of organic reagents, pyridine azo-compounds, finds increasing analytical application. We would draw attention to a recent review, in which for PAR and other reagents of this group, methods are described for the photometric and complexometric determination of about 30 elements.[7]



2(2-pyridylazo)resorcinol

PAR is a sensitive reagent for niobium: the molecular extinction coefficient ε varies from 25,000 to 35,000, depending on the experimental conditions.[8–12]

A colour reaction arises from the presence in solution of a third component: tartaric, citric, oxalic acids, EDTA, hydrogen peroxide, *etc.* Niobium reacts with PAR in the form of complexes with these reagents; the final reaction product evidently consists of the corresponding ternary complex.[10] The same components in various combinations are used as masking substances, which in combination with the possible extraction of the coloured complex, offers a highly selective method for determining niobium with PAR. Niobium forms with PAR two series of complexes. At pH 5·8–6·5 a complex is formed with maximum absorption at 555 mμ and $\varepsilon = 31{,}200$; in 0·1–0·2N Sulphuric acid, the complex has $\lambda_{\max} = 530$ mμ and $\varepsilon = 16{,}500$.[13]

A reagent with a similar functional grouping, 1-(2-pyridylazo)-2-naphthol, also gives a less sensitive colour reaction with niobium at pH 6.

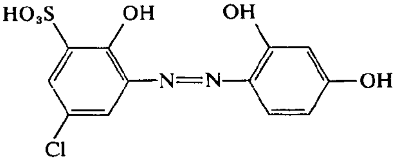
Reagents Containing the O,O′-Dioxyazo Grouping

Mono- and polyazodyestuffs containing the *O,O′*-dioxyazo grouping are widely used in analytical chemistry for the photometric determination or the extraction of a series of elements. As reagents, those most usually employed are the monoazo-compounds, the products of azo-coupling of diazotised aromatic amines with various azo-components, mainly naphthol- and aminonaphtholsulphonic acids: H-acid, chromotropic acid, Chicago CC, Y-acids, R-salt and also β-naphthol, resorcinol and many other compounds capable of azo-coupling.

The functional *O,O′*-dioxyazo grouping is fairly universal; it is characteristic for zirconium, aluminium, magnesium, scandium, molybdenum, zinc, calcium, cadmium, copper, *etc.* However, because in this grouping no salt-producing groups are incorporated except hydroxyl, the conditions (pH) under which colour reactions with the elements are observed are in good agreement with the pH of hydrolysis of these elements. Therefore, in the case of readily hydrolysed elements (niobium, zirconium, *etc.*), it is possible to attain sufficiently high specificity by varying the acidity of the medium.

Lumogallion

From the reagents with this grouping we must first of all consider Lumogallion.[11,13,14]

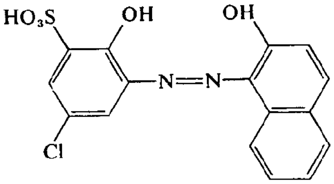


Lumogallion

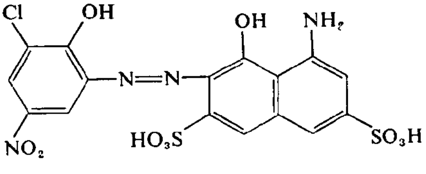
This reagent, proposed for the luminescent determination of gallium, is of special interest for niobium, with which in a sufficiently acidic medium, it forms a stable, intensely coloured compound with a molar extinction coefficient of 16,800. The complex is formed by heating in tartaric acid solution made 0·5–2·0N in sulphuric or hydrochloric acid and it is stable for more than 1 hr. The complex is reasonably stable: tartaric and citric acids do not interfere with the reaction, but strongly by complexing substances, such as EDTA or oxalic acid, can be present only in limited amounts.

The niobium complex with Lumogallion can be extracted from sulphuric acid, over the concentration range of 0·1–6N, by polar solvents. Photometric determination after extraction markedly increases the selectivity of the method.

Approximately the same spectrophotometric characteristics are possessed by the colour reactions of niobium with Magneson and Gallion.



Magneson

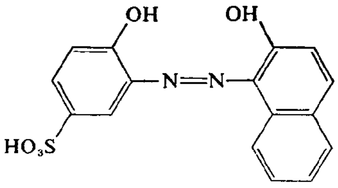


Gallion

The following features of the extraction of the niobium-Gallion complex should be noted.[13] Over the pH range 0·5–3·5, the complex is completely extracted by polar solvents (butyl, isobutyl, amyl, and isoamyl alcohol) only in the presence of diphenylguanidine salts. Non-polar solvents (benzene, chloroform, carbon tetrachloride) do not extract the complex, but mixtures of benzene or chloroform with alcohols in the ratio 1:2 do.

Anthracene Chrome Violet

A feature of the use of the reagent is a fairly high permissible acidity for carrying out the reaction, 0·5–1·5M hydrochloric acid,[13,15,16] but the reaction sensitivity is low ($\varepsilon = 8000$).



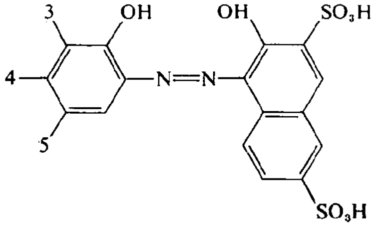
Anthracene Chrome Violet

The reagent and the niobium complex are not very water-soluble, which creates operational difficulties in practical analysis.

Approximately the same properties and spectrophotometric characteristics are possessed by the niobium complexes of similar structure based on β-naphthol.

Reagents Based on R-salt Containing the O,O′-Dioxyazo Group

In contrast to the Anthracene Chrome Violet reagent of this group, those containing two sulphonic acid groups in the naphthalene nucleus possess greater solubility and better spectrophotometric characteristics.[3,17–19] Examples are:



3,5-diNO_2-picramine R

3-NO_2,5-SO_3H-nitrosulphophenol R

3-SO_3H,5-Cl-sulphochlorophenol R

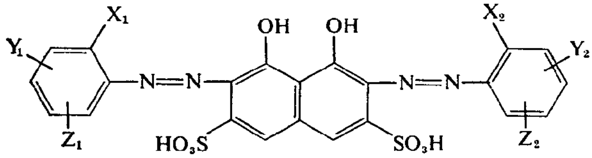
3-Cl,5-NO_2-chloronitrophenol R, *etc.*

The niobium determination is carried out in 1–3*M* hydrochloric acid, in an aqueous, aqueous-acetone or aqueous-alcohol medium; $\varepsilon = 10{,}000$–$15{,}000$. The reaction is selective: the major interferences are zirconium, oxalate, and fluoride in large amounts. The effect of zirconium is overcome by adding EDTA.

The niobium complexes formed with the reagents listed can be extracted by the higher alcohols, which substitute for water of hydration in the complexes.[20–23] To neutralise the negative charge on the complex, salts of heavy organic cations, *e.g.*, diphenylguanidine $[(C_6H_5NH)_2CNH_2]^+$ must be added. In strongly acid media where dissociation of the reagent is slight the heavy organic cations are unnecessary.[23,24] Extraction proceeds with practically no colour fading, so that the absorbance can be measured directly in the organic phase without re-extraction. The method can be used also for the determination of niobium in coloured solutions. With reagents of this type, the extraction variation is evidently preferable to direct photometry.

Bisazo-Dyestuffs Based on Chromotropic Acid

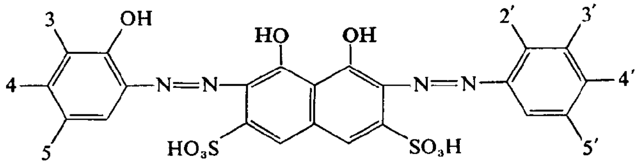
This group of reagents finds an increasing analytical applicability. Most of the papers are devoted to Arsenazo III, from which methods of determination for more than 20 elements have been developed.[6,25–27] Latterly, there has been synthesised and studied a greater number of structural analogues of Arsenazo III, 2,7-bisazo-derivatives of chromotropic acid, both symmetrical and non-symmetrical, containing various substituents:[3,6,18,20,26–31]



where X, Y and Z are H, Cl, Br, NO_2, *O*-alkyl, *N*$_2$-aryl, OH, SO_3H, COOH, PO_3H_2, AsO_3H_2, *etc.*

It seems that these reagents, like Arsenazo III, have the general ability to produce with elements extra stable complexes, exceeding by an order of 2–3 the stability of the complexes with the corresponding mono-azo derivatives. The colour reactions with elements are generally quite sensitive (ε = 30,000–60,000 and for certain systems can reach 130,000) and proceed in strongly acid media. Certain reagents studied for niobium are tabulated in Table I.

TABLE I.—COLOUR REACTIONS OF NIOBIUM WITH BISAZO-DERIVATIVES OF CHROMOTROPIC ACID

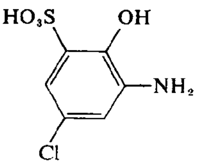


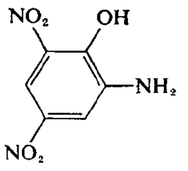
Sequence	Substituents	Name*	$\Delta\lambda$, mμ	Sensitivity, μg/ml
1	2′-OH, 3,3′-diSO_3H, 5,5′diCl	Sulphochlorophenol C	65	0·1
2	3-SO_3H, 5-Cl, 1″-OH, 3″,8″-diSO_3H	Sulphochlorophenol AE	60	0·3
3	3,5-diNO_2, 1″-OH, 3″,8″-diSO_3H	Picraminic AE	60	0·3
4	3-NO_2, 5-SO_3H, 1″-OH, 3″,8″-diSO_3H	Nitrosulphophenol AE	60	0·2
5	2′-OH, 3,3′-diNO_2, 5,5′-diSO_3H	Nitrosulphophenol C	40	0·2
6	3-SO_3H, 5-Cl, 2′-OCH_3, 5′-$SO_2N(CH_3)_2$		45	0·3
7	5-SO_3H, 2′-OH		35	0·6
8	3,5-diNO_2, 3′-SO_3H	Picraminic M	65	0·2
9	3-SO_3H, 5-Cl, 3′-SO_3H	Sulphochlorophenol M	55	0·1
10	5-NO_2, 3′-SO_3H		40	0·3
11	5-Cl, 3′-SO_3H		40	0·3
12	5-SO_3H, 3′-SO_3H		20	0·5
13	3′-SO_3H		10	0·8
14	4-NO_2, 3′-SO_3H		10	0·4

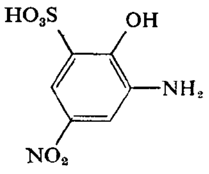
* C is symmetrical; reagents 2–4 instead of the second benzene nucleus contain the radical 1 hydroxy-2-aminonaphthalene-3,8-disulphonicacid—amino-ε-acid (AE); reagents 8–14 contain metanilic acid (M) as a second diazo substituent.

A systematic study of the reagents, azo-dyestuffs based on R-salt and chromotropic acid, has shown that analytical interest rests only in those which contain the diazo moiety electronegative substituents: —NO_2, —Cl, —Br, —SO_3H, *etc.* The location of the substituent exerts an effect: a positive analytical effect is observed on introducing substituents into the 3,3′ and 5,5′ positions, whereas reagents containing such substituents in the 4,4′ position either do not usually give colour reactions with niobium or the reactions produce so little colour contrast that they were of little interest for analytical application. This rule is easily seen in derivatives of metanilic acid (compounds 8–14).

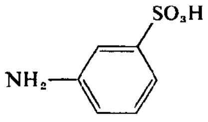
It should also be noted that, other conditions remaining the same, of more interest analytically are the symmetrical reagents (1 and 5) containing as diazo constituents, the amines

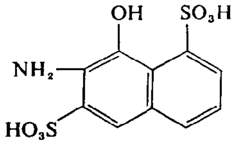






or the non-symmetrical reagents (2–4, 8, 9) containing as the second diazo constituent metanilic or amino-ε-acid:

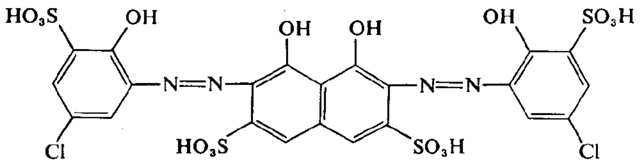




Because of the ease of synthesis and availability of the intermediates, for practical purposes, out of several equivalent reagents (1–4), sulphochlorophenol C was chiefly employed and its properties were studied in more detail.

Properties and analytical application of sulphochlorophenol C

Sulphochlorophenol C consists of a dark red powder, moderately (up to 1 %) soluble in water; the solution is stable indefinitely when kept in air, but powerful reducing or oxidising substances decolourise it. The colour of aqueous acidic solutions is red or violet-red according to the concentration; in the presence of niobium they are deep blue.



Sulphochlorophenol C

Figure 1 shows the absorption spectra of the reagent and its niobium complexes for various degrees of acidity. The maxima are 560 mμ for the reagent and 610 and 615 mμ for the complexes. The colour reaction of niobium with sulphochlorophenol C develops either in water or in aqueous acetone or aqueous ethanol. In the last two cases, reaction sensitivity increases somewhat as does the stability of the solutions.

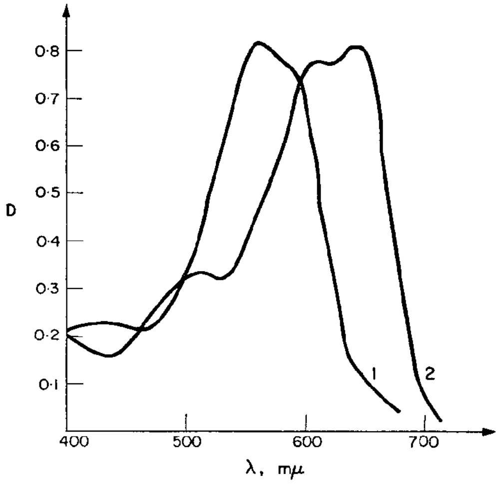


FIG. 1.—Absorption spectra of sulphochlorophenol C [1] and its complex with niobium [2].
Reagent concentration is 1·8 × $10^{-5}M$; niobium is 5·7 × $10^{-5}M$ (SF-4 spectrophotometer, l = 10 mm).

At room temperature, 30 min are needed for the reaction to go to completion, at 40° about 10 min and at 80° less than 5 min.

The pH range of the niobium-sulphochlorophenol C reaction is sufficiently large: 0·5–3*M* hydrochloric acid or 0·5–6*M* nitric acid (Fig. 2). At acidities above 3*M* in hydrochloric acid the reagent precipitates. In nitric acid the solubility is high and solutions are stable in 6*M* solutions. To remove nitrogen oxides, which oxidise the reagent, the nitric acid must receive preliminary treatment with urea or sulphamic acid. Determination of niobium in hydrochloric acid solution is usually carried out in 1*M* hydrochloric acid.

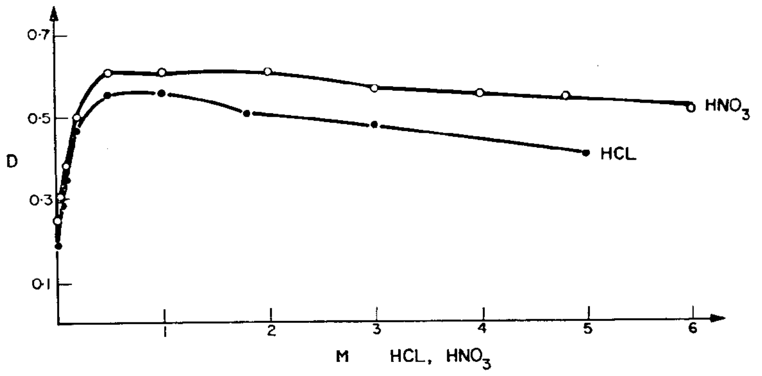


FIG. 2.—Effect of acidity on the colour reaction between niobium and sulphochlorophenol C.
Reagent concentration is 1·86 × $10^{-5}M$; niobium is 1·82 × $10^{-5}M$ (λ = 650 mμ, l = 10 mm, the reagent is the comparison solution).

Under these conditions the effect of certain complexing agents has been studied. The hydroxy acids (citric, tartaric), chloride, sulphate, phosphate, EDTA and other masking and complexing agents have quite a weak effect and in quantities up to 100–500 mg/25 ml do not interfere with the determination of 1–50 μg of niobium. Oxalate and fluoride have a marked effect. The permissible amount of sodium fluoride is 2–3 mg/25 ml. In the presence of aluminium salts or boric acid, fluoride can be tolerated in greater amounts. The feeble effect of anions, especially hydroxy acids (measurements can be made in the presence of tartaric and citric acids), promotes increased stability and reproducibility of results in niobium determinations.

Specificity. Colour reactions with sulphochlorophenol C are given by zirconium, hafnium, scandium, molybdenum, bismuth, copper, zinc, rare earth elements, *etc.*, in addition to niobium. However, under the conditions for the determination of niobium ($> 1M$ hydrochloric or nitric acid) comparable colour reactions only arise in the presence of zirconium and hafnium. Their effect, at least up to a ratio of Nb:Zr = 1:100, may be completely eliminated by the addition of EDTA, potassium fluoride or certain other masking substances.

The effect of iron(III) is overcome by adding to the solution small amounts of ascorbic acid. Titanium does not interfere at a ratio of Nb:Ti = 1:100. Tantalum does not give a contrasting colour reaction, but amounts present greater than 0·1–0·25 mg/25 ml substantially lower the result of a niobium determination. Quantities of tantalum approximately equal to niobium do not interfere. For many other elements the permissible ratio is Nb:Me = 1:100–1000. The selectivity of the reaction is markedly increased by the use of a photometric-extraction procedure.[3,21]

The latter variation can be employed for the determination of niobium in coloured solutions, if the coloured substance is not extracted or with some modification during the determination of niobium in non-aqueous solvents, *e.g.*, after extraction with tributyl phosphate or other extracting agents.

Procedure. For the determination of niobium in non-aqueous solvents, take a 1–2 ml aliquot of the solution containing 3–30 μg of niobium and add up to 10 ml of a mixture containing 0·1% aqueous solution of sulphochlorophenol C, $6M$ hydrochloric acid, 20% aqueous solution of diphenylguanidine chloride, ethyl and butyl alcohols in the volumetric ratio 1:1:0·5:4:20. Heat the solution obtained for several minutes, cool, and measure the absorbance at 650 mμ. Prepare a calibration curve in the usual way.

Composition of the complex. The mechanism of complex formation and the nature of the colour reaction between niobium and sulphochlorophenol C present interesting features, which are being studied at the present time. For practical purposes, it is necessary to know the ratio of the reacting components.

Complexes of multivalent metals (thorium, zirconium, plutonium) with reagents of this type are generally of the form MeR or MeR_2.[26,27,32] The 1:1 complex (MeR) is formed when an excess of the elemental ion is present; the 1:2 complex (MeR_2) is more stable and exists over a wide range of acidity. The complex compounds of thorium, zirconium, plutonium(IV) and the rare earth elements with Arsenazo III have been well studied.[27,30–34] Only in certain cases, with a large excess of reagent, is it possible to propose the existence of more saturated complexes, *e.g.*, MeR_3.[33,34]

Figures 3 and 4 show spectrophotometric titration curves and curves of the isomolar series of the system niobium-sulphochlorophenol C, from which it is apparent

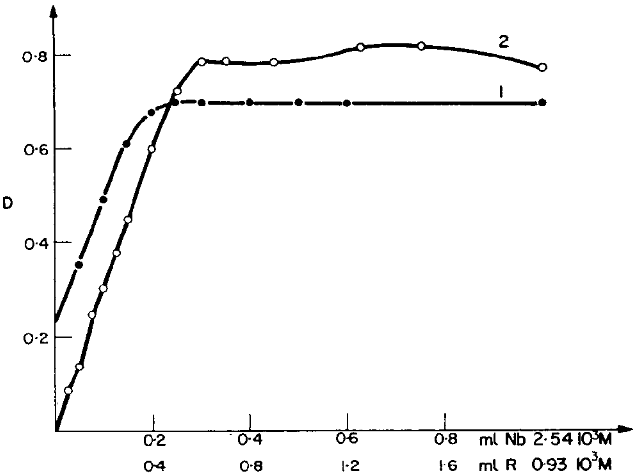


FIG. 3.—Spectrophotometric titration (1M HCl, V = 25 ml):

1. With a constant reagent concentration of $1 \cdot 86 \times 10^{-5}M$ (found Nb:R = 1:0·99).
2. With a constant niobium concentration of $1 \cdot 86 \times 10^{-5}M$ (found Nb:R = 1:1·04).

that the composition of the complex corresponds to a ratio of 1:1. The molar absorption coefficient for the complex is 33,000 at 650 mμ.

Some practical examples of the use of sulphochlorophenol C. Some practical methods are discussed for the determination of niobium in solutions of complex composition,[3] of zirconium-base alloys[35,39] and alloy steels.[3,6,37,39]

For the determination of 0·5–3 % of niobium in a zirconium-base alloy, dissolve a 50-mg sample of alloy by warming with 3 ml of conc. sulphuric acid and 2 g of ammonium sulphate. Evaporate the solution to dryness, and dissolve the residue by warming in 100 ml of 5 % tartaric acid solution. Transfer an aliquot portion containing 5–50 μg of niobium to a 25-ml volumetric flask, add 6 ml of 6·0M hydrochloric acid, 0·5 ml of 5 % EDTA solution, 2 ml of acetone, 1 ml of a 0·05 % solution of sulphochlorophenol C and make up almost to the mark with water. Heat for 10–15 min at 50–60°.

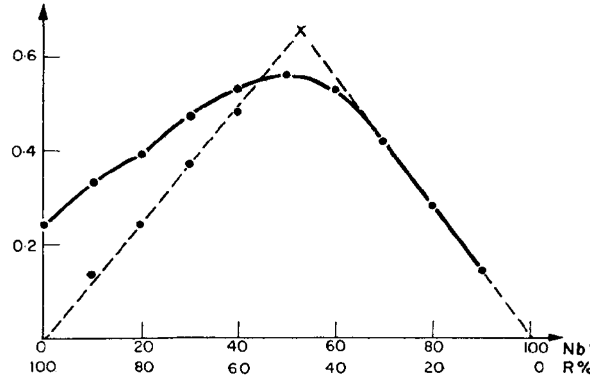


FIG. 4.—Graph of the isomolar series [Nb] + [R] = $3 \cdot 7 \times 10^{-5}M$ (1MHCl, l = 10 mm, λ = 640 mμ).

Cool and add water to the mark. Measure the absorption at 650 mμ in 10-mm cells. The niobium content is read from a calibrated curve prepared in the usual way.

For the determination of niobium in steels containing 0·05–2·5% of niobium, dissolve a 0·25-g sample in 30 ml of 20% sulphuric acid, add 1–1·5 ml of phosphoric acid and nitric acid dropwise. Evaporate to near dryness twice with sulphuric acid to remove any nitric acid. Add 15 ml of 20% tartaric acid solution and water until the salts dissolve completely, then make the whole up to 100 ml with water. Transfer an aliquot of 1–2 ml to a 50-ml flask, add 24 ml of hydrochloric acid (1 + 1), 1 ml of 0·1% sulphochlorophenol C solution and water almost to the mark. Heat for 5 min at 80°, cool and make up to the mark with water, then measure photometrically at 650 mμ using 10- or 20-mm cells. Prepare a calibration curve by taking a series of weighed amounts of steel free from niobium corresponding to the weights used for the analysis and add a known amount of niobium at the final stage.

The photometric-extraction variation for the determination of niobium in steel embodies extraction of the diphenylguanidine salt of the coloured niobium-sulphochlorophenol C complex with butanol when the acidity of the aqueous phase is equal to 1·5*M* hydrochloric acid. The coloured extract is measured photometrically and the niobium content is read from a calibrated graph.[37] The reproducibility and accuracy of the method are evident from the data of Table II.

TABLE II.—THE DETERMINATION OF NIOBIUM IN ALLOY STEELS

Nb found, %		
Gravimetric methods using phenylarsonic acid or by hydrolytic methods (mean)	Photometric method using sulphochlorophenol C	Photometric-extraction method using sulphochlorophenol C
0·8	0·76, 0·8	
	0·8	
0·36	0·36, 0·37	
0·40	0·41, 0·40	
	0·39, 0·40	
1·05	1·05, 1·04	
	1·04, 1·06	
0·99		0·97
0·037		0·035

Synthesis of sulphochlorophenol C. Synthesis of the reagent is carried out by reacting chromotropic acid with the diazonium compound of the corresponding aromatic amine, used in excess over the stoichiometric quantity, in a medium containing sodium carbonate, caustic soda or calcium hydroxide.[25,28,30] In the synthesis of sulphochlorophenol C, coupling proceeds satisfactorily in a calcium hydroxide medium even with equimolar ratios of the azo-coupling components.[3]

Stir 14 g of 2,4,6-aminochlorosulphophenol with 20 ml of concentrated hydrochloric acid and 150 ml of water. Cool, and through a narrow glass tube which reaches the bottom of the vessel, add, with thorough stirring, 3·9 g of sodium nitrite in 20 ml of water. As the material diazotises, it dissolves almost completely; filter off the small residue and discard it.

Dissolve 10 g of chromotropic acid disodium salt in 50 ml of water, place it in a vessel containing ice and, with thorough stirring, add simultaneously the solution of diazonium 2,4,6-aminochlorosulphophenol and a suspension of 20 g of calcium oxide in 150 ml of water, ensuring that the medium is always alkaline. The solution acquires at first a red-violet and then a deep blue colour. Allow to stand at room temperature for 1–2 hr. Acidify the reaction mixture by adding 1/5 of its volume of concentrated hydrochloric acid with careful mixing. Filter off the precipitated reagent and wash with dilute hydrochloric acid, water, and ethanol. Reprecipitate 2–3 times after dissolving in water by addition of sodium carbonate followed by the addition of hydrochloric acid. Paper chromatography is used to establish the homogeneity and purity of the product.

By a similar procedure other niobium bisazodyestuff reagents, based on chromotropic acid, are synthesised, in particular, nitrosulphophenol C, Arsenazo—amino-ε-acid, etc.

Zusammenfassung—Es wird eine Übersicht über die Azofarbstoffe mit der analytisch wesentlichen *O,O′*-Dioxyazogruppe gegeben, die weithin als photometrische Reagentien für Niob verwendet werden. Zwei neue Gruppen von Reagentien werden beschrieben: Monoazofarbstoffe auf Basis R-Salz und 2,7-Bisazofarbstoffe auf Basis Chromotropsäure. Die Reaktion mit Niob ist empfindlich ($\epsilon = 20000$–40000), selektiv und findet in stark saurer Lösung statt (0,5–6 *M* Salz- oder Salpertesäure). Man kann mit Butanol das Diphenylguanidinsalz des entsprechenden Niob-Komplexes extrahieren und die Extinktion des Extraktes messen.

Résumé—On passe en revue les colorants azoïques qui contiennent le groupe fonctionnel O,O′-dioxyazo et sont très utilisés comme réactifs photométriques du niobium. On décrit deux nouveaux groupes de réactifs: colorants monoazoïques basés sur le Sel R et colorants 2,7-bisazoïques basés sur l'acide chromotropique. La réaction avec le niobium est sensible ($\varepsilon = 20{,}000 - 40{,}000$), sélective et a lieu en solution fortement acide (acides chlorhydrique ou nitrique 0,5–6 *M*). On peut extraire le sel de diphénylguanidine du complexe correspondant du niobium au moyen de butanol et mesurer l'absorption de l'extrait.

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QUANTITATIVE GASCHROMATOGRAPHISCHE BESTIMMUNG DER INHALTSSTOFFE DES TECHNISCHEN DIVINYLBENZOLS

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(*Eingegangen am* 20. *September* 1965. *Angenommen am* 22. *November* 1965)

Zusammenfassung—Mit einer neuentwickelten Anordnung lassen sich aus technischem Divinylbenzol die reinen *m*- und *p*-Isomeren des Divinyl-und des Äthylvinylbenzols erfolgreich präparativ-gaschromatographisch trennen. Mit den so isolierten reinen Inhaltsstoffen war es möglich, stoffspezifische Korrekturfaktoren zu ermitteln, Eichdiagramme aufzunehmen und ein quantitatives Bestimmungsverfahren für die einzelnen Stoffe auszuarbeiten. In Genauigkeit und Zeitaufwand ist die Methode der bisher bekannten weitgehend überlegen. Darüber hinaus konnte für die vollständige gaschromatographische Analyse der Isomeren in Betone 34 + Silikonöl DC 550 eine neue Trennflüssigkeit gefunden werden.

Zur Trennung der Inhaltsstoffe des technischen Divinylbenzols wurde von Blasius und Beushausen[1] die Gaschromatographie eingesetzt. Im Mittelpunkt dieser vorhergehenden Arbeit standen vorwiegend qualitative Untersuchungen. Für eine quantitative Auswertung sind jedoch die Reinsubstanzen erforderlich, die, wie die vorliegende Arbeit zeigt, präparativ-gaschromatographisch isoliert werden können. Damit besteht auch die Möglichkeit einer Überprüfung der bisher verwendeten klassischen titrimetrischen und gravimetrischen Bestimmungsmethoden nach Marquardt und Luce.[2,3]

Unter vereinfachenden Voraussetzungen ist das Verhältnis Fläche einer Bande zur Gesamtfläche aller Banden ein direktes Maß für die prozentuale Zusammensetzung einer Mischung. Dies gilt in guter Näherung für chemisch sehr ähnliche Stoffe bei gleichzeitiger Verwendung gut wärmeleitender Trägergase. Dieses als "direkte Flächenmethode" bezeichnete Verfahren ist besonders für Analysen innerhalb homologer Reihen[4] wertvoll. Je heterogener die Stoffe einer Analysenmischung sind, um so größere Fehler sind zu erwarten.[5–8] Für diesen Fall ist es notwendig, durch Eichmessungen stoffspezifische Korrekturfaktoren zu bestimmen. Mit diesen Korrekturfaktoren[4] multiplizierte Flächenwerte sind für gleiche Mengen verschiedenster Stoffe gleich groß. Es wird eine Bezugssubstanz festgelegt, deren stoffspezifischer Korrekturfaktor den Wert 1,000 erhält.

Neben Blasius und Beushausen[1] hatten sich auch Wolf, Losse und Schwachula[9] mit dem genannten Problem beschäftigt. Quantitative Messungen mit Äthylbenzol als Eichsubstanz ergaben einen Fehler von ±4%, allerdings sind keine Korrekturfaktoren angegeben. Polymerisation des Divinylbenzols und anderer Komponenten konnte auf der Trennsäule nicht festgestellt werden. Trennflüssigkeit war Dinonylphthalat. "The Dow Chemical Co." gibt ein halbquantitatives Analysenverfahren[10] mit Apiezon L als Trennflüssigkeit an.

Zur Trennung der Isomeren des Diäthylbenzols verwendete Blake[11] als Trennflüssigkeit eine Mischung aus Bentone 34 und Silikonöl DC 550. Bentone 34 verursacht meist eine starke Schwanzbildung, so daß die Banden sehr unsymmetrisch werden. Die Schwanzbildung läßt sich durch den Zusatz von Siliconölen,[11] Siliconfett,[12] Apiezonfett,[12] Dinonyl-[13] oder Diisodecylphthalat[14] weitgehend einschränken. Nach Mortimer und Gent[13] wird die hervorragende Selektivität des Bentone 34 durch die Zusätze vermindert, deren Menge eine entscheidende Rolle spielt.

Bayer und Mitarbeiter[15–18] zeigten, daß zwischen der Trennwirksamkeit analytischer und präparativer Säulen kein prinzipieller, sondern nur ein gradueller Unterschied besteht. Sie untersuchten Säulen bis zu 100 mm Durchmesser und fanden einen Abfall der Trennwirksamkeit präparativer Säulen gegenüber entsprechenden analytischen um maximal 26 %.

EXPERIMENTELLER TEIL

Arbeitstechnik

Für die Untersuchungen stand technisches Divinylbenzol der Firma Dow Chemical zur Verfügung. Die für die Eichmessungen notwendigen präparativen Mengen an reinen Isomeren des Divinyl- und des Äthylvinylbenzols wurden aus dem technischen Produkt mit Hilfe eines Eigenbau-Gaschromatographen gewonnen. Die Trennsäulen aus Edelstahl mit 27,2 mm Innendurchmesser wurden in einem Luftumwälzthermostaten mit *ca.* 0,1 m³ nutzbarem Raum untergebracht. Die Dosierung der Substanz erfolgte über einen Probenverdampfer nach Bayer.[16] Als Trägermaterial diente Kieselgur (Merck 0,2–0,3 mm), als Detektor eine Wärmeleitfähigkeitszelle vom Typ 30 S der Firma Gow Mac. Zur Isolierung der einzelnen Substanzen wurden Kühlfallen in Eis-Kochsalzmischungen von *ca.* −20° am Detektorausgang in den Gasweg eingeschaltet. Eine in der Falle befindliche Rohrschlage zwingt dem durchströmenden Gas eine kreisförmige Bewegung auf, wodurch eine bessere Abscheidung erzielt wird.

Die Isolierung des Diäthylbenzols (DÄB) entfiel, da *m*- und *p*-Diäthylbenzol in genügender Reinheit im Handel (Firma Fluka) erhältlich ist.

Die Reinheit der isolierten Substanzen hängt von der Güte der Trennung und vom Zeitpunkt der Einschaltung der Kühlfallen ab. Diese werden, sobald die entsprechende Bande auf dem Schreiber erscheint, angeschlossen.

Für die analytischen Arbeiten stand das Gerät MK II B der Firma Griffin und George zur Verfügung.

Präparative Trennung

Optimale Arbeitsbedingungen für die präparative Trennung:

Säulenlänge:	5,2 m
Säulen-Durchmesser:	27,5 mm
Temperatur:	145°
Gasmengenstrom:	25 l./hr
Trennflüssigkeit:	20 % Hochvakuumfett R (Fa. Leybold, Köln)
Probenmenge:	4 ml

Allgemein ist die Auftrennung der *m*- und *p*-Isomeren in einem Arbeitsgang nicht vollständig.

Die Kühlfalle muß bei der Gewinnung des *m*-Äthylvinylbenzols (*m*-ÄVB) kurz nach Erreichung des Bandenmaximums entfernt werden. Für das *m*-Divinylbenzol (*m*-DVB) liegt dieser Zeitpunkt infolge der besseren Auftrennung später. Er befindet sich in halber Höhe zwischen dem Bandenmaximum und dem Minimum, das zwischen der *m*- und *p*-DVB-Bande auftritt. Nach der Entfernung der Kühlfalle für die *m*-Verbindung wird ein Auffanggefäß für das entsprechende *p*-Isomere in den Gasweg eingeschaltet.

Durch sehr spätes Einschalten der Kühlfallen lassen sich die *p*-Isomeren zwar rein isolieren, allerdings nur in Ausbeuten von *ca.* 10 % des eingesetzten technischen Divinylbenzols. Vorteilhafter ist es, zunächst die *p*-Verbindungen mit einer kleinen Menge der entsprechenden *m*-Verbindung zusammen aufzufangen. Die Isolierung der reinen *p*-Isomeren geschieht nach nochmaliger Aufgabe der angereicherten Substanzen.

Sie enthalten dann nur noch relativ geringe Mengen an entsprechenden *m*-Verbindungen (Abb. 1). Die Hauptmenge der *p*-Verbindungen läßt sich rein isolieren. Die Banden kurz nach dem Startpunkt sind dem Lösungsmittel Benzol (BZL) zuzuordnen.

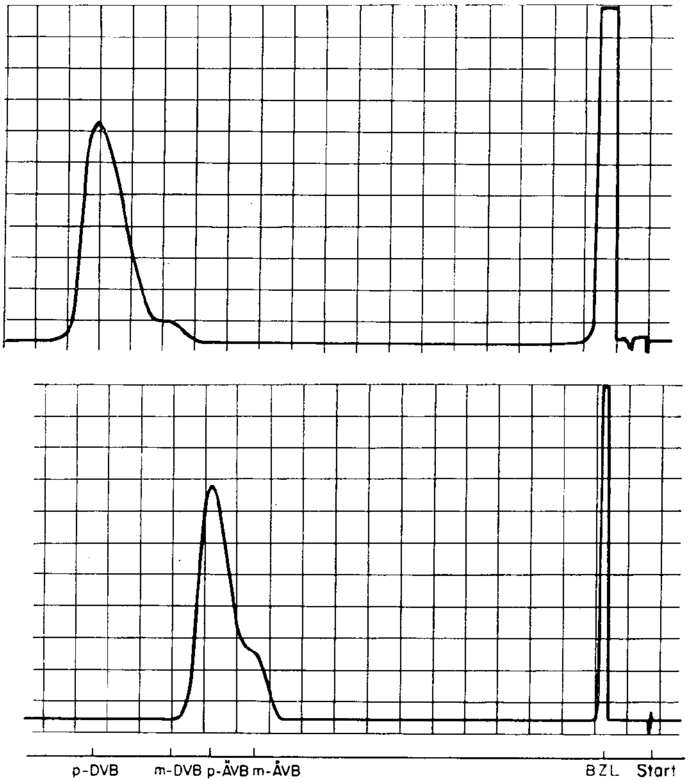

Abb. 1.—Isolierung der reinen Isomeren

Wenn alle Inhaltsstoffe in einer Kühlfalle gesammelt werden, liegt die Ausbeute zwischen 60 und 70%. Die Ausbeuten für die reinen Isomeren sind geringer. Sie betragen für *m*-ÄVB und *m*-DVB *ca.* 55%. Für *p*-ÄVB und *p*-DVB schwankt der Wert zwischen 40 und 50%.

Die relativ geringe Ausbeute ist auf nicht quantitative Abscheidung und unvollständige Auflösung der Isomerenbanden zurückzuführen. Ferner polymerisiert ein kleiner Teil der dosierten Probe in der Verdampfungskammer. Im Gegensatz zu analytischen treten bei präparativen Proben in der Verdampfungskammer hohe Substanzkonzentrationen auf, die Polymerisationserscheinungen verständlich machen.

Analytische Trennung

Hohe Trennleistungen erzielt man mit Bentone 34 (Fa. F & M Scientific) als eine Komponente der Trennflüssigkeit. Selbst die Isomeren werden bei starker Verminderung der Schwanzbildung und unter Verkürzung der Retentionszeiten vollständig aufgetrennt (Abb. 2).

Arbeitsbedingungen:

Säulenlänge: 2,5 m
Temperatur: 145°
Säulenausgangsdruck: 260 mm Hg
Säuleneingangsdruck: 673 mm Hg
Gasmengenstrom: 3,0 l.He/hr
Säulenfüllung: 2,0 g Bentone 34 + 1,30 g Siliconöl DC 550 + 40 g Kieselgur
Probenmenge: 3 µl
Heizstrom des Detektors: 200 mA
Empfindlichkeit: 1/3 des Vollausschlages
Papiervorschub: 36 inch/hr

Die gesamte Trennflüssigkeitsmenge beträgt 7,6 Gew.-% und das Gewichtsverhältnis Bentone 34/Silikonöl 1,54:1.

Unter den obigen Arbeitsbedingungen wurden die isolierten Fraktionen untersucht. Die getrennten Isomeren sind vollkommen rein (Abb. 3). Es ist jeweils nur die entsprechende Bande zu erkennen. Verunreinigungen müßten unterhalb der Empfindlichkeitsgrenze des Detektors liegen. Die bei *p*-DVB (Fp. 31°) zusätzlich auftretende Bande gehört dem Benzol, das als Lösungsmittel zur besseren Dosierung der Probe Verwendung fand.

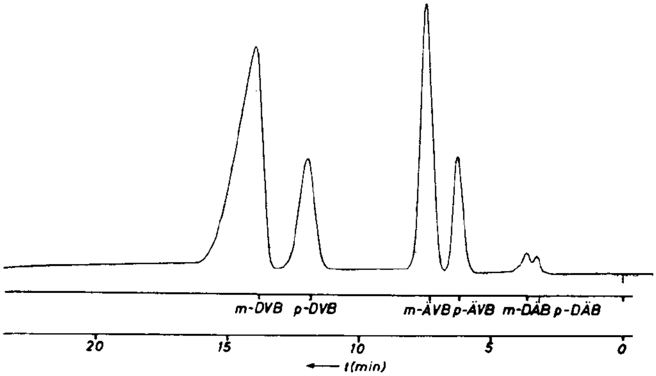

ABB. 2.—Bentone 34 + Siliconöl DC 550 als Trennflüssigkeit

Quantitative Auswertung

Es wurden acht Modellgemische unterschiedlicher Konzentrationen aus denpräparativ isolierten reinen Komponenten eingewogen. Als Bezugssubstanz diente eine definierte Menge Äthylbenzol. Von jeder Eichmischung wurden acht Chromatogramme angefertigt. Die Bandenflächen wurden planimetrisch aus je acht Einzelmessungen und anschließender Mittelswertsbildung bestimmt.

Die Arbeitsbedingungen sind die gleichen wie im Kapitel Analytische Trennung.
Tabelle I zeigt die gefundenen Korrekturfaktoren.

TABELLE I.—ZUSAMMENSTELLUNG DER KORREKTURFAKTOREN (BEZUGSSUBSTANZ ÄTHYLBENZOL)

	f_i	rel. Fehler, %
m-DVB	1,115 ± 0,028	±2,5
p-DVB	1,136 ± 0,024	±2,1
m-ÄVB	1,078 ± 0,025	±2,3
p-ÄVB	1,098 ± 0,010	±1,0
DÄB	1,082 ± 0,015	±1,5

Die Auswertung der Chromatogramme kann auch graphisch[19] vorgenommen werden. In diesem Fall trägt man in Eichdiagrammen das Bandenflächenverhältnis Stoff i/Eichsubstanz gegen den Prozentgehalt an Stoff i auf. Der Prozentgehalt an Eichsubstanz wird dabei nur auf die Analysenprobe (*nicht* auf Analysenprobe plus Eichsubstanz) bezogen. Der prozentuale Anteil der Eichsubstanz am Analysengemisch muß konstant bleiben. Mit diesem Auswertungsverfahren läßt sich überprüfen, ob die Analysenprobe vollständig verdampfbar ist.

Mit Hilfe der Korrekturfaktoren erfolgte die quantitative Bestimmung der Inhaltsstoffe eines im

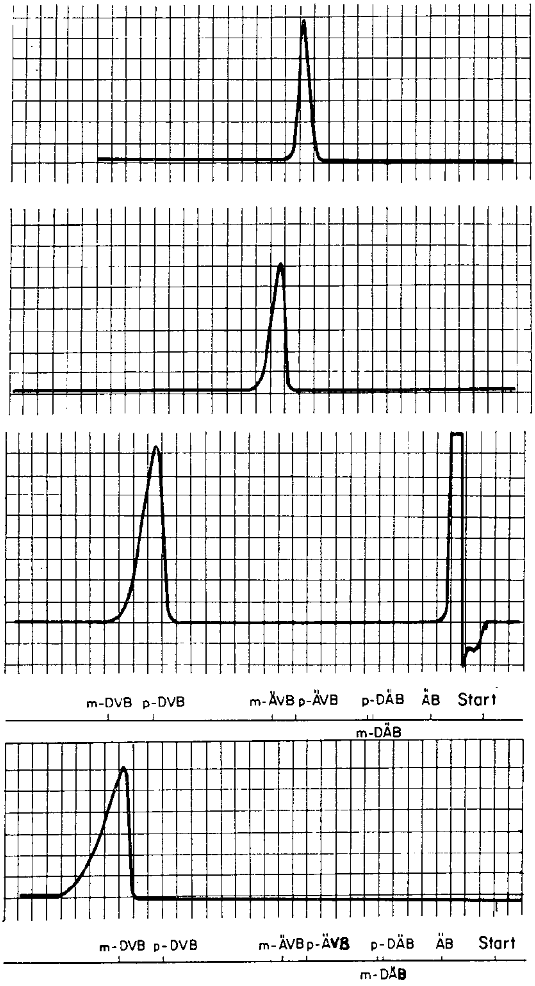

Abb. 3.—Reinheit der isolierten Verbindungen

Handel erhältlichen Divinylbenzols. Zur Berechnung dient die Beziehung:

$$\text{Gew.-\% vom Stoff 1} = \frac{A_1 \times f_i}{A_n \times f_n} \qquad A = \text{Bandenfläche}$$

Tabelle II zeigt die Zusammensetzung des Gemisches (Chromatogramm 1 und 2). Naphthalin (Naphth.) wurde gesondert und nur nach der direkten Flächenmethode bestimmt, da es bei den angewandten Arbeitsbedingungen (s. Abb. 2) keineaus wertbare Bande ergibt. Zu seiner Bestimmung wurde nur eine Säule (0,88 m) eingesetzt, die Arbeitstemperatur lag bei 165°.

Chromatogramm 3 gibt die mit Hilfe der Eichdiagramme bestimmte Zusammensetzung des gleichen Produkts an.

Die Werte der Chromatogramme 1–2 stimmen gut überein. Die Auswertung über Eichdiagramme ist ungenauer; da die Ablesung mit einem zusätzlichen Fehler behaftet ist. Das Analysengemisch ist vollständig verdampft.

TABELLE II.—ZUSAMMENSETZUNG EINES IM HANDEL ERHÄLTLICHEN TECHNISCHEN DIVINYLBENZOLS

	Chromatogramm 1 (Gew. %)	Chromatogramm 2 (Gew. %)	Chromatogramm 3 (Gew. %)
m-DVB	47,2	47,2	46,5
p-DVB	14,3	14,5	14,0
m-ÄVB	25,5	25,3	25,5
p-ÄVB	9,3	9,5	9,0
DÄB	3,2	3,0	3,5
Naphth.	0,6	0,6	0,6

VERGLEICH DES KLASSISCHEN ANALYSENVERFAHRENS MIT DER GASCHROMATOGRAPHISCHEN METHODE

In Tabelle III sind die Ergebnisse der beiden Methoden gegenübergestellt. Die Ergebnisse nach Marquardt und Luce[2,3] stellen Mittelwerte aus 5 Einzelbestimmungen dar.

TABELLE III.—VERGLEICH DES GASCHROMATOGRAPHISCHEN VERFAHRENS MIT DER METHODE VON MARQUARDT UND LUCE

	Gaschromatogr. (Gew.-%)	Methode nach Marquardt (Gew.-%)
DVB	61,6	57,6
ÄVB	34,8	36,3
Gesättigte Verbindungen	3,7	6,1

Die gaschromatographisch ermittelten Werte sind infolge der vorhergehenden Eichmessungen als die genaueren anzusehen. Bei dem titrimetrischen und gravimetrischen Verfahren sind die Abweichungen vor allem auf die Löslichkeit des Divinylpseudonitrosits und die Ermittlung des Divinylbenzolgehaltes aus der Eichkurve[2,3] zurückzuführen. Besonders groß ist der relative Fehler bei den gesättigten Verbindungen, die nach Marquardt und Luce nur als Differenz zu 100% indirekt berechnet, während sie gaschromatographisch direkt bestimmt werden.

Die größere Genauigkeit ist aber nicht der einzige Vorteil des gaschromatographischen Verfahrens. Mit ihm sind die Isomeren des DVB und des ÄVB sowie die verschiedenen gesättigten Verbindungen einzeln bestimmbar. Bei der älteren Methode kann jeweils nur die Summe ermittelt werden. Eine vollständige Analyse nach Marquardt und Luce dauert *ca.* einen Tag. Nach dem gaschromatographischen Verfahren benötigt man für eine Analyse mit Auswertung *ca.* eine Stunde. Ein weiterer Vorteil des gaschromatographischen Verfahrens liegt in den geringen Probemengen.

Für die Bereitstellung von Mitteln und Apparaten danken wir der Deutschen Forschungsgemeinschaft und dem Bundesministerium für Wissenschaftliche Forschung.

Summary—A new arrangement has been developed to separate *m*- and *p*-isomers of divinyl- and ethylvinylbenzene from technical divinylbenzene by preparative gas chromatography. Using the pure constituents so isolated, it was possible to ascertain correction factors, calibration curves and methods of quantitative analysis. The described method is more exact and requires less time than those previously known. A new liquid phase (Bentone 34 and Siliconoil DC 550) has also been investigated for the complete gas chromatographic analysis of the isomers.

Résumé—On a élaboré un nouveau dispositif pour séparer les isomères *m*- et *p*- du divinyl- et de l'éthylvinyl-benzène à partir du divinylbenzène technique par chromatographie en phase vapeur préparative. En utilisant les constituants purs ainsi isolés, il a été possible de déterminer les facteurs de correction, les courbes d'étalonnage et les méthodes d'analyse quantitative. La méthode décrite est plus précise et nécessite moins de temps que celles connues jusqu'à présent. On a également étudié une nouvelle phase liquide—(Bentone 34 et Siliconoil DC 550) pour l'analyse complète des isomères par chromatographie en phase vapeur.

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Talanta, 1966, Vol. 13, pp. 709 to 714. Pergamon Press Ltd. Printed in Northern Ireland

STRUCTURES OF THE URANYL 8-HYDROXYQUINOLATES

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(*Received* 9 *August* 1965. *Accepted* 5 *December* 1965)

Summary—An X-ray investigation of the two uranyl 8-hydroxyquinolates

$$UO_2{\cdot}(C_9H_6NO)_2{\cdot}C_9H_6NOH \text{ (dark red)}$$

and

$$[UO_2{\cdot}(C_9H_6NO)_2]_2{\cdot}C_9H_6NOH \text{ (orange)},$$

has been carried out on the untreated compounds and after recrystallising them from chloroform. The unsolvated compound $UO_2{\cdot}(C_9H_6NO)_2$ and the residue remaining after dissolving the orange compound in chloroform have also been examined. The investigation shows that the crystals obtained from the red and orange compounds, respectively, after dissolving in chloroform and recrystallising, are identical. The untreated red and orange compounds are different, the latter showing evidence of existing as a polymer, whereas the former is crystalline. On the basis of the results obtained, a structure for the orange compound is proposed.

IN 1961, Bordner *et al.*[1] prepared uranium(VI) 8-hydroxyquinolate from homogeneous solution with 8-hydroxyquinoline generated by hydrolysis of 8-acetoxyquinoline. Two different compounds were obtained depending on the pH of precipitation. At pH 5·0 a dark red compound was obtained, while at pH 6·8 the resulting compound was orange in colour. On the basis of the analytical data, the authors claimed that the composition of the two compounds was different, the formula for the dark red compound being given as $UO_2{\cdot}Q_2{\cdot}HQ$ (where $Q = C_9H_6NO$), while for the orange compound the formula $(UO_2{\cdot}Q_2)_2{\cdot}HQ$ fitted the data.

Recently, in order to attempt an elucidation of their structure, infrared studies[2] and diffuse reflectance[3] studies were carried out on the compounds, but differences were so slight that it could not be definitely proved that the two compounds possessed different structures.

In the past, evidence has been given by a number of authors that uranium forms two different compounds with 8-hydroxyquinoline[4,5]—the dark red $UO_2{\cdot}Q_2{\cdot}HQ$ and the "normal" unsolvated chelate, dark green in colour, $UO_2{\cdot}Q_2$. Few, however, appear to have observed the orange compound obtained by Bordner *et al.* Bullwinkle and Noble[5] studied the dark red compound and came to the conclusion that it was an acid which could be written as $[H(UO_2{\cdot}Q_3)]$. For this compound they proposed the structure shown in Fig. 1, *i.e.*, the three 8-hydroxyquinoline groups lie in a plane through the uranium atom with the uranyl oxygen atoms (not shown in the figure) above and below this plane. One of the three hydroxyquinoline units is attached to the uranium atom only through the nitrogen, so that the acidic hydrogen is free to link to the uranyl oxygen of another molecule. By this means, long chains may arise. Hall *et al.*,[6] on the other hand, from a crystal structure determination on the

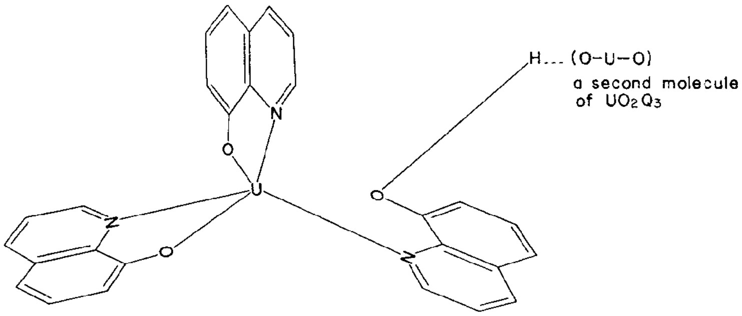

FIG. 1

dark red compound came to the conclusion that the suggestion of Bullwinkle and Noble was not correct.

In the structure proposed by Hall *et al.*, all three 8-hydroxyquinoline molecules are co-ordinated to the uranium atom, but they are not equivalent. All three phenolic oxygen atoms are co-ordinated, but only in two ligand molecules is the nitrogen also bonded to the uranium. The proposed structure is shown in Fig. 2.

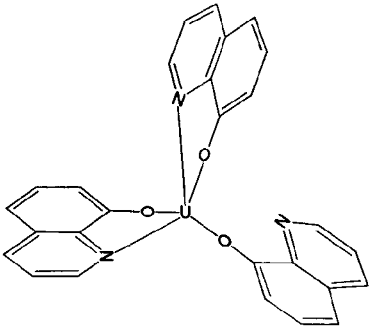

FIG. 2

Neither Hall *et al.* nor Bullwinkle and Noble appear to be familiar with the orange compound, $(UO_2 \cdot Q_2)_2 \cdot HQ$. In view of this and the disagreement between the two sets of workers it was considered desirable to investigate by X-ray diffraction the orange, red and dark-green "normal" uranium 8-hydroxyquinolates. The results of this investigation are now reported.

EXPERIMENTAL

For the X-ray investigation on the red compound, Hall *et al.* used crystals grown from chloroform. In the present work, the following specimens were examined:

I. *Red single crystals.* These were grown from a solution of the red compound $UO_2 \cdot Q_2 \cdot HQ$ (where $Q = C_9H_6NO$) in chloroform, as prepared by Hall *et al.*[6] for their investigation.

II. *Red single crystals.* These were grown from the solution of the orange compound $(UO_2 \cdot Q_2)_2 \cdot HQ$, as prepared by Bordner *et al.*,[1] in chloroform.

III. *The red compound.* $UO_2 \cdot Q_2 \cdot HQ$, was prepared as by Bordner *et al.*[1] and used without further treatment.

IV. *The orange compound.* $(UO_2 \cdot Q_2)_2 \cdot HQ$, was prepared as by Bordner *et al.*[1] and used without further treatment.

V. *The dark green compound.* $UO_2 \cdot Q_2$, was prepared as by Magee and Gordon[2] and others, and used without further treatment.

VI. *A dark brown compound.* Not previously reported, and prepared as follows. A sample of the orange compound (IV) [which is less soluble than the red compound (III)] was shaken thoroughly with chloroform and left overnight. The undissolved portion was centrifuged, washed and dried. It was dark brown in colour.

All photographs were taken with Cu Kα radiation on a 6-cm diameter single crystal goniometer. Single crystal rotation photographs were taken of specimens I and II. For the remaining compounds, no single crystals could be obtained and powder photographs only were possible.

Single crystal specimens were mounted on a glass fibre with cellulose in amyl acetate and acetone. This was also used as a binding agent for the powders. However, because it gives some low angle scattering and a diffuse halo, when present in bulk, it was used as sparingly as possible and a control photograph of the adhesive alone was prepared. As an additional check in the case of the orange powder, further specimens, bound with seccotine and vaseline, were examined.

No attempt was made to index reflections or define cell dimensions from the powder photographs.

Unfortunately, all the photographs obtained, although establishing the points mentioned in the paper, were not such as to permit calculations of cell dimensions. This frequently happens with a complex powder pattern.

RESULTS

Examination of the films indicated the following:

1. Samples I and II were identical with the crystals described by Hall *et al.*[6] This was established by the *b*-axis periodicity and the spacings of the thirteen *h0l* reflections, with $\theta < 16{\cdot}5°$, which were measured.

2. The remaining specimens all gave diffraction patterns differing from the above and from each other.

3. The red compound (III), $UO_2 \cdot Q_2 \cdot HQ$, gave good powder rings up to $\theta \simeq 45°$, showing that this compound is fully crystalline. The unit cell is fairly large.

4. The orange compound (IV), $(UO_2 \cdot Q_2)_2 \cdot HQ$, showed no powder lines. Two haloes corresponding to spacings of about 4·2 and 8·5 Å were present. The specimen is undoubtedly amorphous.[7] However, the compound may well be a polymer with chains or layers in which the uranium atoms are separated by about 8·5 and 4·2 Å.

5. The dark green compound (V), $UO_2 \cdot Q_2$, also appears to be fully crystalline. Although the lines of the pattern were not distinguishable much beyond $\theta = 20°$, no evidence of line broadening was apparent.

6. The dark brown compound (VI) showed considerable low-angle scattering, suggesting that some of the scattering material is colloidal. Two very faint rings, much obscured by this, could be due to $UO_2 \cdot Q_2$ (V), but were too faint for exact measurement. Stationary and oscillation photographs indicated that some small crystals were also present, giving reflections which did not lie on the powder rings of any of the other compounds studied.

DISCUSSION

Hall *et al.*[6] pointed out that the red crystals grown from chloroform for the structure determination of $UO_2 \cdot Q_2 \cdot HQ$ contain molecules of chloroform, present as solvent of crystallisation. It is not surprising, therefore, that the diffraction pattern of the red crystals (I and II) is different from that of the red powder (III). Further, the fact that the red and orange powders (III and IV) give different diffraction patterns is supporting evidence for the claim of Bordner *et al.*, that these compounds are of different compositions, although in itself this is not conclusive, because it might merely indicate the existence of allotropic forms.

The fact that the orange powder yields two compounds on dissolution in chloroform is important. Further, because it was established that the red crystalline compound produced is identical with $UO_2{\cdot}Q_2{\cdot}HQ{\cdot}CHCl_3$, the implication is that molecules of $UO_2{\cdot}Q_2{\cdot}HQ$ are present in the solution. The composition of the other product (VI) can only be guessed, but because the red powder (III) yields red crystals only, its formation may be regarded as further evidence that the red and orange powders are of different composition.

If the formula given by Bordner *et al.*[1] for the orange compound, based on analytical data, *i.e.*, $(UO_2{\cdot}Q_2)_2{\cdot}HQ$, is accepted, it would appear that the compound must break up into two constituents on dissolution in chloroform. The slow rate of dissolution and the diffraction pattern provide supporting evidence for a polymeric structure. The break-up in solution might be envisaged as follows:

$$(UO_2{\cdot}Q_2)_2{\cdot}HQ \rightarrow UO_2{\cdot}Q_2{\cdot}HQ{\cdot}CHCl_3 + UO_2{\cdot}Q_2 \text{ (or } UO_2{\cdot}Q_2{\cdot}x\ CHCl_3).$$

However, when one of the suggested fragments, $UO_2{\cdot}Q_2$, is prepared[2] by direct heating *in vacuo* of $UO_2{\cdot}Q_2{\cdot}HQ$ or $(UO_2{\cdot}Q_2)_2{\cdot}HQ$, it is very dark green in appearance. On the other hand, the residue obtained on dissolving the orange powder in chloroform is dark brown in colour.

Several reasons may be suggested as possibly accounting for this change in colour. First, the dark brown compound could be a mechanical mixture of a small amount of minute red crystals of $UO_2{\cdot}Q_2{\cdot}HQ{\cdot}CHCl_3$ with the green compound $UO_2{\cdot}Q_2$. The faint rings in the X-ray photograph afford some evidence of the presence of the latter, but there is no X-ray evidence for the presence of the former. Secondly, the dark brown compound is partly colloidal, and may consist of mainly $UO_2{\cdot}Q_2$ in that form, and as such not necessarily identical in colour with the crystalline $UO_2{\cdot}Q_2$. Finally, the compound, and also the small crystals observed to be present in the sample, might be $UO_2{\cdot}Q_2{\cdot}x\ CHCl_3$, or a mixture of constituents such as $UO_2{\cdot}Q_2{\cdot}x'$ $UO_2{\cdot}Q_2{\cdot}HQ{\cdot}x''\ CHCl_3$. However, none of these possible structures could be shown to be the correct one.

From the evidence now available, what conclusions can be drawn about the structure of the orange compound, $(UO_2{\cdot}Q_2)_2{\cdot}HQ$? It is clear that it is polymeric and, further, the breakdown in chloroform solution discussed above, and the structure obtained by Hall *et al.* for the red crystals, give useful pointers. We suggest that the orange compound is composed of a molecule of $UO_2{\cdot}Q{\cdot}HQ$ in which all three phenolic oxygens are co-ordinated, but only in two ligand molecules is the nitrogen also bonded to the uranium. The unattached nitrogen is co-ordinated to the uranium of a second molecule $(UO_2{\cdot}Q_2)$, with the proton delocalised and able to form a hydrogen bond between a uranyl oxygen in the $UO_2{\cdot}Q_2$ molecule and the uranyl oxygen of another molecule of $UO_2{\cdot}Q_2$, which is in turn co-ordinated through the nitrogen atom to a molecule of $UO_2{\cdot}Q_2{\cdot}HQ$. In this way a polymer of chains or layers would be built up. The basic unit of this proposed structure is shown in Fig. 3. When this compound is dissolved in chloroform, a break at the hydrogen bond occurs first, producing the unit $(UO_2{\cdot}Q_2){\cdot}HQ$. Migration of the proton to the vicinity of the nitrogen atom on the $UO_2{\cdot}Q_2{\cdot}HQ$ portion of the molecule results, and a second break between the co-ordinated nitrogen and uranium atoms takes place. As a result, two compounds are produced, $UO_2{\cdot}Q_2{\cdot}HQ$ having the structure given by Hall *et al.* for the red compound, and $UO_2{\cdot}Q_2$.

It is interesting to note that the orange compound has not been prepared by any

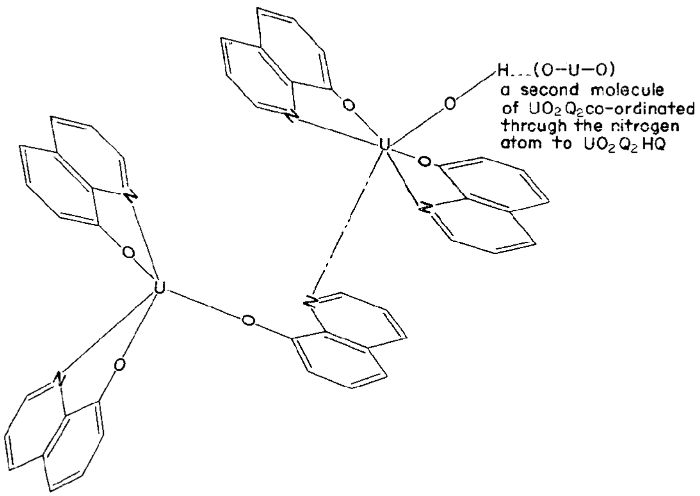

FIG. 3

method other than precipitation from homogeneous solution (PFHS), a method characterised by the slow formation of ligand and complex. Under such conditions a chain-like structure could well have the time to form, whereas time is not available when the reagent and the metal compound are mixed in the conventional manner. Further, formation of this compound occurs at pH 6·8, *i.e.*, when the hydrogen ion concentration is reduced. Magee and Gordon[3] have also shown that for its formation a 2-fold excess of reagent is required, while for the red compound a 20-fold excess is used: however, if the amounts of reagents are reversed, the orange compound is not obtained; instead the red one results. Thus, it is apparent that the conditions necessary for the formation of the orange compound are critical and well-defined.

Acknowledgement—The authors wish to thank Professor L. Gordon, Department of Chemistry, Case Institute of Technology, Cleveland, Ohio, U.S.A., for ideas which stimulated the work and for his interest in it.

Zusammenfassung—Die beiden Uranyl-8-hydroxychinolate $UO_2(C_9H_6NO)_2\cdot C_9H_6NOH$ (dunkelrot) und $[UO_2(C_9H_6NO)_2]_2\cdot C_9H_6NOH$ (orange) wurden im unbehandelten Zustand und nach Umkristallisation aus Chloroform rontgenographisch untersucht. Auch die nicht solvatisierte Verbindung $UO_2(C_9H_6NO)_2$ und der Rückstand, der nach dem Lösen der orangefarbigen Verbindung in Chloroform hinterbleibt, wurden in die Untersuchung einbezogen. Es zeigt sich, daß die Produkte der Umkristallisation der roten und orangefarbigen Verbindung aus Chloroform identisch sind. Die nicht behandelte rote und orangefarbige Verbindung sind verschieden; die erstere ist kristallin, wogegen es Anzeichen dafür gibt, daß die letztere ein Polymeres ist. Auf Grund der erhaltenen Ergebnisse wird eine Struktur für die orangefarbige Verbindung vorgeschlagen.

Résumé—Pour les deux 8-hydroxyquinoléinates d'uranyle, $UO_2(C_9H_6NO)_2C_9H_6NOH$ (rouge foncé) et $[UO_2(C_9H_6NO)_2]_2C_9H_6NOH$ (orangé) on a mené une recherche aux rayons X sur les composés non traités et ceux obtenus après dissolution et recristallisation en chloroforme. On a aussi examiné le composé non solvaté $UO_2(C_9H_6NO)_2$

et le résidu restant après dissolution du composé orangé en chloroforme. La recherche montre que les cristaux obtenus à partir des composés rouge et orangé, respectivement, après dissolution en chloroforme et recristallisation, sont identiques. Les composés rouge et orangé non traités sont différents, le dernier se révélant exister comme un polymère, cependant que le premier est cristallin. Sur la base des résultats obtenus, on propose une structure pour le composé orangé.

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STABILITY OF HYPOBROMITE SOLUTIONS

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(*Received* 24 *November* 1965. *Accepted* 28 *December* 1965)

Summary—The stability of hypobromite solutions is governed by such factors as the concentration of hypobromite and hydroxide, light, temperature, and the presence of foreign substances. From a review of the literature it is concluded that it is impossible to obtain perfectly stable solutions. The preparation of more or less stable hypobromite solutions is described, and the dependence of the stability on various factors is determined.

INTRODUCTION

Solutions of hypochlorite and hypobromite have long been used as titrants; first for estimating ammonia salts[1–3] and urea,[4] and later for other easily oxidised species such as arsenite,[5] iodide,[6,7] bromide,[8] thiosulphate,[5] thiourea,[9] thiocyanate[5,10] and several others.[5,11–16] Hypobromite is a powerful oxidant, and although it has a lower oxidation potential[17] than the more stable hypochlorite, it is more reactive. Hypobromite solutions (like hypochlorite solutions) are thermodynamically unstable with respect to disproportionation. In an alkaline medium the result is a mixture of bromide and bromate:

$$3BrO^- \rightleftharpoons 2Br^- + BrO_3^-.$$

This reaction does not lead to errors in titration, however, because if a back-titration is used all the bromine compounds present can be reduced to bromide without loss in titre. There is another mode of decomposition, however, which occurs in both acid and alkaline media, and can cause serious error:

$$2HBrO \rightleftharpoons 2HBr + O_2$$

$$2BrO^- \rightleftharpoons 2Br^- + O_2.$$

The resultant loss of oxygen precludes the use of hypobromite in titrations where oxidation is slow or requires an increased temperature.

The literature on the preparation, standardisation and stability of hypobromite solutions is full of contradictions, and is worth reviewing. All the early work refers to solutions prepared by adding bromine to a solution of an alkali metal hydroxide; the method of adding alkali to an acidified solution of bromate and bromide was not used in analysis till much later.[18,19]

The stability of hypobromite solution with respect to total oxygen content is influenced by the concentration of hypobromite, concentration of hydroxyl ions, traces of foreign substances, light, temperature, and the method of preparation used. Some authors state that their solutions of hypobromite are completely stable,[20,21] others report a decrease in titre with time. Estimates of the rate of decrease vary widely, and the recommended frequency of checking the titre ranges from daily to monthly. Most authors either make no attempt to assign a cause for the decrease, or merely refer to other papers. Table I shows some of the estimates of stability.

Kolthoff and Stenger[28] and others[29,30] have tried to combine the stability of hypochlorite with the reactivity of hypobromite by adding bromide to the sample to be titrated, and using sodium or calcium hypochlorite as titrant. In this way hypobromite is thought to be produced *in situ*. If a prolonged back-titration is necessary, however, decomposition with loss of oxygen may occur, though this is not mentioned in the literature.

TABLE I.—DECREASE IN TITRE (TOTAL OXYGEN CONTENT) OF HYPOBROMITE SOLUTIONS ACCORDING TO DIFFERENT AUTHORS

Reference	Authors	OBr^-, N	OH^-, N	Decrease in titre after certain time intervals, %		
4	Hamburger	0·72	0·02	0·5 in 13 weeks		
3	Artmann and Skrabal	0·5	0·5	0·2 in 3 weeks		
22,23	Willard and Cake	0·6	0·1	0·2 in 1 day	2 in 2 days	15 in 20 days
24	Tomíček and Jašek	0·1	0·5	0·0 in 8 days	16·7 in 13 weeks	30·2 in 26 weeks
25	Rechmann	0·05	0·5	0·8 in 5 days	4·2 in 22 days	4·6 in 26 days
26	Solymosi	0·1	0·3–0·5	6·0 in 4 weeks		
21	Rupp and Rössler	0·4	0·1	stable		
27	Farkas and Lewin	0·08	0·1	0·0 in 5 days (at 0°)		

Factors affecting stability of hypobromite solutions

Concentration of hypobromite. No information is available from the literature, and the analogy of hypochlorite must be used. Kolthoff and Stenger[28] found a strong decrease in stability as the concentration of hypochlorite was decreased. Others have found hypochlorite to be stable.

Hydroxyl ion concentration. Kretzschmar[31] found that 0·5M hypobromite gave least disproportionation when the hydroxyl concentration was 0·5M. Increasing the hydroxyl concentration or raising the temperature increased the extent of disproportionation. A more dilute solution of hypobromite (0·06M) in 0·1 or 0·4M sodium hydroxide was comparatively stable. On the other hand, the oxygen loss was reduced by increasing the hydroxyl concentration. The conclusion is that the oxygen loss is least in 2M sodium hydroxide, but the rate of disproportionation into bromide and bromate is comparatively rapid. Tomíček and Jašek[15] stated that stability of 0·1N hypobromite diminished with increasing alkalinity of the solution, and recommended 0·5M sodium hydroxide as giving least loss of oxygen content.

Traces of foreign substances. Decomposition of hypobromite solutions is accelerated by a small number of substances. Fleury[32] found that traces of nickel, cobalt and copper had a marked effect on the stability. His results for the effect of copper ions at 36° are shown in Table II. He gave no results for nickel and cobalt, but said they had the same effect. He also said that the solution could be stabilised by addition of iodide or iodate. Willard and Cake[23] attempted to confirm this observation, but obtained contradictory results depending on the concentration of hypobromite used. They considered that when the oxygen content remained constant all the hypobromite had been converted into bromate. They also found that iron and other heavy metal ions, besides copper, cobalt and nickel, caused decomposition of the solution. They recommended that the alkali solution should be aged for 2·5 days, then filtered before the bromine was added to it, but even then their solutions were not stable. Erdey and Buzas[5] considered the influence of heavy metal ions on the stability to be very small, but suggested eliminating them by using water distilled in an all-glass apparatus.

TABLE II.—EFFECT OF COPPER ON STABILITY OF HYPOBROMITE SOLUTION[32]

Copper, *mg/l.*	Decrease (%) in titre after		
	1 day	2 days	4 days
0·00	0·2	0·8	1·2
0·25	1·4	2·2	3·7
1·25	3·4	6·7	9·7
2·50	9·3	15·2	23·9
10·0	43·0	60·0	68·4

Kolthoff[33] states that charcoal completely decomposes hypobromite solutions, and that metal oxides cause instability, though he quotes no evidence for the statement.

Mains and Raggett[34] agree with Fleury that nickel and copper catalyse the decomposition of hypohalites, and consider that traces of these metals are introduced mainly by the water and sodium hydroxide used, the amount generally found in a hypohalite bleach solution being 0·02–0·80 ppm. Concentrations higher than 0·40 ppm are regarded as a primary cause of unstable bleach solutions.

Light. The influence of light on the stability of hypobromite solutions was first mentioned by Tomíček and Jašek,[15] who showed that exposure of the solutions to light decreased the titre. They suggested storage in dark coloured glass bottles. The decrease in titre of 0·1*N* hypobromite in 0·5*M* and 1*M* sodium hydroxide was 1·4% and 3·7% (total oxygen content) in a month when stored in clear glass, but 0·0% and 1·6% when stored in dark glass.

Temperature. From Willard and Cake's work it appears that the rate of decomposition increases with an increase of the temperature at which the solution is kept. A 0·6*N* hypobromite solution showed no change in titre during 5 days storage at 0° whereas a similar solution stored at 22° decreased in titre by 3·5% in 3 days. Kretzschmar[31] found that decomposition was rapid at 50–60°.

Method of preparation. There are several modifications that can be made to Tomíček and Jašek's standard method.[15] These include adding bromine water instead of bromine, altering the amount of cooling, aging the alkali solution for 2–3 days before adding the bromine to the alkali, *etc.* None of these changes leads to a more stable solution. Preparation of the reagent by adding alkali to an acidic solution of bromate and bromide[18,19] is said by Claeys and Sion[35] to give a stable solution.

EXPERIMENTAL

A systematic investigation was made of the factors which affect the stability of hypobromite solutions. Some of the earlier work in this field was necessarily repeated.

Influence of reagents used

To see whether the reagents used themselves affected the stability of the hypobromite solutions, chemicals from various suppliers were used to prepare the test solutions. The suppliers used were:

A. British Drug Houses Ltd. (Analar NaOH and KOH),

B. British Drug Houses Ltd. (Laboratory Reagent NaOH, KOH and LiOH),
C. Merck, West Germany (*pro analysi* NaOH, KOH and LiOH),
D. Fluka (*purum* LiOH),
E. E.K.A., Sweden (*purum* NaOH and KOH).

Lithium hydroxide was included because Pierron[36] had shown that hypochlorites increased in stability in the order KOCl, NaOCl, LiOCl.

A $0{\cdot}1\,N$ hypobromite solution was made by the standard method.[15] Bromine (16 g, B.D.H. Analar) was added to 2 l. of alkali solution through a funnel. The alkali solution was cooled beforehand to −4° and thoroughly shaken during and after addition of the bromine. The water used was distilled in an all-glass apparatus, and the solutions were stored in dark brown glass bottles at room temperature. Solutions were prepared which were 0·01, 0·1 and $1M$ in alkali, and were standardised iodometrically at intervals. About 2 g of potassium iodide and 10 ml of dilute sulphuric acid (the dilution depending on the hydroxyl concentration of the hypobromite) were added to 25 ml of the hypobromite solution in a stoppered flask, and the iodine liberated was titrated with sodium thiosulphate. Some results are given in Table III.

Table III.—Loss of oxidative power of $0{\cdot}1N$ hypobromite in different alkali metal hydroxide solutions

Supplier	Time of standing, *days*	Decomposition (%) in KOH			Decomposition (%) in NaOH			Decomposition (%) LiOH		
		$0{\cdot}01N$	$0{\cdot}1N$	$1N$	$0{\cdot}01N$	$0{\cdot}1N$	$1N$	$0{\cdot}01N$	$0{\cdot}1N$	$1N$
A	7	0·4	0·6	0·7	0·2	—	—	—	—	—
	30	4·5	9·1	33·2	1·5	—	—	—	—	—
	100	10·3	24·6	75·0	3·3	—	—	—	—	—
B	7	0·3	0·4	5·0	0·1	0·0	4·2	0·0	0·0	0·1
	30	1·6	2·7	18·0	1·5	2·6	14·6	0·0	0·0	0·0
	100	2·2	5·5	31·0	5·2	5·2	38·6	0·1	0·0	0·0
C	7	0·1	0·1	0·4	0·0	0·1	0·4	0·1	0·1	0·0
	30	0·2	0·1	0·7	0·0	0·1	0·6	0·1	0·0	0·0
	100	0·6	0·4	0·1	0·0	0·4	0·9	0·2	0·0	0·1
D	7	—	—	—	—	—	—	0·0	0·0	0·0
	30	—	—	—	—	—	—	0·0	0·1	0·1
	100	—	—	—	—	—	—	0·1	0·1	0·0
E	7	0·6	0·6	5·3	1·5	4·2	8·0	—	—	—
	30	1·3	2·4	16·7	3·6	45·0	66·0	—	—	—
	100	4·1	3·0	42·3	7·3	64·0	86·1	—	—	—

It is obvious from the results that all the lithium hydroxides gave completely stable solutions, whereas with a few exceptions the sodium and potassium hydroxides gave unstable solutions which decomposed at rates that increased with increase in the hydroxide concentration. The conclusion drawn was that the alkalis that caused decomposition contained impurities which catalysed the decomposition, and that these were probably metal ions.

Influence of metal ions

Aliquots of a stable $1M$ hypobromite solution prepared with Fluka lithium hydroxide were allowed to stand in the dark at room temperature for an hour with 2, 5 or 10 drops of 1% solutions of various cations, and then were titrated iodometrically. Metals with more than one oxidation state were either added in the reduced form or a blank titration made to determine the amount of iodine equivalent to the metal ion added. Of the ions Fe^{2+}, Cr^{3+}, Al^{3+}, Mn^{2+}, Ba^{2+}, Ca^{2+}, Sr^{2+}, $Hg_2{}^{2+}$, Bi^{3+}, Mg^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Sn^{2+}, Ag^{+}, As^{3+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, only copper, cobalt, nickel and iron had any effect on the titre of the solutions. Some quantitative results for the effect of these four ions on $0{\cdot}1M$ hypobromite in $0{\cdot}1M$ lithium hydroxide (Fluka) are given in Table IV. The minimum concentration of cation needed to produce a 1% reduction in titre of this solution in 4 hr at room temperature was found to be $1{\cdot}6 \times 10^{-6}M$ for copper, $8 \times 10^{-7}M$ for cobalt, $2{\cdot}4 \times 10^{-6}M$ for nickel and $1{\cdot}9 \times 10^{-6}M$ for iron.

The alkalis used were then examined spectrographically for these metals. The alkali was mixed with spectrochemically pure carbon powder, and about 50 mg were arced (d.c.) between carbon electrodes (8-mm gap) on a Hilger large spectrograph fitted with a three-step sector. Qualitative analysis showed the presence of iron, magnesium, aluminium, copper and silicon, but no cobalt or nickel was found in any of the samples. A quantitative analysis was then made for copper and iron.

The results are shown in Table V. From these results and those obtained earlier, it seems likely that copper was the cause of the decomposition, although it is difficult to see why the lithium solutions should be more stable even though they contain more copper than the sodium and potassium solutions. Tests with silica-free alkali to which silica was added showed that the silicate did not affect the titre of the hypobromite.

Evidence that the instability of hypobromite solutions is not due to the method of preparation was obtained by repeating the stability tests on hypobromite solutions made by the method of Claeys and Sion.[35] Potassium bromate (15 g) and potassium bromide (80 g) were dissolved in 2 l. of distilled water. Sulphuric acid (6N, 100 ml) was then added and the solution was well shaken. After an hour, 10N alkali metal hydroxide (120 ml) was added and the solution was diluted to 5 l. The results given in Table VI show the same pattern as those in Table III, the lithium solutions again being the most stable. It seems likely that Claeys and Sion obtained stable solutions because they used reagents free from the catalysts that cause the decomposition.

TABLE IV.—DECREASE OF TITRE OF 0·1N HYPOBROMITE IN 0·1M HYDROXIDE SOLUTION WHEN COPPER, COBALT, NICKEL OR IRON IS PRESENT

Time of standing, *hr*	Decrease of titre (%) in the presence											
	[Cu].$10^{-4}M$			[Co].$10^{-4}M$			[Ni].$10^{-4}M$			[Fe].$10^{-4}M$		
	4	20	40	4	20	40	4	20	40	4	20	40
1	0·5	0·7	1·9	4·7	26·3	46·8	3·6	19·0	36·7	1·7	9·3	17·5
2	1·3	2·3	4·6	8·1	39·4	56·0	12·5	40·4	65·4	1·9	10·4	21·3
3	1·2	4·4	6·4	11·5	46·6	64·0	17·0	66·1	77·9	2·1	10·8	20·6

TABLE V.—AMOUNT OF COPPER AND IRON PRESENT IN SOME HYDROXIDES

Supplier	Reagent	Cu, %	Fe, %
A	NaOH	$<10^{-4}$	$<10^{-4}$
	KOH	$<10^{-4}$	$<10^{-4}$
B	LiOH	$\sim10^{-3}$	$<10^{-4}$
	NaOH	$<10^{-4}$	$<10^{-4}$
	KOH	10^{-3}–10^{-4}	$\sim10^{-4}$
C	LiOH	$<10^{-4}$	$\sim10^{-4}$
	NaOH	$\sim10^{-3}$	$<10^{-4}$
	KOH	$\sim10^{-4}$	$\sim10^{-4}$
D	LiOH	$\sim10^{-3}$	$<10^{-4}$
E	NaOH	$\sim10^{-4}$	$<10^{-4}$
	KOH	$<10^{-4}$	$<10^{-4}$

TABLE VI.—DECOMPOSITION OF 0·1N HYPOBROMITE MADE ACCORDING TO CLAEYS AND SION[35] IN DIFFERENT 0·01M ALKALI SOLUTIONS

Supplier	Time of standing, *days*	Decomposition (%) in		
		LiOH	NaOH	KOH
A	4	—	0·8	0·8
	10	—	1·9	1·8
	60	—	5·8	4·6
B	4	0·0	0·8	1·1
	10	0·0	2·5	1·9
	60	0·1	4·3	4·7
D	4	0·0	—	—
	10	0·2	—	—
	60	0·1	—	—
E	4	—	1·3	0·3
	10	—	2·9	1·7
	60	—	7·9	2·2

Influence of hydroxyl concentration

Although it was shown that 0·1*N* lithium hypobromite in 0·1, 0·5, and 1*M* lithium hydroxide was stable in terms of total oxygen content, it remained to be known whether the solutions were also stable to disproportionation. The extent of disproportionation can be measured by titrating two aliquots of hypobromite, one iodometrically to give the total titre, and the other with arsenite to give the hypobromite alone. The end-point of the arsenite titration is determined potentiometrically with platinum and calomel electrodes. An arsenite solution (0·1*N*) was prepared by dissolving 2·5 g of arsenious oxide (previously dried at 110° for 2 hr) in 15 ml of 6*N* sodium hydroxide in an atmosphere of nitrogen. The solution was then diluted to 500 ml with water freed from oxygen by passage of nitrogen. The results shown in Table VII indicate that disproportionation occurs even during the first day after preparation, but is minimal for concentrations of lithium hydroxide between 0·1 and 0·5*N*. All the solutions were stable with respect to total oxygen content. The solutions could obviously be used for any hypobromite reaction without restandardisation, even in an alkaline medium, provided the reaction took not more than 1 day to reach completion.

TABLE VII.—AMOUNT OF DISPROPORTIONATION OF 0·1*N* HYPOBROMITE (2·5 mequiv) IN VARIOUS LITHIUM HYDROXIDE CONCENTRATIONS

LiOH, *M*	Days after preparation	a*	b†	a–b	Disproportionation, %
0·001	1	2·510	2·465	0·045	1·8
	2	2·512	2·459	0·053	2·1
	9	2·512	2·399	0·113	4·5
	30	2·504	2·296	0·208	8·3
0·01	1	2·419	2·228	0·191	7·9
	2	2·419	2·208	0·211	8·4
	9	2·417	2·200	0·217	8·4
	30	2·418	2·145	0·273	11·3
0·1	1	2·591	2·577	0·014	0·5
	2	2·592	2·575	0·017	0·7
	9	2·590	2·565	0·015	0·6
	26	2·585	2·539	0·046	1·7
0·5	1	2·558	2·537	0·021	0·8
	2	2·562	2·544	0·018	0·7
	9	2·561	2·518	0·043	1·7
	30	2·556	2·485	0·071	2·8
1·0	1	2·526	2·475	0·051	2·0
	2	2·531	2·478	0·055	2·2
	9	2·527	2·465	0·062	2·4
	30	2·527	2·422	0·105	4·2
2·0	1	2·468	2·431	0·037	1·4
	2	2·467	2·428	0·039	1·5
	9	2·463	2·401	0·062	2·5
	30	2·459	2·347	0·112	4·5

* a = mequiv ($OBr^- + BrO_3^-$)
† b = mequiv OBr^-

Influence of hypobromite concentration

Solutions of various concentrations of lithium hypobromite were prepared in 0·1*M* lithium hydroxide (Fluka), and tested for stability with respect to total titre and to disproportionation. The results in Table VIII show that the amount of disproportionation increases with increasing concentration of hypobromite, although all the solutions are otherwise completely stable.

It is, therefore, recommended that the hypobromite concentration should be between 0·01 and 0·1*N*.

Effect of temperature

In the analysis of substances that are difficult or slow to oxidise, decomposition of the hypobromite may occur. If the reagent could be used at a higher temperature so that the oxidation was accelerated, this risk might be avoided. The total oxygen loss and the amount of disproportionation of hypobromite solutions stable at room temperature were measured after the solutions had been kept for various periods at temperatures of 50° and 75°. The results are shown in Tables IX and X.

TABLE VIII.—AMOUNT OF LOSS OF OXYGEN AND DISPROPORTIONATION OF VARIOUS HYPOBROMITE CONCENTRATIONS IN 0·1M LITHIUM HYDROXIDE

OBr^-, N	Days after preparation	a*	b*	a–b	Disproportionation, %
0·001	1	0·05196	0·04879	0·00317	6·3
	5	0·05232	0·04985	0·00247	4·9
	10	0·05249	0·04710	0·00539	6·8
	25	0·05163	0·04621	0·00542	6·8
0·01	1	0·5151	0·5060	0·0091	1·8
	5	0·5104	0·5035	0·0069	1·4
	10	0·5104	0·5015	0·0089	1·8
	35	0·5081	0·4975	0·0106	2·1
0·05	1	2·599	2·549	0·030	1·2
	5	2·574	2·537	0·037	1·5
	10	2·574	2·536	0·038	1·5
	35	—	—	—	—
0·1	1	2·591	2·577	0·014	0·6
	5	2·590	2·572	0·018	0·7
	10	2·590	2·565	0·025	1·0
	35	2·587	2·526	0·061	2·4
0·2	1	2·006	1·988	0·018	0·9
	5	2·007	1·985	0·022	1·1
	10	2·010	1·957	0·053	2·7
	35	2·009	1·917	0·092	4·6
0·5	1	2·493	2·456	0·037	1·5
	5	2·496	2·401	0·095	3·8
	10	2·493	2·315	0·178	7·2
	35	2·498	1·962	0·536	21·4

* a and b have the same meaning as in Table VII

TABLE IX.—INFLUENCE OF TEMPERATURE (50° AND 75°) ON THE STABILITY OF 0·1N LITHIUM HYPOBROMITE IN LITHIUM HYDROXIDE

OH^-, M	Time of standing, *hr*	T = 50°		Disproportionation, %	T = 75°		Disproportionation, %
		a*	b*		a*	b*	
0·001	0	2·509	2·465	1·8	2·509	2·465	1·8
	1	2·508	2·462	1·8	2·506	2·387	4·7
	2½	2·505	2·416	3·5	2·501	1·776	29·0
0·01	0	2·408	2·145	10·9	2·408	2·145	10·9
	1	2·406	2·132	11·3	2·399	2·076	13·5
	2½	2·398	2·122	11·5	2·385	1·879	21·2
0·1	0	2·573	2·504	2·6	2·573	2·504	2·6
	1	2·572	2·503	2·6	—	—	—
	2½	2·573	2·491	3·2	2·556	2·365	7·5
0·5	0	2·545	2·473	3·0	2·545	2·473	3·0
	1	2·541	2·475	2·6	2·539	2·458	3·2
	2½	2·542	2·450	3·6	2·539	2·254	11·1
1·0	0	2·509	2·396	4·5	2·509	2·396	4·5
	1	2·508	2·399	4·3	2·507	2·371	5·4
	2½	2·509	2·376	5·3	2·508	2·208	12·0
2·0	0	2·447	2·328	4·9	2·447	2·328	4·9
	1	2·448	2·327	4·9	2·445	2·317	5·2
	2½	2·446	2·313	5·4	2·421	2·164	10·6

* a and b have the same meaning as in Table VII

Table X.—Influence of temperature (50° and 75°) on the stability of lithium hypobromite in 0·1*M* lithium hydroxide

OBr⁻, *N*	Time of standing, *hr*	T = 50°		Disproportionation, %	T = 75°		Disproportionation, %
		a*	b*		a*	b*	
0·001	0	0·05249	0·04712	10·2	0·05249	0·04712	10·2
	1	0·05124	0·04490	12·4	0·05153	0·04702	8·8
	2½	0·05172	0·04731	8·5	0·05047	0·04591	9·0
0·01	0	0·5106	0·5076	0·8	0·5106	0·5076	0·8
	1	0·5096	0·4984	2·2	0·5086	0·5015	1·4
	2½	0·5096	0·5005	1·8	0·5106	0·4975	2·7
0·05	0	2·576	2·536	1·6	2·576	2·536	1·6
	1	2·574	2·530	1·8	2·577	2·517	2·3
	2½	2·577	2·519	2·3	2·575	2·480	3·7
0·1	0	2·573	2·504	2·6	2·573	2·504	2·6
	1	2·572	2·503	2·6			
	2½	2·573	2·491	3·2	2·556	2·365	7·5
0·2	0	2·010	1·957	2·6	2·010	1·957	2·6
	1	2·010	1·944	3·3	2·004	1·900	5·0
	2½	2·007	1·928	3·6	2·000	1·605	19·8
0·5	0	2·493	2·315	7·9	2·493	2·315	7·1
	1	2·488	2·300	7·6	2·470	2·181	11·7
	2½	2·485	2·250	9·4	2·423	1·858	23·5

* a and b have the same meaning as in Table VII.

It is evident that 0·1*N* lithium hypobromite is stable for up to 2·5 hr at 50° or 75° over a wide range of alkalinity, although the amount of disproportionation increases with time and temperature. The anomalous result for 0·01*M* hydroxide is obviously due to some other cause than the effect of temperature changes. Hypobromite solutions ranging from 0·01 to 0·2*N* retain their titre in 0·1*M* lithium hydroxide at 50° and 75° for up to 2·5 hr, but again the amount of disproportionation increases with time and temperature.

For work at higher temperatures it is recommended that 0·1–0·2*N* lithium hypobromite in 0·1–0·5*M* lithium hydroxide should be used. No blanks are needed if the heating period is less than 1 hr. For higher temperatures or longer heating periods, blanks should be run.

Similar experiments on solutions made with sodium or potassium hydroxide showed that a considerable loss of oxygen and a large amount of disproportionation occurred.

Effect of light

Two freshly prepared solutions of 0·1*M* lithium hypobromite in 0·5 and 1*M* lithium hydroxide were divided and stored in dark glass (D) and clear glass (C) bottles, and standardised iodometrically at intervals. The results in Table XI show that light decomposes hypobromite solutions, the effect decreasing as the hydroxyl concentration is increased.

Table XI.—Influence of light on 0·1*N* hypobromite

Time of standing, *days*	Decrease in titre (%) of 0·1*N* hypobromite in 0·5*M* LiOH		1·0*M* LiOH	
	D	C	D	C
1	0·1	0·4	0·0	0·3
3	0·0	0·9	0·1	1·0
17	0·0	3·7	0·2	2·6
27	0·0	5·7	0·1	3·6

DISCUSSION

The results obtained substantiate the claims in the literature that the instability of hypohalite solutions can be caused by light, by raising the temperature, or by the presence of certain catalytic ions, notably copper, iron, cobalt and nickel. Of these causes the last-named is normally predominant, and most of the conflicting statements in the earlier literature almost certainly arise from the use of reagents of different standards of purity and freedom from these ions. That the mechanism is not a simple one is shown by the fact that lithium hypobromite/hydroxide solutions were stable even in the presence of an amount of copper that caused instability in sodium or potassium hypobromite/hydroxide solutions. A further source of these catalytic ions may be the glass of the storage bottles by interaction with the alkaline solution.

Hypohalite solutions that are unstable at room temperature are made more unstable by raising the temperature, but solutions stable at room temperature can tolerate higher temperatures for some time without losing their titre, though more or less disproportionation then occurs.

Lithium hypobromite in lithium hydroxide solution is a good oxidimetric reagent and need be standardised only once each week. It can be used at temperatures of 50–75° for periods of 1–2 hr; if the analysis is completed in an acidic medium, no blank is necessary, but if alkaline conditions are used throughout, then a blank should be run.

Zusammenfassung—Die Stabilität von Hypobromitlösungen ist durch Faktoren wie Hypobromit- und Hydroxydkonzentration, Licht, Temperatur und Gegenwart von Fremdsubstanzen bestimmt. Aus einer Literaturdurchsicht wird geschlossen, daß völlig stabile Lösungen nicht zu erhalten sind. Die Herstellung mehr oder weniger stabiler Hypobromitlösungen wird beschrieben und die Abhängigkeit der Stabilität von verschiedenen Einflüssen bestimmt.

Résumé—La stabilité des solutions d'hypobromite est régie par des facteurs tels que la concentration en hypobromite et en hydroxyde, la lumière, la température et la présence de substances étrangères. En se basant sur une revue de la littérature, on conclut qu'il est impossible d'obtenir des solutions parfaitement stables. On décrit la préparation de solutions d'hypobromite plus ou moins stables, et l'on détermine la dépendance entre divers facteurs et la stabilité.

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SOME NEW HETEROCYCLIC COMPOUNDS AS ANALYTICAL REAGENTS

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(*Received* 7 *October* 1965. *Accepted* 3 *January* 1966)

Summary—A survey of the metal-complexing reactions, as determined by reactions on chromatography paper, of 44 compounds with a substituted or modified 4-(2-pyridylazo)-resorcinol (PAR) or 1-(2-pyridylazo)-2-naphthol (PAN) structure is reported.

INTRODUCTION

4-(2-PYRIDYLAZO)-RESORCINOL (PAR) and 1-(2-pyridylazo)-2-naphthol (PAN) are now well known successful sensitive, non-selective reagents for metal ions.[1–3] Since their development, the azo-dyes of thiazole have also been investigated[4–6] and found to be more useful in complexometric titrations, yet not quite as sensitive as their pyridyl analogues. In a previous paper we have reported the use of these dyes and related azomethine compounds as non-selective spray reagents in chromatography.[7] We have also shown that co-ordination by PAR involves the pyridine nitrogen, the *ortho*-hydroxyl group and the azo nitrogen furthest from the heterocyclic ring.[8] Reported here are two further series of ligands:

1. Ligands where the groups in PAR involved in co-ordination are unaltered, but other modifications to the molecule are made.
2. Ligands where the co-ordinating groups in PAR are modified, either by changing their position, their chemical nature, or by eliminating them.

These compounds have been synthesised by unambiguous methods* and preliminary investigations have been made into their properties as analytical reagents, particularly with respect to their use in chromatography. The disk chromatogram method of Pollard *et al.*[7] was used, and in addition direct spot tests were made by spotting sheets of chromatography paper (Whatman No. 54) with solutions of about fifty cations of known strength and spraying with an alcoholic solution of the ligand. The colours developed were recorded for comparison and the sheets viewed under ultraviolet light for fluorescences. In nearly every case the colours had to be developed fully by exposure to ammonia.

SERIES 1: $=N-\overset{\|}{C}-N=N-\overset{\|}{C}-\overset{\|}{C}-OH$ GROUP UNALTERED

Table 1 shows a qualitative summary of results obtained for the first series of ligands. From it some general observations concerning the ligands can be made.

Removal of the *para*-hydroxyl group in PAR produces a much paler dye that gives a better colour contrast on chelation with metals. Compound 3† is isomeric with PAN, yet is a derivative of α-naphthol. It is just as sensitive as PAN, but the dye, its anion and metal complexes all absorb at longer wavelengths.

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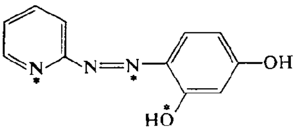
* Details of synthesis will be presented in full in a subsequent paper.

† Numbers refer to compounds in tables.

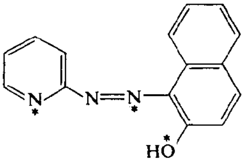
TABLE I.—LIGANDS WITH A HETEROCYCLIC NITROGEN ATOM AND A HYDROXYL GROUP BOTH ORTHO TO AN AZO GROUP

No.	Ligand	Solubility		Colour				Sensitivity *cf.* PAR	Selectivity *cf.* PAR
		Water	Ethanol	Acid	Neutral	Alkaline	Complexes		
1.	2-(2-pyridylazo)-phenol	sl.sol.	sol.	yl.	pl.yl.	or.	r.,vl.,gr.	same	same
2.	2-(2-pyridylazo)-5-methylphenol	v.sl.sol.	sol.	yl.	pl.yl.	or.	r.,vl.,gr.	same	same
3.	2-(2-pyridylazo)-1-naphthol	insol.	sol.	yl.	or.	cherry r.	vl.,bl.,gr.	same	same
4.	2-(2-pyridylazo)-1-naphthol-4-sulphonic acid	f.sol.	sl.sol.	yl.	or.yl.	or.r.	mag.,vl.,gr.	same	same
5.	2-(2-pyridylazo)-1-naphthol-5-sulphonic acid	f.sol.	sl.sol.	yl.	or.yl.	r.	pr.,bl.,gr.	same	same
6.	2-(2-pyridylazo)-1-naphthol-6-sulphonic acid	f.sol.	sl.sol.	yl.	or.	r.	vl.,bl.,gr.	l.less	same
7.	2-(2-pyridylazo)-1-naphthol-7-sulphonic acid	f.sol.	sl.sol.	yl.	or.	r.	vl.,bl.,gr.	l.less	same
8.	2-(2-pyridylazo)-1-naphthol-8-sulphonic acid	f.sol.	sl.sol.	yl.	or.	mag.	vl.,bl.,gr.	same	same
9.	2-(2-pyrimidylazo)-phenol	sl.sol.	sol.	pl.yl.	pl.yl.	or.r.	r.,br.,bl.,gr.	same	Gps. IIa & IIIa better
10.	2-(2-pyrimidylazo)-5-methylphenol	sl.sol.	sol.	pl.yl.	pl.yl.	or.r.	mr.,br.,gr.	same	Gps. IIa & IIIa better
11.	2-(2-pyrimidylazo)-1-naphthol	insol.	sol.	or.yl.	or.yl.	car.	pr.,vl.,gr.	same	Gps. IIa & IIIa better
12.	2-(2-pyrimidylazo)-1-naphthol-4-sulphonic acid	sol.	insol.	yl.	yl.	r.	mag.,pr.,gr.	l.greater	Gps. IIa & IIIa better
13.	2-(2-pyrimidylazo)-1-naphthol-5-sulphonic acid	sol.	insol.	yl.	yl.	car.	pr.,vl.,gr.	same	Gps. IIa & IIIa better
14.	2-(2-pyrimidylazo)-1-naphthol-6-sulphonic acid	sol.	insol.	cr.yl.	cr.yl.	car.	pr.,bl.,gr.	same	Gps. IIa & IIIa better
15.	2-(2-pyrimidylazo)-1-naphthol-7-sulphonic acid	sol.	insol.	yl.	yl.	car.	pr.,bl.,gr.	l.greater	Gps. IIa & IIIa better
16.	2-(2-pyrimidylazo)-1-naphthol-8-sulphonic acid	sol.	insol.	yl.	yl.	mag.	vl.,bl.,gr.	same	Gps. IIa & IIIa better
17.	2-(2-benzothiazolylazo)-phenol	insol.	sol.	yl.	yl.	mag.	vl.,br.,gr.	l.less	Gp. IIa better
18.	2-(2-benzothiazolylazo)-5-methylphenol	insol.	sol.	yl.	yl.	or.	vl.,bl.,br.	same	Gp. IIa better
19.	2-(2-benzothiazolylazo)-1-naphthol	insol.	sol.	or.r.	or.r.	vl.	bl.,gr.	same	Gp. IIa better
20.	2-(2-benzothiazolylazo)-1-naphthol-4-sulphonic acid	sl.sol.	f.sol.	or.	or.r.	mag.	bl.,gr.	l.less	Gp. IIa better
21.	2-(2-benzothiazolylazo)-1-naphthol-5-sulphonic acid	sl.sol.	f.sol.	or.	or.r.	vl.	bl.,gr.	l.less	Gp. IIa better
22.	2-(2-benzothiazolylazo)-1-naphthol-6-sulphonic acid	sl.sol.	f.sol.	or.yl.	or.r.	vl.	bl.,gr.	l.less	Gp. IIa better
23.	2-(2-benzothiazolylazo)-1-naphthol-7-sulphonic acid	sl.sol.	f.sol.	or.	or.r.	vl.	bl.,gr.	l.less	Gp. IIa better
24.	2-(2-benzothiazolylazo)-1-naphthol-8-sulphonic acid	sl.sol.	f.sol.	or.yl.	or.r.	vl.bl.	bl.,gr.	l.less	Gp. IIa better

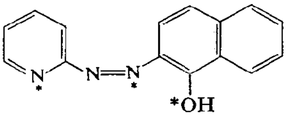
Key					
Key	yl.—yellow	vl.—violet	car.—carmine	wh.—white	sl.—slightly
	mag.—magenta	mr.—maroon	r.—red	bl.—blue	v.—very
	cr.—cream	or.—orange	br.—brown	bf.—buff	f.—fairly
	gr.—green	pr.—purple	pl.—pale	dk.—dark	l.—little



PAR



PAN



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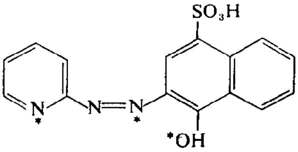
The effect of sulphonating the α-naphthol dyes was (i) to make them more water soluble and (ii) produce lower p*K*a values. However, the 4-substituted (and to a lesser extent the 5-substituted) dyes, with their complexes tend to absorb at shorter wavelengths, whereas the 8-substituted dyes have higher p*K*a values, their anions and some of the complexes absorbing at longer wavelengths.



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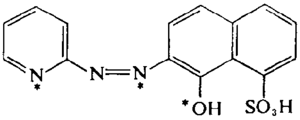

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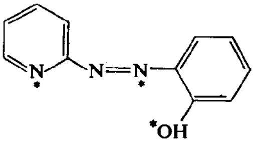
Differences between the heterocyclic residues may be summarised as follows.

1. The pyrimidylazo dyes are more water soluble than their pyridylazo analogues, whereas the benzothiazolylazo dyes are less water soluble.

2. The pyrimidylazo dyes produce stronger colours than any of the other dyes with metals in Groups IIa and IIIa. Otherwise little difference in selectivity was noticed, although the benzothiazolylazo dyes are slightly less sensitive.

3. Under neutral conditions, the pyrimidylazo dyes are more yellow, and the benzothiazolylazo dyes more red than their pyridylazo analogues. The pyrimidylazo dyes therefore produce the largest colour change on chelation under these conditions. In the presence of alkali though, the pyridylazo dyes are the most useful, because they undergo the smallest change in colour on ionisation.

4. Pyrimidine and benzothiazole being weaker bases than pyridine, their azo derivatives should form less stable metal complexes. This is evident when the dyes are used in complexometric titrations; the pyridylazo dye complexes are often too stable to be dissociated by EDTA at the end-point, in cases where the pyrimidylazo or benzothiazolylazo analogues are not.



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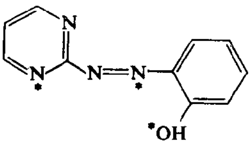

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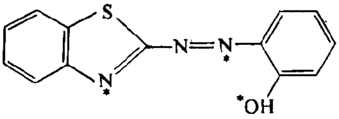

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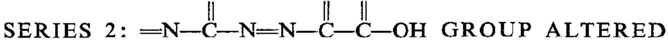
* Asterisks mark probable centres of chelation

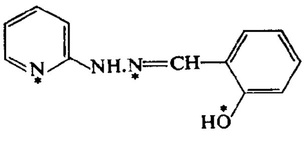
Under ultraviolet light, some of the complexes give an orange-pink to orange-red fluorescence. This is most noticeable with the metals in Groups IIa and IIIa, and with the sulphonated pyridylazo-dyes.



SERIES 2: $=N-\overset{\|}{C}-N=N-\overset{\|}{C}-\overset{\|}{C}-OH$ GROUP ALTERED

Results for the second series of ligands are summarised in Table II. The first observation that can be made is that any alteration of the PAR co-ordinating structure immediately destroys the general sensitivity of ligands of that type.

PAR generally forms two five-membered rings on chelation with metals. In the case of the hydrazones and the 8-quinolyl derivatives, one or both rings become six-membered. This appears to weaken considerably the colour sensitivity of the ligand towards metals, although preliminary potentiometric studies show that most of them form quite stable complexes.



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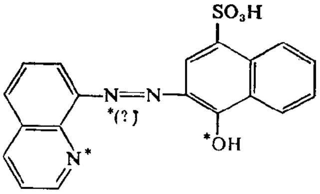

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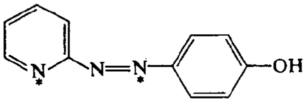
Replacement of the *ortho*-hydroxyl group with a *para*-hydroxyl group in any of the azo dyes or hydrazones causes the ligand to become almost specific for the Group VIII and Ib metals when used as a chromatographic spray reagent. Compounds 25 and 26 are just as sensitive (more sensitive in the case of the nickel group) as their *ortho*-isomers, but the other ligands lose sensitivity with increased selectivity. The chelating properties of 28 have been investigated by Betteridge, Todd, Fernando and Freiser[9] who recommend the ligand for use in solvent extraction.



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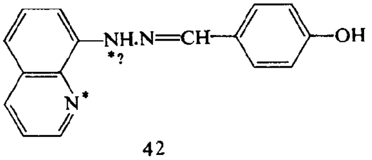

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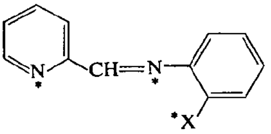

43: X = OH
44: X = SH

Compound 43 has been reported previously as a chromatographic spray reagent,[7] but is included here in order that its properties may be compared with those of 44. The former is very similar to 1 in its selectivity and sensitivity, but the latter shows a marked selectivity towards transition metals from group VIIa to IIb inclusive, also

TABLE II.*—LIGANDS WITH A CO-ORDINATING STRUCTURE OTHER THAN THAT OF PAR

No.	Ligand	Solubility		Colour				Sensitivity *cf.* 1	Selectivity *cf.* 1	Fluorescence
		Water	Ethanol	Acid	Neutral	Alkaline	Complexes			
25.	4-(2-pyridylazo)-phenol	sl.sol.	sol.	yl.	cr.	dk.yl.	br.,vl.,bl.	greater	Gps. VIII, Ib, Zn^{2+}, Cd^{2+}	—
26.	4-(2-pyrimidylazo)-phenol	f.sol.	sol.	cr.	cr.	yl.or.	r.,vl.	greater	Gps. VIII, Ib, Zn^{2+}, Cd^{2+}, but not Fe^{3+}, Fe^{2+}	—
27.	4-(2-benzothiazolylazo)-phenol	insol.	sol.	yl.	yl.	r.	vl.,br.	less	Gps. VIII and Ib	—
28.	4-(2-pyridylazo)-1-naphthol	sl.sol.	sol.	dk.yl.	yl.	car.	vl.,gr.	less	Gps. VIII and Ib Zn^{2+}, but not Fe	—
29.	4-(2-pyrimidylazo)-1-naphthol	sl.sol.	sol.	yl.	yl.	car.	pr.,bl.	less	Gps. VIII, and Ib but not Fe, Ru	-
30.	4-(2-benzothiazolylazo)-1-naphthol	insol.	sol.	or.r.	or.r.	bl.vl.	vl.,br.	much less	Gps. VIII and Ib	—
31.	2-(8-quinolylazo)-1-naphthol	insol.	f.sol.	or.r.	or.r.	mag.	pr.,bl.,gr.	much less	Most metals	Sc^{3+} (weak)
32.	2-(8-quinolylazo)-1-naphthol-4-sulphonic acid	sl.sol.	f.sol.	or.r.	r.	or.r.	bl.,gr.,bf.	less	Most metals	Most metals visible
33.	4-(8-quinolylazo)-1-naphthol	insol.	f.sol.	or.r.	or.r.	mag.	bl.,pr.,br.	much less	Gps. VIII and Ib but not Fe, Ru	—
34.	salicylaldehyde-2-pyridylhydrazone	insol.	sol.	cr.	wh.	cr.	yl.,br.	less	Not IIa, REs, Tl, Pb^{2+}, Bi^{3+}	Ca^{2+}, Mg^{2+}, Sr^{2+}, Sc^{3+}
35.	2-hydroxy-1-naphthaldehyde-2-pyridylhydrazone	insol.	f.sol.	yl.	cr.	yl.	dk.yl.,br.	less	Not IIa, REs, Tl, Pb^{2+}, Bi^{3+}	Al^{3+}, Sc^{3+}, Ca^{2+}
36.	4-hydroxybenzaldehyde-2-pyridylhydrazone	insol.	sol.	cr.	wh.	cr.	yl.,br.,br.	less	Co^{2+}, Pd^{2+}, $PtCl_4^{2-}$, $PtCl_6^{2-}$, Cu^{2+}	Ca^{2+}, Sr^{2+}, Ce^{4+}, Sn^{4+}
37.	salicylaldehyde-2-pyrimidylhydrazone	insol.	sol.	wh.	wh.	cr.	grey,dk.yl.	less	Not IIa, REs, Tl, Pb^{2+}, Bi^{3+}	—
38.	2-hydroxy-1-naphthaldehyde-2-pyrimidylhydrazone	insol.	f.sol.	cr.	cr.	yl.	br.,dk.yl.,or.	less	Not IIa, REs, Tl, Pb^{2+}, Bi^{3+}	yl. quenched by complexing with metals
39.	4-hydroxybenzaldehyde-2-pyrimidylhydrazone	insol.	sol.	wh.	wh.	cr.	yl.br.,br.	less	Fe, Ru, Co^{2+}, Pt, Pd^{2+}, Cu^{2+}	—
40.	salicylaldehyde-8-quinolylhydrazone	insol.	sol.	or.r.	pl.yl.	dk.yl.	br.,pr.	less	Cu^{2+}, (Gps. VIII & Ib much less)	—
41.	2-hydroxy-1-naphthaldehyde-8-quinolylhydrazone	insol.	f.sol.	or.r.	yl.	dk.yl.	br.,pr.	less	Cu^{2+}, (Gps. VIII & Ib much less)	yl. quenched by Cu^{2+}, Au^{3+}, Tl^{3+}
42.	4-hydroxybenzaldehyde-8-quinolylhydrazone	insol.	sol.	or.r.	yl.	dk.yl.	br.,pr.	less	Most metals	—
43.	2-pyridylidene-*o*-aminophenol	insol.	sol.	yl.	cr.	yl.	or.,br.	same	same	Sc^{3+}, Mg^{2+}, Ca^{2+}
44.	2-pyridylidene-*o*-aminothiophenol	insol.	sol.	cr.	wh.	cr.	br.,gr.,pr.	l. less	Gps. VIIa to IIb, In^{3+}, Tl, Pb^{2+}, Bi^{3+}	—

* Key as for Table I.

to indium, thallium, lead and bismuth. Compound 44 produces a large colour change on chelation, but is slightly less sensitive. The reagent is very easily oxidised by the air.

Under ultraviolet light fluorescence is observed with the following ligands: 35, 38 and 41(yellow), 36(blue) and 32(pink). These fluorescences are quenched by most heavy and transition metal ions. In addition fluorescence is observed with 32, 34, 35, 36 and 43 when in the presence of most cations in Groups IIa and IIIa. It is of interest to note that 32 under ultraviolet light is as general in its ability to detect metal ions as PAR, either by forming bright blue fluorescent complexes or by its fluorescence being quenched by the metal to form a dark blue or black spot.

Most of the results presented above are based on the use of the ligands as chromatographic spray reagents. That they may have applications in other branches of analytical chemistry is very likely. Work is therefore being actively carried out in this department on their use in spectrophotometric and complexometric analysis. Formation constants with metals are being measured by potentiometric titration and calculation on an Elliott 503 computer. Results of these investigations will be published in due course.

Zusammenfassung—Es wird eine Übersicht über Komplexbildungsreaktionen mit Metallen gegeben, die mit 44 Verbindungen von substituierter oder modifizierter 4-(2-pyridylazo)-resorcin-(PAR) oder 1-(2-pyridylazo)-2-naphthol-(PAN)-struktur auf Chromatographiepapier ausgeführt wurden.

Résumé—On décrit une étude des réactions de complexation des métaux, effectuée par réactions sur papier pour chromatographie et portant sur 44 composés de structures 4-(2-pyridylazo) résorcinol (PAR) ou 1-(2-pyridylazo) 2-naphtol (PAN) substituées ou modifiées.

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Talanta, 1966, Vol. 13, pp. 731 to 734. Pergamon Press Ltd. Printed in Northern Ireland

ELECTRON MICROSCOPE INVESTIGATION OF THE THERMAL AGING OF BARIUM SULPHATE PRECIPITATES

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(*Received* 25 *October* 1965. *Accepted* 5 *January* 1966)

Summary—Barium sulphate precipitates, formed by four different analytical methods, dried and ignited at different temperatures, have been examined with an electron microscope. The study of the dissolution of precipitates has been found useful for the investigation of thermal aging. On heating the precipitates, diffusion, which takes place at temperatures depending on structure, permits structural changes such as reordering to take place. Consequently, the structure of the ignited precipitates approaches the ideal arrangement.

INTRODUCTION

IT IS a frequent question in connection with the precipitation methods of gravimetric analysis, which of the recommended methods ensures the ideal experimental conditions for the formation of pure precipitates. We have chosen barium sulphate as a model substance to study the problem by the derivatographic[1] and the new gas-thermoanalytical methods[2] and have found[3] that foreign ions and water molecules are always built into the crystal structure of barium sulphate in amounts depending on the experimental conditions of the precipitation. Barium sulphate forms a solid solution with its contaminants. The defect sites of the crystal cause a distortion in the lattice and a marked self-diffusion occurs at about 300°. The defect sites of the crystal migrate to the surface and decomposition processes take place forming hydrochloric acid, sulphur trioxide, ammonia and water. These processes are usually complete at about 1000°. It was assumed that the regularity of the crystal structure increased as a result of these processes, although no changes of the characteristic habit of the crystals could be observed.

Electron microscope examination reveals that the surface of the crystals markedly changes as a result of dissolution if the crystals are left in water for 1–2 days. This phenomenon was also noticed by Takiyama.[4] We have used this phenomenon to detect the change in crystal structure on heating.

EXPERIMENTAL

The preparations studied represented the four most important types of precipitation. The precipitations were effected

(1) from extremely dilute solution, according to Hahn and Otto[5] by very slow mixing of dilute solutions of barium hydroxide and sulphuric acid (Fig. 1)

(2) with concentrated reagents, according to Njegovan and Marjanovic,[6] with rapid addition of barium chloride solution to ammonium sulphate solution (Figs. 2–4)

(3) from a standard solution (pH 2, 1% ammonium chloride), according to Winkler[7] (Figs. 5–12) by reversed precipitation

(4) from a homogeneous medium, according to Wagner and Wuellner[8] with amidosulphonic acid (Figs. 13 and 14). We have already reported[2,3] on the derivatograms and gas-analytical results referring to the conditions of the production and to the removal of the volatile contaminants.

The electron microscope observations were made using a Tesla BS 242 B Type electron microscope. Drop-preparations were made on formvar films from suspensions of the precipitates. Preparations of the precipitates, dried at 110° and ignited at various temperatures in the usual way and after storing the samples under water for 1–2 days, were examined with the electron microscope. We have attempted to study the behaviour of the same crystal as it dissolved in water. For this purpose certain points of the specimen grid were deformed by a pin. The position of the chosen crystals with reference to these points was noted, and in this way the same crystal could be found after the dissolution experiment (Figs. 5, 7 and 13).

A one-step carbon replica was also made of the surface of the crystals. This was carried out as follows. The suspension of the precipitate was dropped on a formvar carrier membrane placed on a microscope slide. When the drop was dry a carbon film was evaporated on to the surface and shadowed with gold. The layer prepared in this way was refloated on a basic EDTA solution which dissolved the barium sulphate crystals between the carbon layer and the formvar membrane (Figs. 4, 11 and 12).

The results of the experiments are summarised in Table I.

TABLE I

Method of preparation	Morphology of precipitate		Morphology of precipitate after soaking in water	
	dried	ignited	dried	ignited
Precipitated from dilute solution	square, with straight edges	unchanged	step-dissolved parallel to certain edges	no essential change
Precipitated by concentrated reagent	small, iso-dimensional particles	particle-size increased by 1–2 orders of magnitude, isodimensional	no characteristic dissolution form	certain surfaces are dissolved directionally
Winkler's method	dendrites, cross shape	unchanged	mosaic structure, chiefly internal parts are dissolved	certain planes are dissolved, stepwise
Precipitated from homogeneous medium with amidosulphonic acid	square, spindle shape	unchanged	mosaic structure, chiefly internal parts are dissolved	certain planes are dissolved, stepwise

DISCUSSION

It has been stated in our previous paper[3] that the best experimental conditions for the purest barium sulphate precipitate are ensured by the method of Hahn and Otto, by precipitation from extremely dilute solutions. This precipitate [method (1)] forms rectangular crystals having straight edges and planes. It has also been observed that the dissolving effect of water is oriented, in the direction of one of the axes of the crystal, while planes parallel to this remain practically undisturbed. This phenomenon can be observed in Figs. 1(a) and (b). The toothed structure of the dissolution surfaces shows that the dissolution did not proceed at a constant rate but stepwise even in the given direction. According to Stransky[9] an inverse proportionality exists between the direction and rate of the growth and dissolution of the crystal. From the step structure of the dissolved surface we can conclude that under given conditions the crystals have grown in accordance with Kossel's theory. The results of our experiments show that the regularity of the crystals did not change on heating. No volatile contaminant except water has left the precipitate[3] on heating and no change of habit of the crystals

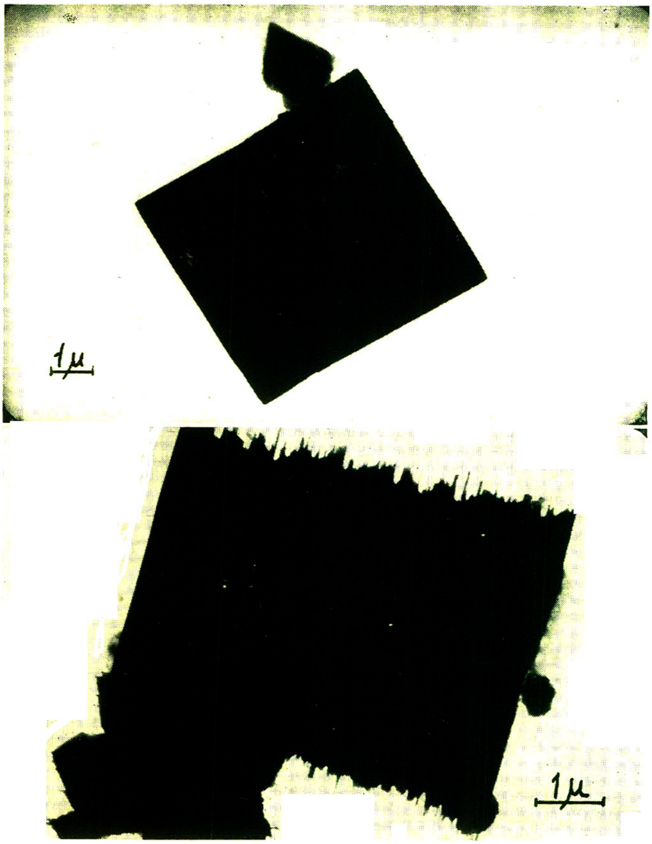

FIG. 1.—Precipitate (1), (a) dried; (b) after dissolution.

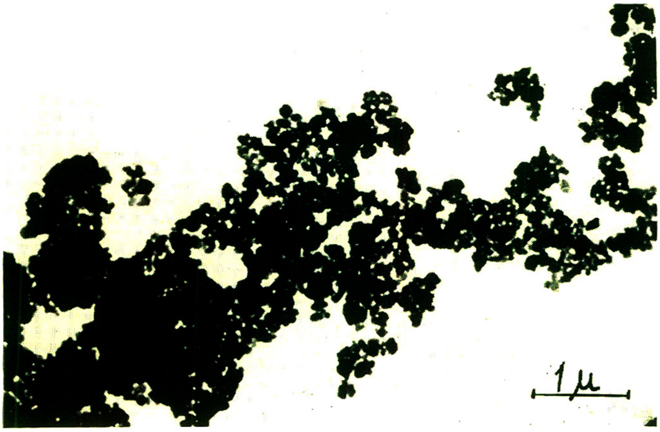

FIG. 2.—Precipitate (2), dried.

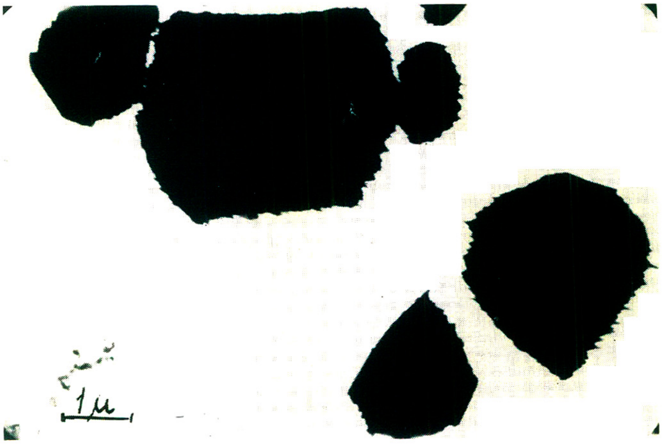

FIG. 3.—Precipitate (2), ignited, after dissolution.

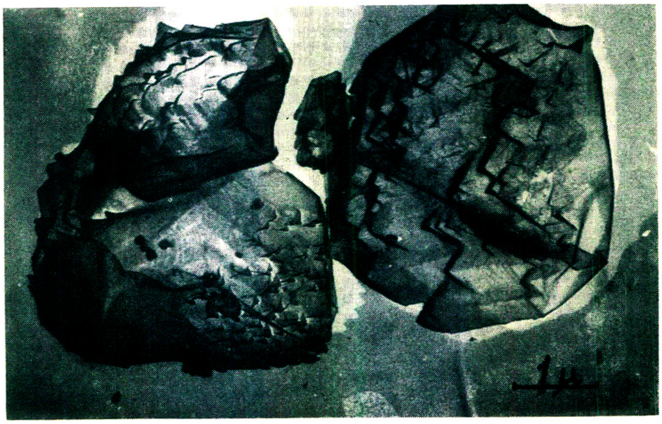

FIG. 4.—Precipitate (2), ignited, after dissolution, replica.

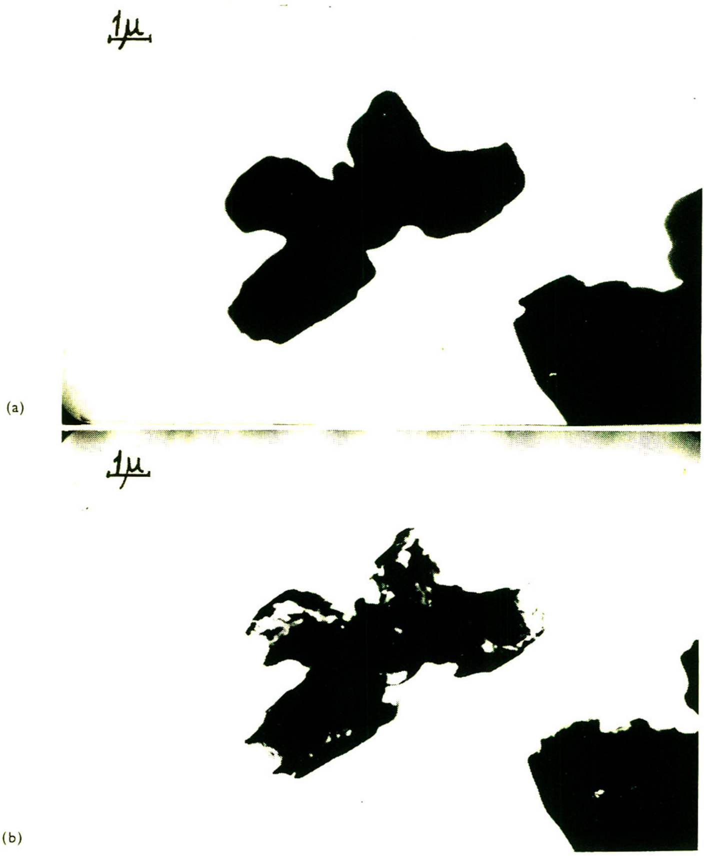

FIG. 5.—Precipitate (3), (a) dried; (b) after dissolution.

FIG. 6.—Precipitate (3), dried, after dissolution.

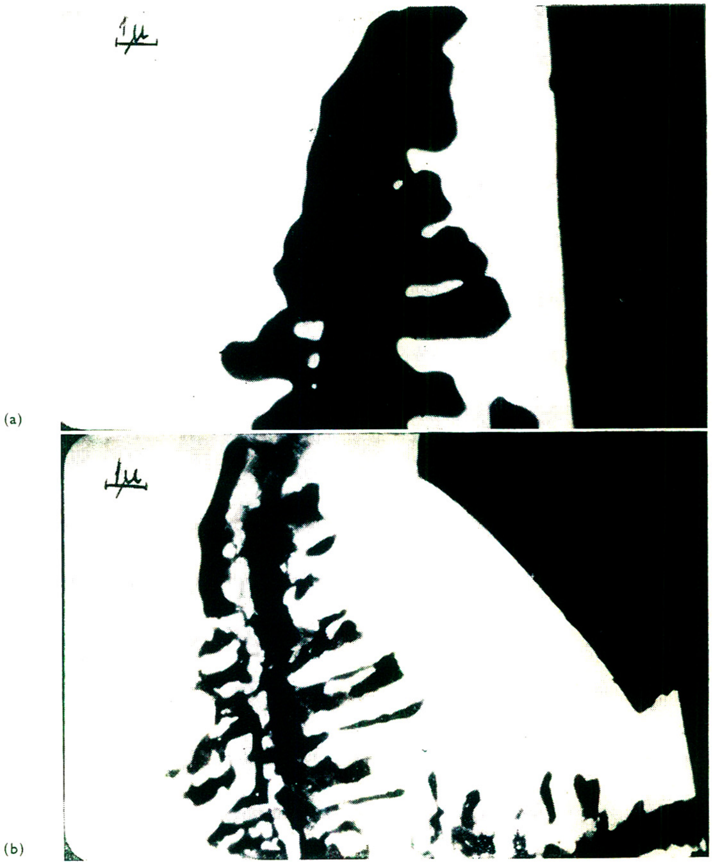

FIG. 7. Precipitate (3), (a) dried; (b) after dissolution.

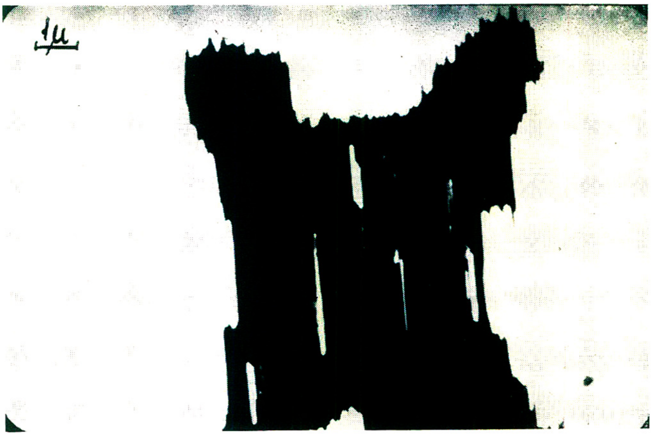

FIG. 8.—Precipitate (3), ignited, after dissolution.

FIG. 9.—Precipitate (3), ignited, after dissolution.

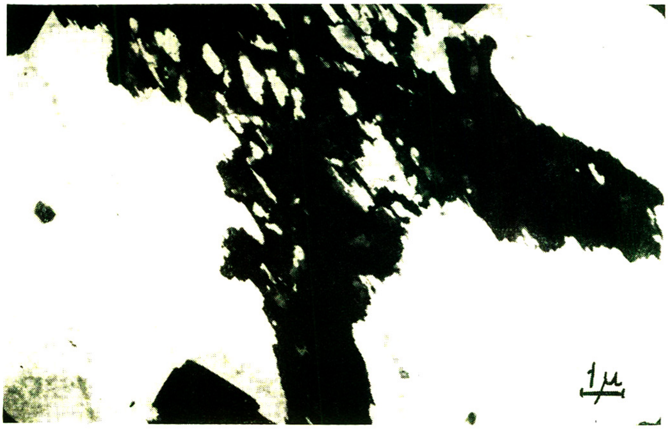

FIG. 10.—Precipitate (3), ignited at 300°, after dissolution.

FIG. 11.—Precipitate (3), dried, replica.

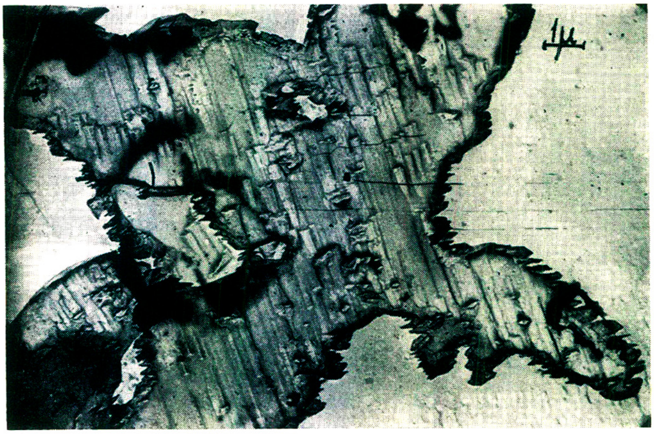

FIG. 12.—Precipitate (3), ignited, after dissolution, replica.

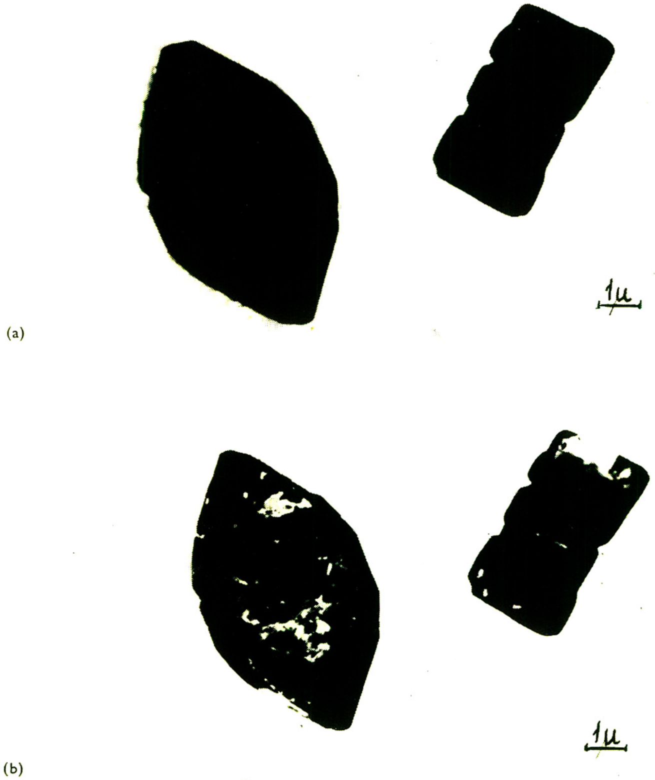

FIG. 13.—Precipitate (4), (a) dried; (b) after dissolution.

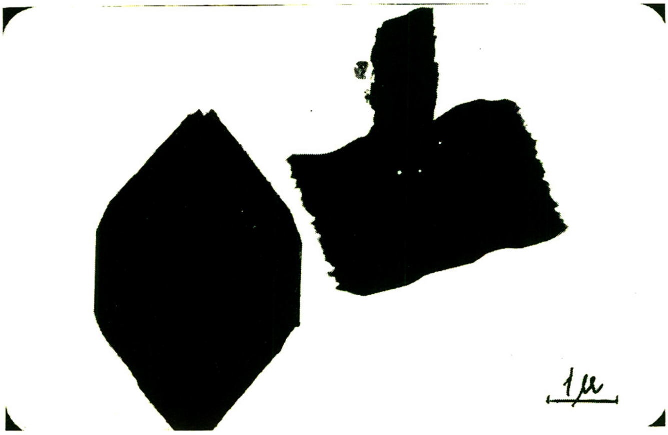

FIG. 14.—Precipitate (4), ignited, after dissolution.

could be observed; also the dissolution of the heated crystals proceeded as described above.

Considering the great purity and regularity of these crystals, the form and dissolution properties of these were taken as reference for the evaluation of phenomena observed with other precipitates.

Less favourable conditions (concentrated solution, quick precipitation, *etc.*) for obtaining a pure and ordered precipitate are ensured by the method of Njegovan and Marjanovic. It has been shown by thermoanalytical examination[3] that this precipitate contains most contaminant. The product precipitated in this way [method (2)] consists of small particles without characteristic form (Fig. 2).

After soaking the dried precipitate in water it can be observed that only the smallest particles dissolve. On heating, the small particles form larger ones to an extent depending on the temperature. The growth of the particle size proceeds up to 800°; above that the aggregate of crystals becomes sintered. According to the dissolution experiments the structure of these crystals shows a uniform arrangement (Fig. 3). The direction of the maximal rate of dissolution can easily be observed in Fig. 4. The increase in particle size becomes apparent at 300°, the regularity only at 600°.

From the point of view of the quantitative determination of sulphate ions Winkler found precipitation in the presence of an excess of ammonium chloride advantageous. However, the foreign ions affected both the purity and loss on ignition,[3] and the morphology of the precipitate.

Crystal forms of dendritic habit, shown in Figs. 5 and 7, are characteristic of precipitation method (3). Water begins to dissolve the dried precipitate without any order at various points of the crystal [Figs. 5(b) and 6]. In this way the primary and secondary branches, having been formed at the beginning of the precipitation and covered by small crystals later, become observable [Figs. 7(a) and 7(b)]. The two pictures show the mosaic structure of the crystals and also the irregular arrangement of the mosaic particles. The crystals, however, as shown by Figs. 8 and 9, recrystallise entirely on heating. Water causes step-dissolved surfaces similar to those on the ideal crystal of Hahn and Otto. The recrystallisation process has already started at 300° (Fig. 10). It can also be stated that all the small particles of all the crystals are of the same orientation, after heating, no matter what their original shape. The edges of the dissolution surfaces are perfectly parallel. On the surface of crystals shown in Fig. 11, parallel grooves can be observed, which can be explained by stepwise growth. Hence the direction of growth is perpendicular to the grooves. According to Fig. 12 the direction of the maximal rate of dissolution is perfectly perpendicular to the grooves. However, Figs. 5(b) and 7(b) illustrating dried precipitates, do not conform with this idea, because no regularity could be found on dissolution.

With the precipitation from a homogeneous medium [method (4)] the reagent appears in the solution very slowly, by the decomposition of the precipitation agent (small relative supersaturation), which ensures the formation of pure precipitates according to earlier assumptions. The results of our thermoanalytical measurements contradict this assumption,[3] and our electron-microscope observations show that the crystals reach their ideally regular arrangement only after heating to 1000°.

Precipitate (4) formed under these conditions consists of well-grown crystals of brick and spindle shape [Fig. 13(a)]. The crystal structure is a mosaic consisting of many differently oriented small crystals. This conclusion can be drawn from the fact that water dissolves it in small areas without any regularity [Fig. 13(b)]. The ignition did not change the habit of the crystal, but markedly changed the internal structure. The parallelism of the edges of the dissolution surfaces shows the great anisotropy of the crystal. As is shown by Fig. 14, the precipitate is already in the recrystallisation state at 500°. On dissolution of the crystals ignited at 300° the mosaic structure predominates.

Therefore, the barium sulphate precipitates can be classified in three groups from the point of view of thermal aging.

(1) Ignition has not caused any change in the particle size or in the structure of barium sulphate crystals precipitated very slowly from dilute solutions.

(2) On heating a precipitate consisting of small particles and formed from a concentrated precipitant, the increase of particle size and the formation of internal regularity proceed simultaneously.

(3) and (4) Heating changes neither particle size nor habit of the dendritic mosaic precipitates, but increases their internal regularity.

Acknowledgements—We thank E. Mucsy (Csepel Metal Works) for helping us with preparation of the replicas.

Zusammenfassung—Mit vier verschiedenen analytischen Methoden hergestellte, bei verschiedenen Temperaturen getrocknete und geglühte Bariumsulfatniederschläge wurden unter einem Elektronenmikroskop untersucht. Die Untersuchung der Ausflösung von Niederschlägen wurde als nützlich zur Erforschung der thermischen Alterung befunden. Beim Erhitzen der Niederschläge gestattet die bei von der Struktur abhängigen Temperaturen einsetzende Diffusion Strukturänderungen, wie z.B. Ausheilungen. Demzufolge nähert sich die Struktur der geglühten Niederschläge der Idealanordnung.

Résumé—On a examiné, au moyen d'un microscope électronique, des précipités de sulfate de baryum formés par quatre méthodes analytiques différentes, séchés et calcinés à différentes températures. On a trouvé que l'étude de la dissolution des précipités est utile pour les investigations relatives au vieillissement thermique. Par chauffage des précipités, la diffusion, qui se produit à des températures dépendant de la structure, permet à des changements structuraux tels que le réarrangement de se produire. En conséquence, la structure des précipités calcinés approche de l'arrangement idéal.

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Talanta, 1966, Vol. 13, pp. 735 to 744. Pergamon Press Ltd. Printed in Northern Ireland

HYDROXAMIC ACIDS AS COLORIMETRIC REAGENTS

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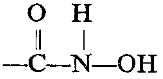
(*Received* 3 *December* 1965. *Accepted* 6 *January* 1966)

Summary—Thirty-three hydroxamic acids and three *N*-substituted hydroxamic acids or structurally similar compounds have been studied as possible colorimetric reagents for metal ions. They were tested with 78 ions under varying conditions of acidity and basicity. Aliphatic, substituted aliphatic, aromatic, substituted aromatic, and heterocyclic hydroxamic acids were represented in the compounds studied. An attempt was made to correlate the activity towards metal ions with variations in the molecular structure of the hydroxamic acids. The studies with *C*-substituted hydroxamic acids indicate that the preferential formation of a colour or a precipitate depends on pH, the solvent, and reagent concentration, and is not a function of the presence or absence of a substituent on the nitrogen atom. A number of the compounds offer promise of being useful colorimetric reagents under proper reaction conditions.

THE purpose of this investigation was to examine systematically the reactions of a variety of hydroxamic acids, particularly those likely to give colour reactions with metal ions, to see if they could be used in developing new spectrophotometric methods of analysis. There has been an increasing interest in hydroxamic acids recently, and a large number of them have been described in the literature. It seemed advantageous to undertake an investigation of as many as possible using the same conditions, with the intention of classifying their reactions systematically and correlating reactivity with variations in structure. In this way it was hoped that a large body of information could be unified and thus indicate useful areas for further investigation.

During the course of our work, vanadium(V) was used as the main test ion because of its high degree of reactivity with hydroxamic acids. A spectrophotometric method for trace quantities of vanadium(V) was developed as a result of the study, using one of the compounds synthesised for our studies.[1]



The class of organic compounds containing the reactive group $-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-OH$ and known as the hydroxamic acids has been widely studied by organic chemists and shows many reactions characteristic of the functional group in the molecule. The coloured complex given with ferric ions by a molecule containing this group has long been known, and has been made the basis for qualitative tests for a number of related organic compounds. During the past 15 years, much experimental work has been done with hydroxamic acids for the detection, separation and determination of a number of metal ions. The most popular compound for this purpose is *N*-phenylbenzohydroxamic acid. It has been reported as a gravimetric reagent for 16 metal ions including copper, iron, aluminium, and titanium;[2] cobalt and nickel;[3] and uranium.[4] Extraction of the precipitates into chloroform has provided colorimetric methods for some of these ions. Other hydroxamic acids which have been used in gravimetric determinations are benzohydroxamic acid,[5] salicylhydroxamic acid[6] and oxaldihydroxamic acid.[7]

Many hydroxamic acids have been applied to the spectrophotometric determination of metal ions. The iron-benzohydroxamic acid system has been extensively investigated;[7–9] benzohydroxamic acid has also been used for the spectrophotometric determination of molybdenum,[10] vanadium,[10,11] uranium,[12] and manganese.[13] Other reported colorimetric reagents are salicylhydroxamic acid,[14] nicotinohydroxamic acid,[15] oxaldihydroxamic acid,[7] *N*-acetyl-*N*-phenylhydroxylamine,[16] and *N*-cinnamyl-*N*-phenylhydroxylamine.[17] A series of complex-forming hydroxamic acids was studied by Dutta,[18–22] who worked out analytical procedures for manganese, iron, vanadium and molybdenum. Wise[23] and Holkeboer[24] have also reported hydroxamic acid studies.

In the present investigation, 33 hydroxamic acids and 3 *N*-substituted hydroxamic acids or structurally similar compounds were studied.[25] Eleven are commercially available, 13 were privately obtained and 12 were compounds synthesised for this work. They are listed in Tables I–V, separated into 5 categories according to structure. These 36 compounds were tested with 78 ions, under varying conditions of acidity and basicity, using the spot-test procedure developed by Yoe.[26] If a reaction appeared to warrant further investigation, the absorbance curve of the metal complex was obtained. On the basis of these tests, certain observations were made and in the following paragraphs the results are described separately for each structural category.

Aliphatic hydroxamic acids

Colour reactions were given or precipitates formed by most of these compounds with vanadium(V), iron(III), copper(II), uranium(VI), titanium(III), and thallium(III); osmium(VI) and manganese(II) showed only slight reactivity. The absorption of light by those vanadium complexes which showed appreciable absorbance at the wavelength of maximum colour intensity, 440 mμ to 460 mμ, varied as shown in Table VI. Noteworthy is the considerably greater absorbance of the sorbohydroxamic acid complex and the relatively close grouping of most of the other complexes.

Substituted aliphatic hydroxamic acids

These compounds were nearly all unreactive. No vanadium reactions were observed. Ethylhydroxycarbamate reacted weakly with iron(III) and copper(II). Glycinohydroxamic acid gave colours or precipitates with iron(III), cobalt(II), copper(II), nickel(II), osmium(VI), and uranium(VI); this was one of the few compounds which reacted with nickel.

Aromatic hydroxamic acids

Of these 5 compounds, *N*-hydroxybenzenesulphonamide and 1-naphthohydroxamic acid showed very slight reactivity. The remaining 3 compounds reacted with vanadium, iron, thallium, uranium, osmium, titanium, and copper. The comparative intensities of the vanadium complexes are shown in Table VII. Notable are the high intensity of the vanadium-2-naphthohydroxamic acid complex, and the decreased absorption of the vanadium complex formed with 1-naphthoacethydroxamic acid.

TABLE I.—ALIPHATIC HYDROXAMIC ACIDS

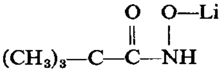
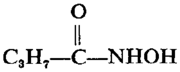
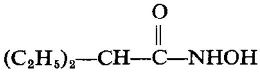
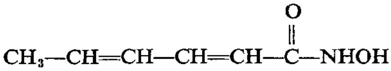
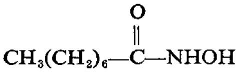
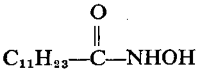
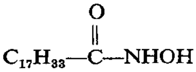
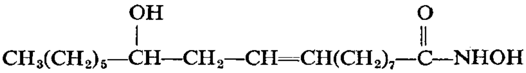
Lithium pivalhydroxamate	 $(CH_3)_3\text{—}\overset{\overset{O}{\|}}{C}\text{—}\overset{\overset{O\text{—}Li}{\mid}}{C}\text{—}NH$
Butyrohydroxamic acid	 $C_3H_7\text{—}\overset{\overset{O}{\|}}{C}\text{—}NHOH$
2-Ethylbutyrohydroxamic acid	 $(C_2H_5)_2\text{—}CH\text{—}\overset{\overset{O}{\|}}{C}\text{—}NHOH$
Sorbohydroxamic acid	 $CH_3\text{—}CH{=}CH\text{—}CH{=}CH\text{—}\overset{\overset{O}{\|}}{C}\text{—}NHOH$
Caprylohydroxamic acid	 $CH_3(CH_2)_6\text{—}\overset{\overset{O}{\|}}{C}\text{—}NHOH$
Laurohydroxamic acid	 $C_{11}H_{23}\text{—}\overset{\overset{O}{\|}}{C}\text{—}NHOH$
Oleohydroxamic acid	 $C_{17}H_{33}\text{—}\overset{\overset{O}{\|}}{C}\text{—}NHOH$
Ricinoleohydroxamic acid	 $CH_3(CH_2)_5\text{—}\overset{\overset{OH}{\mid}}{C}H\text{—}CH_2\text{—}CH{=}CH(CH_2)_7\text{—}\overset{\overset{O}{\|}}{C}\text{—}NHOH$
Cinnamylacethydroxamic acid	 $C_6H_5\text{—}CH{=}CH\text{—}CH_2\text{—}\overset{\overset{O}{\|}}{C}\text{—}NHOH$
C_{16}—C_{18} Fatty hydroxamic acid	

TABLE II.—SUBSTITUTED ALIPHATIC HYDROXAMIC ACIDS

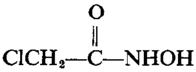
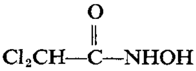
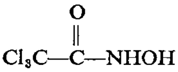
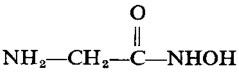
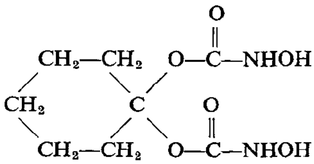
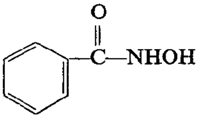
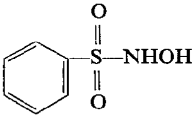
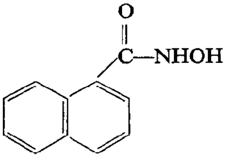
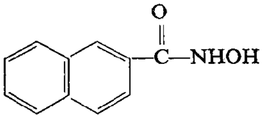
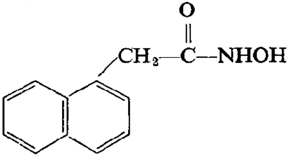
Chloracethydroxamic acid	 $ClCH_2\text{—}\overset{\overset{O}{\|}}{C}\text{—}NHOH$
Dichloracethydroxamic acid	 $Cl_2CH\text{—}\overset{\overset{O}{\|}}{C}\text{—}NHOH$
Trichloracethydroxamic acid	 $Cl_3C\text{—}\overset{\overset{O}{\|}}{C}\text{—}NHOH$
Glycinohydroxamic acid	 $NH_2\text{—}CH_2\text{—}\overset{\overset{O}{\|}}{C}\text{—}NHOH$
Cyclohexanone-bis(carbohydroxamic acid)ketal	

TABLE III.—AROMATIC HYDROXAMIC ACIDS

Benzohydroxamic acid	
N-Hydroxybenzenesulphonamide	
1-Naphthohydroxamic acid	
2-Naphthohydroxamic acid	
1-Naphthoacethydroxamic acid	

Substituted aromatic hydroxamic acids

These reagents reacted, in general, with the same ions as the other groups. Vanadium, iron, uranium, and copper complexes predominated; titanium, thallium, and osmium reacted in a few instances. 2,3-Dichlorobenzenohydroxamic acid was one of the least reactive compounds in this series; it gave colours with vanadium and iron but showed no other reactions. *N*-Laurylphthalamohydroxamic acid gave no colour reaction with any of the ions tested. Anilinohydroxamic acid, like its analogue glycinohydroxamic acid, gave no colour with vanadium but did react with several other ions, including iron, osmium, and uranium; the colours were all of low intensity.

The absorption intensities of the vanadium complexes in this group have a fairly narrow range and show no sharp divisions (see Table VIII). Moreover, most of the complexes in this group, as well as those in the preceding group, have a greater absorption than those in the aliphatic group.

Heterocyclic hydroxamic acids

In this group of 5 compounds, a considerable disparity among reactivities was observed. The last 3 compounds listed in Table V gave no colour with vanadium and only very weak colours with iron, copper or uranium. Nicotinohydroxamic acid and isonicotinohydroxamic acid, however, showed extensive reactivity. The former reacted with vanadium, iron, thallium, palladium, silver, mercury, platinum, iridium, gold, lead, bismuth, selenium, and nickel; and the latter with vanadium, iron, uranium, thallium, cerium, manganese, cobalt, nickel, copper, molybdenum, silver, osmium, and mercury. The vanadium complexes were low in colour intensity.

TABLE IV.—SUBSTITUTED AROMATIC HYDROXAMIC ACIDS

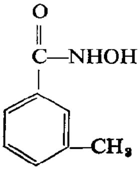
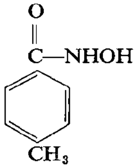
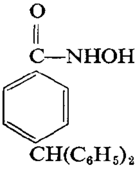
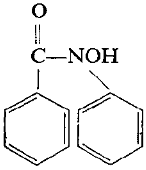
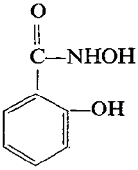
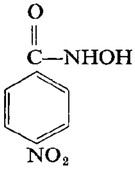
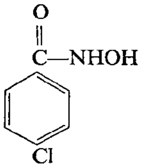
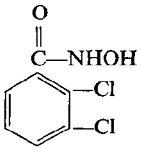
m-Toluohydroxamic acid	
p-Toluohydroxamic acid	
p-(Diphenylmethyl)benzohydroxamic acid	
N-Phenylbenzohydroxamic acid	
Salicylhydroxamic acid	
p-Nitrobenzohydroxamic acid	
p-Chlorobenzohydroxamic acid	
2,3-Dichlorobenzohydroxamic acid	

TABLE IV. (*cont.*)

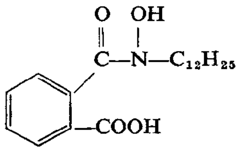
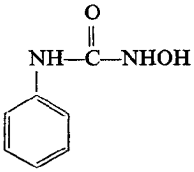
N-Laurylphthalamohydroxamic acid	
Anilinohydroxamic acid	

TABLE V.—HETEROCYCLIC HYDROXAMIC ACIDS

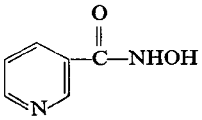
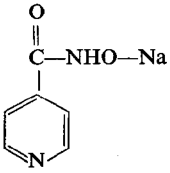
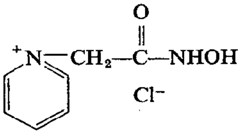
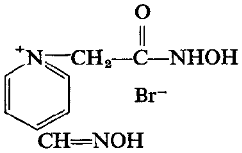
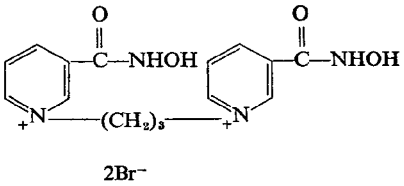
Nicotinohydroxamic acid	
Sodium isonicotinohydroxamate	
α-*N*-Pyridinacethydroxamic acid hydrochloride	
α-*N*-Oximinopyridinacethydroxamic acid hydrobromide	
1,3-(2-Carbhydroxamic acid pyrido)propane dihydrobromide	

TABLE VI.—COMPLEXES OF VANADIUM(V) WITH ALIPHATIC HYDROXAMIC ACIDS

Hydroxamic acids	Absorption at 450 mμ (5 ppm vanadium), %
Sorbohydroxamic acid	36
Cinnamylacethydroxamic acid	28
Laurohydroxamic acid	28
2-Ethylbutyrohydroxamic acid	27
Ricinoleohydroxamic acid	24
Butyrohydroxamic acid	19

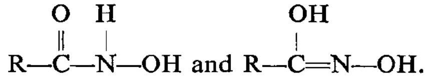
TABLE VII.—COMPLEXES OF VANADIUM(V) WITH AROMATIC HYDROXAMIC ACIDS

Hydroxamic acids	Absorption at 450 mμ (5 ppm vanadium), %
2-Naphthohydroxamic acid	45
Benzohydroxamic acid	38
1-Naphthohydroxamic acid	36
1-Naphthoacethydroxamic acid	27

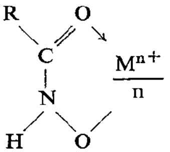
TABLE VIII.—COMPLEXES OF VANADIUM(V) WITH SUBSTITUTED AROMATIC HYDROXAMIC ACIDS

Hydroxamic acids	Absorption at 450 mμ (5 ppm vanadium), %
p-(Diphenylmethyl)benzohydroxamic acid	41
Salicylhydroxamic acid	40
p-Toluohydroxamic acid	38
p-Chlorobenzohydroxamic acid	38
p-Nitrobenzohydroxamic acid	37
m-Toluohydroxamic acid	36
N-Phenylbenzohydroxamic acid	35
2,3-Dichlorobenzohydroxamic acid	31

DISCUSSION



Hydroxamic acids exist in the two forms, $\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{H}{|}}{N}{-}OH}$ and $\mathrm{R{-}\overset{\overset{OH}{|}}{C}{=}N{-}OH}$. Such keto-enol tautomerism provides a number of sites for chelation. Because the keto form predominates in an acidic medium,[27] which is required for most precipitates or colours to form, it is probable that the structure of the majority of hydroxamic acid-metal ion complexes is



This is borne out by the fact that the vanadium-benzohydroxamic acid complex is readily extracted from an acidic medium by organic solvents and is, therefore, presumably neutral, while the species formed in an alkaline medium cannot be extracted.[23] The alkaline form is probably analogous to the manganese-benzohydroxamic acid complex, which has been shown to be anionic and which is formed in an ammoniacal medium with the enol form of the reagent.[28] When the keto form is the primary reactive group, the similarity of the reactions between *N*-substituted hydroxamic acids and those which retain the unsubstituted structure is explained, because the complex structure would be essentially the same for both types. However, as Brandt has pointed out,[8] it is probable that a number of different mechanisms can occur, depending on the metal ion, the reaction medium and other conditions.

With regard to the experimental results obtained, certain conclusions can be drawn from the observed variations in reactivity. In general, the group of ions with which most of the hydroxamic acids react shows the similarity of these compounds to the closely related cupferron compounds; and the reactivity differences within each group follow the established rules of organic chemistry. Among the aliphatic hydroxamic acids, little correlation appears between their structures and the colour intensities of their complexes. The presence of a conjugated system of double bonds in sorbohydroxamic acid probably contributes to its higher reactivity with vanadium. Table VI shows that this compound gives a more intense colour with vanadium than any of the other compounds in this group, all of which contain a saturated carbon atom *alpha* to the reactive group.

In the substituted aliphatic compounds, the electronegativity of the chlorine or oxygen atoms near the reactive group evidently decreases the availability of electrons for chelation and thus prevents many complexes from forming. In glycinohydroxamic acid, the substituent is removed by one $—CH_2$ group from the site of chelation and the electron-withdrawing effect is diminished enough to permit a reaction.

With the aromatic compounds, the importance of the  $—\overset{\text{O}}{\overset{\|}{\text{C}}}—$ group for chelation is shown by the fact that the substitution of sulphur for carbon in the reactive group prevents reaction almost completely. The difference in reactivity of the 1- and 2-positions of the naphthalene nucleus is responsible for the enhanced reactivity of 2-naphthohydroxamic acid as compared with 1-naphthohydroxamic acid. With 1-naphthoacethydroxamic acid the decreased reactivity is probably due to the saturated carbon atom intervening between the aromatic portion of the molecule and the reactive group.

The general similarity of intensities among the colour-complexes of substituted aromatic hydroxamic acids with vanadium indicates that the hydroxamic acid group on a benzene ring is sufficiently reactive to be little affected by a single substituent on the ring, regardless of the nature or position of the substituent. Two electronegative substituents (as in 2,3-dichlorobenzohydroxamic acid) apparently decrease the reactivity somewhat.

Reactions of the heterocyclic compounds indicate that halogen-acid pyridine derivatives of hydroxamic acids are very insensitive. With the two nicotinic acid derivatives it is possible that the colour reactions, all of which were of low intensity, are due to oxidation-reduction rather than to chelation.

A distinction has often been made between *N*-substituted hydroxamic acids as gravimetric reagents and unsubstituted compounds as colorimetric reagents. This distinction appears, however, to have originated more from convenience or habit than from a fundamental difference between the two types of compound. Our work with hydroxamic acids indicates that the preferential formation of a colour or a precipitate depends on pH, the solvent, and reagent concentration, and is not a function of the presence or absence of a substituent on the nitrogen atom.

Acknowledgements—We wish to express our thanks and appreciation to Dr. Arthur L. Fox who synthesised twelve hydroxamic acids for our studies. Thanks are also due to the U.S. Army Chemical Corps and the Jackson Laboratory of E. I. du Pont de Nemours & Co. for supplying a number of compounds. One of us (V. C. B.) gratefully acknowledges a fellowship awarded by the John Lee Pratt Trace Analysis Laboratory during her 3 years of graduate studies and the National Science Foundation for financial assistance during one summer.

Zusammenfassung—Dreiunddreißig Hydroxamsäuren und drei *N*-substituierte Hydroxamsäuren oder strukturell verwandte Verbindungen wurden auf ihre mögliche Eignung als kolorimetrische Reagentien auf Metallionen untersucht. Sie wurden mit 78 Ionen bei wechselnden pH-Werten geprüft. Under den untersuchten Verbindungen waren aliphatische, substituierte aliphatische, aromatische, substituierte aromatische und heterocyclische Hydroxamsäuren vertreten. Es wurde versucht, die Aktivität gegenüber Metallionen mit den Änderungen in der Molekularstruktur der Hydroxamsäuren in Beziehung zu setzen. Die Untersuchungen an *C*-substituierten Hydroxamsäuren zeigen, daß die Ausbildung einer Farbe oder Fällung von pH, Lösungsmittel und Reagenskonzentration abhängt und nicht von An- oder Abwesenheit eines Substituenten am Stickstoffatom. Eine Anzahl der Verbindungen verspricht unter geeigneten Reaktionsbedingungen nützliche kolorimetrische Reagentien.

Résumé—On a étudié trente trois acides hydroxamiques et trois acides hydroxamiques N-substitués ou composés de structure similaire en tant que réactifs colorimétriques possibles des ions métalliques. Ils on été essayés avec 78 ions dans des conditions variables d'acidité et de basicité. Des acides hydroxamiques aliphatiques, aliphatiques substitués, aromatiques, aromatiques substitués et hétérocycliques figuraient dans les composés étudiés. On a tenté de relier l'activité vis-à-vis des ions métalliques à des variations dans la structure moléculaire des acides hydroxamiques. Les études avec des acides hydroxamiques *C*-substitués montrent que la formation préférentielle d'une coloration ou d'un précipité dépend du pH, du solvant et de la concentration en réactif, et n'est pas une fonction de la présence ou de l'absence d'un substituant sur l'atome d'azote. Un certain nombre de composés promettent d'être des réactifs colorimétriques utiles dans des conditions convenables de réaction.

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BEHAVIOUR OF GLASS AND SILVER/SILVER CHLORIDE ELECTRODES IN SOME NON-AQUEOUS MEDIA

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(*Received* 19 *July* 1965. *Accepted* 10 *January* 1966)

Summary—The stability of glass electrodes and silver/silver chloride electrodes in isopropanol, methyl ethyl ketone and a mixture of equal volumes of these has been measured, and found to be of the order of 1 mV. Changes in the electrode potential due to addition of water and to addition of supporting electrolyte have been investigated. The glass electrode responded reversibly to hydrogen ion activity changes in buffers of picric acid-tetraethylammonium picrate, and perchloric acid-di-isopropylamine. The autoprotolysis constants at 25° were calculated to be 2×10^{-19} in isopropanol, 2×10^{-26} in the ketone and 8×10^{-19} in the mixture.

INTRODUCTION

THE recently increased output of papers dealing with the more fundamental aspects of acid-base chemistry in non-aqueous solvents has resulted in an increased understanding of the phenomena. The acid-base behaviour in acetonitrile,[1] ethylenediamine[2] and *t*-butanol[3] has been treated as well as conductometric measurements in a variety of solvents. Fundamental data are often too scarce for a complete evaluation of the conditions for a successful titration. The conditions for non-aqueous titrations have therefore usually been found by trial and error. This approach is not applicable when a high accuracy is required. Accordingly, an electrode system with high stability and accuracy must be evaluated. Hills[4] has described electrode systems, for use in some anhydrous media, which were reversible, reproducible and suitable as reference electrodes.

This paper deals with an investigation of the glass–silver/silver chloride system for coulometric titration in isopropanol, methyl ethyl ketone and a mixture of both. In the same solvents the titration end-point was earlier[5] than that located by the indicator Thymol Blue or potentiometrically using the glass-aqueous calomel electrode system. Carson and Ko[6] described a method for base generation in 70% isopropanol medium. As a reference they used the silver/silver chloride electrode placed directly in the titration solution. After changing the acid concentration the glass electrode needed 2 min to reach the equilibrium potential. The silver/silver chloride electrode has been used in the potentiometric titration of bases in acetic acid, chlorobenzene, nitrobenzene, ethyl acetate, chloroform and acetonitrile.[7,8]

EXPERIMENTAL

Solvents

Methyl ethyl ketone, for chromatography, was dried with anhydrous calcium sulphate and distilled. Isopropanol, "Baker Analyzed", was used without further purification. The water content was determined by Karl Fischer titration. In a mixture of isopropanol and methyl ethyl ketone the water content increased due to the formation of 1-ethyl-1,1-dipropoxyethane.[9] The amount of water changed from $2{\cdot}7 \times 10^{-2}M$ to $4{\cdot}0 \times 10^{-2}M$ during 0·5 hr in a mixture of equal volumes of the solvents, and further to $18 \times 10^{-2}M$ after 48 hr. For this reason the mixtures were prepared immediately before use. Carbon dioxide was expelled by purified nitrogen.

Supporting electrolyte

Sodium perchlorate, *pro analysi*, was recrystallised and dried at 130°. The solubility of sodium perchlorate in a mixture of 50% methyl ethyl ketone and 50% isopropanol was about 30 g/l. and in pure isopropanol about 5 g/l. Tetraethylammonium perchlorate and the isosteric fluoroborate are very suitable as supporting electrolytes but for use in routine analysis they are too expensive. Lithium perchlorate was also rejected because of the acidic properties of the lithium ion.

Apparatus

A Beckman Research pH-meter was used for the potentiometric measurements. The cell consisted of a Metrohm titration vessel EA615. All electrodes and a motor driven Teflon stirrer were inserted through the ground glass joints on the top. The lower part of the vessel was double-walled so that water could be circulated. All measurements were made at 25·0°.

Electrodes

The glass electrodes were Beckman Type pH 0–11 and Metrohm Type U. After use in non-aqueous solutions the electrodes were rinsed and stored in distilled water.

A bridge to an aqueous calomel electrode was prepared according to Marple and Fritz.[10] The vessels were arranged concentrically, however, which resulted in a high internal resistance (1 mΩ). The reproducibility of the glass electrode–calomel electrode system reported by Marple and Fritz was 2 mV over a considerable time. Measurements have shown that the reproducibility of this electrode system was less than that of the glass–silver/silver chloride (Table II). The liquid–liquid junctions in the calomel electrode system which caused diffusion potentials were probably the reason for this lower reproducibility.

Silver/silver chloride electrodes were prepared by electrolytic deposition of silver and silver chloride on a platinum support, as recommended by Ives and Janz.[11] The silver/silver chloride electrode was inserted into a tube with a glass filter disk in the bottom and provided with a ground joint on the stem. The tube was filled with the chloride solution with or without supporting electrolyte and sealed to the electrode proper by a rubber stopper. The internal resistance was 75 kΩ when the solution was 0·05*M* sodium perchlorate in isopropanol.

RESULTS

Reference electrode stability

The aging of silver/silver chloride electrodes of different shapes and origin is shown in Table I. Different amounts of sodium perchlorate added to the lithium chloride solution had no influence on the stability of the electrode potential. The potential increased 5 mV when the amount of sodium perchlorate was changed from 2·5 g/l. to 5·0 g/l. Diffusion potentials and a change in the ionic strength of the medium accounted for this difference.

Addition of water to the reference electrode solution shifted the potential to more positive values depending on the diminished association of sodium chloride, which tended to compensate for the decrease in activity coefficients of the chloride ions. An increase of the water content from 0·06% to 0·25% and further to 1·0% changed the potential to 4·4 mV and 10·4 mV respectively. The stability of the electrode was of the same order as before.

Glass electrode stability

If the glass electrode has been stored in water for a month or more it takes 2 hr to reach the equilibrium potential in the non-aqueous solvents investigated. When reconditioned in water overnight, after use in non-aqueous solution, 15 min was sufficient to obtain a stable potential. When equilibrium had been obtained the response was very fast. Intercomparison of two glass electrodes showed that the potential difference was the same in water, isopropanol and in methyl ethyl ketone, *i.e.*, the asymmetry potential remained the same independent of the solvent. The influence of water on electrode potentials in a mixture of 50% isopropanol and

TABLE I.—POTENTIAL DIFFERENCE BETWEEN Ag/AgCl ELECTRODES AS A FUNCTION OF THE TIME FROM THE IMMERSION OF THE NEW ELECTRODE. (SOLVENT: 0·01*M* LiCl IN ISOPROPANOL)

Time *hr*,	A *mV*	B *mV*	C *mV*	D *mV*
0·1	0	−1·2	−2·1	−1·2
0·25	0	−0·6	−2·6	−0·9
0·50	0	−0·4	−2·7	−0·8
1·50	0	−0·3	−2·8	−0·8
2·0	0	−0·2	−2·8	−0·8
3·0	0	−0·3	−2·8	−0·7
4·0	0	−0·3	−2·8	−0·9
6·0	0	−0·3	−2·7	−0·8
8·5	0	−0·3	−2·7	−0·8
22·0	+0·2	−0·4	−2·3	−0·7
70·0	+0·2	−0·4	−1·2	−0·9

A. Intercomparison of two new wire electrodes prepared simultaneously.
B. One new wire electrode compared to an aged wire electrode.
C. One commercial wire electrode, previously used but dried before the new immersion, compared to two old wire electrodes.
D. One new disk electrode, 0·8 cm^2, compared to an aged wire electrode.

50% methyl ethyl ketone is shown in Fig. 1. The water was added to 50 ml of 0·001*M* picric acid solution containing 5 g of sodium chloride. The potentials became stable immediately.

Glass-reference electrode system

The reproducibility of the glass–silver/silver chloride electrode system in the mixture of isopropanol and methyl ethyl ketone was determined in 0·001*M* picric acid (5 g of sodium perchlorate/l.). Table II shows the results of three runs on three consecutive days. The decrease of potential with time can be quantitatively explained by the formation of water. In spite of the liquid junction potentials and the problem of crystallisation of salts in the filter, the reference electrode containing 0·01*M* lithium chloride was more reproducible and stable over a longer period than that containing sodium chloride and sodium perchlorate. This is probably due to the very low solubility of sodium chloride.

When the amount of supporting electrolyte was increased from 2·5 g/l. to 5·0 g/l. in a weak acid solution the potential became 10 mV more positive. The glass electrode was compared to a reference containing no sodium perchlorate.

Electrode calibration in buffer systems

Because of the low solubility of salts very few buffer systems are suitable. This applies especially to isopropanol but also in methyl ethyl ketone. Picric acid-tetraethylammonium picrate buffer, previously used by Coetzee and Padmanabhan[12] in acetonitrile, seemed to be satisfactory in our solvents. The perchloric acid-di-isopropylamine buffer was also suitable for investigating the hydrogen ion response of the glass electrode. The reference electrode solution was 0·01*M* lithium chloride.

Conductometric measurements made by the present author[13] confirmed that simple dissociation

$$HPi + SH \rightleftharpoons SH_2^+ + Pi^- \qquad (1)$$

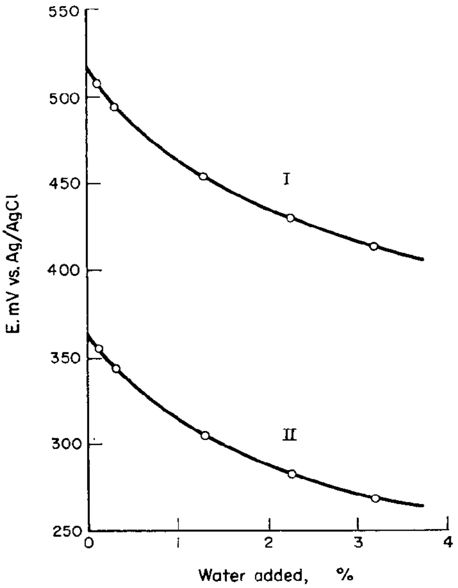

FIG. 1.—The influence of water on electrode potentials in 0·001*M* picric acid—5 g $NaClO_4$/l. Solvent: a mixture of 50% isopropanol and 50% methyl ethyl ketone. I: Reference electrode solution 0·01*M* LiCl. II: Reference electrode solution 0·0002*M* NaCl—5 g $NaClO_4$/l.

dominated for picric acid in isopropanol and in the mixture of 50% isopropanol and 50% methyl ethyl ketone. In methyl ethyl ketone, on the other hand, association of the picrate ion with picric acid occurs in accordance with the following conductance equation

$$\text{HPi} + \text{Pi}^- \rightleftharpoons \text{Pi-H-Pi}^- \tag{2}$$

developed by French and Roe.[14]

The hydrogen ion activity in the solvents may be expressed by

$$a_{\text{H}^+} = K_a \cdot \frac{[\text{HPi}]}{[\text{Pi}^-]} \cdot \frac{f_s}{f_a} \tag{3}$$

TABLE II.—GLASS-Ag/AgCl POTENTIALS IN 0·001*M* PICRIC ACID IN THE MIXTURE OF ISOPROPANOL AND METHYL ETHYL KETONE

Electrode system	Time, *min*	1 *mV*	2 *mV*	3 *mV*
I	10	+519·6	+519·0	+518·9
	200	+519·5	+518·8	+518·6
	600	+518·7	+517·9	+517·9
II	10	+353·4	+360·5	+362·1
	200	+349·0	+364·8	+364·1
	600	+337·4	—	—

I. Reference electrode solution of 0·01*M* LiCl.
II. Reference electrode solution of 0·0002*M* NaCl and 5 g of $NaClO_4$/l.

For methyl ethyl ketone this expression is valid only at the half-neutralisation point. The activity coefficients were calculated from the Debye-Hückel equation

$$\log f_i = -C_1 . Z_i^2 D^{-3/2} \sqrt{I} \qquad (4)$$

D is the dielectric constant, which is 18·3 for isopropanol, and 18·1 for methyl ethyl ketone at 25·0°, calculated from the value measured at 20·0°.[15] Using these values as calibration points, the dielectric constant of the mixture was measured at 5 mc, giving a value of 18·0 at 25·0°. The constant C_1 in equation (4) is 279, 281 and 314 in the alcohol, the ketone and the mixture, respectively.

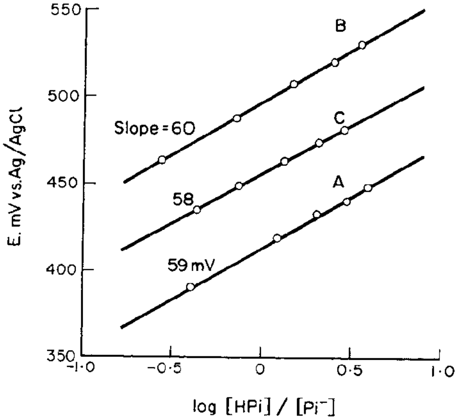

Fig. 2.—Response of the glass electrode in picric acid-tetraethylammonium picrate buffer. The tetraethylammonium picrate concentration constant at 1·5 × $10^{-3}M$ in isopropanol (A), 2·5 × $10^{-3}M$ in methyl ethyl ketone (B), and 2·6 × $10^{-3}M$ in 50% isopropanol and 50% methyl ethyl ketone (C).

The potential of the glass-silver/silver chloride electrodes was plotted *vs.* log HPi/Pi⁻. A straight line with slope 59 mV proves that the glass electrode obeys the Nernst equation

$$E_{glass} = C_2 + 59 \log a_{H^+} \qquad (5)$$

The constant C_2 can be determined by substituting K_a (Table III), the half-neutralisation potential (Fig. 2) and the activity coefficients.

The perchloric acid-di-isopropylamine buffer was used for investigating the Nernst equation in the alkaline region. The amine was titrated with 0·19*M* perchloric acid which contained 2% of water. The water content was about 0·2% at the end of the titration. The base dissociation gives

$$B + SH_2^+ \rightleftharpoons BH^+ + SH \qquad (6)$$

$$K_{BH^+} = \frac{B}{BH^+} \cdot \frac{f_s}{f_a} \cdot a_{H^+} \qquad (7)$$

Formation of BHB^+ will make the slope of the plot of the Nernst equation higher than 59 mV. At the half-neutralisation point, however, $B/BH^+ = 1$ independent of the hydrogen bonding. The electrode potential was plotted *vs.* log x/(100 — x) where

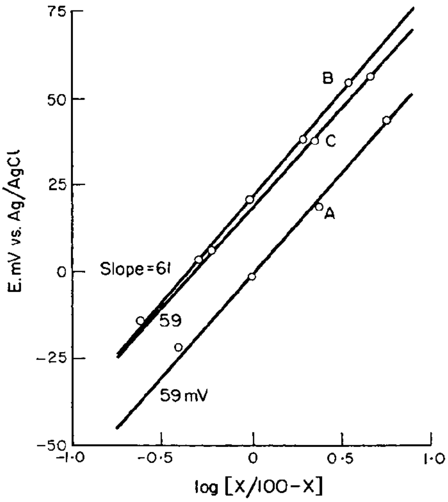

FIG. 3.—Response of the glass electrode in perchloric acid-di-isopropylamine buffer. The ionic strength at the half-neutralisation point is $4{\cdot}5 \times 10^{-3}$ in isopropanol (A), 5×10^{-3} in methyl ethyl ketone (B), and 5×10^{-3} in 50% isopropanol and 50% methyl ethyl ketone (C).

x is the percentage of B titrated (Fig. 3). The half-neutralisation potential was read from this plot and substituted into equation (5) to give the proton activity; K_{BH^+} was then calculated from equation (7). The values are given in Table III.

TABLE III

Buffer system	Solvent	K_a resp. K_B	C_2	K_{BH^+}	K_S
Picric acid-tetraethylammonium picrate	isoPropanol	$2{\cdot}5 \times 10^{-4}$	617		2×10^{-19}
	Methyl ethyl ketone	$6{\cdot}4 \times 10^{-9}$	971		2×10^{-26}
	50% isoPropanol 50% Methyl ethyl ketone	$2{\cdot}3 \times 10^{-4}$	656		8×10^{-19}
Perchloric acid-di-isopropylamine	isoPropanol	$3{\cdot}1 \times 10^{-9}$		$6{\cdot}0 \times 10^{-11}$	
	Methyl ethyl ketone	$1{\cdot}7 \times 10^{-10}$		$1{\cdot}5 \times 10^{-16}$	
	50% isoPropanol 50% Methyl ethyl ketone	$2{\cdot}6 \times 10^{-8}$		$3{\cdot}1 \times 10^{-11}$	

The autoprotolysis constant, K_S, can be found from K_{BH^+} and K_B, the latter being determined conductometrically[13]

$$2\,SH \rightleftharpoons SH_2^+ + S^- \tag{8}$$

$$K_S = a_{S^-} \, . \, a_{SH_2^+} = K_B \, . \, K_{BH^+} \tag{9}$$

DISCUSSION

The glass–silver/silver chloride electrode combination has proved to be suitable as an indicator system for titration of acids and bases in isopropanol, methyl ethyl ketone and a mixture of both.

A buffer solution of picric acid-tetraethylammonium picrate containing sodium perchlorate as supporting electrolyte has been taken as a standard against which changes in the asymmetry potential of the glass electrode and shifts of the reference liquid junction potential were adjusted. The silver/silver chloride potential itself was reproducible within 1 mV. The stability of a single electrode was of the order of 0·1 mV after 25 min in the solution. After calibration against the buffer the composite electrode system is stable within 1 mV during a day. The temperature coefficient was +0·8 mV/° in the range 18·0–27·0°. It responds reversibly to changes in the hydrogen ion activity. In a weak acid solution the potential shifted less than 10 mV if the water content was doubled from 0·06% to 0·12%.

Brønsted[16] has characterised solvents on the basis of three properties which have an important bearing on the acid-base behaviour of solutions in these media. These properties are proton-donating power (acidity), proton-accepting power (basicity) and ionising power (high dielectric constant). Because the dielectric constants of the three solvents are about the same, simple qualitative statements can be made. Methyl ethyl ketone has an autoprotolysis constant of the order of 10^{-7} times as great as in isopropanol or the mixture. From this and the values of dissociation constants (Table III) it can be inferred that the pH break at the end-point is larger in the pure ketone than in the isopropanol or in the mixture. Methyl ethyl ketone has a very small autoprotolysis constant; hence acids and bases with an extraordinarily wide range of proton energies can exist unlevelled in it. A mixture of isopropanol and methyl ethyl ketone is to be preferred as a solvent because of the higher solubility of solutes. The differentiating action of isopropanol is not changed by mixing with methyl ethyl ketone.

Acknowledgement—The author thanks Docent Gillis Johansson for valuable help and discussions. She is also indebted to Professor K. J. Karrman for his interest in this work.

Zusammenfassung—Die Stabilität von Glaselektroden und Silber-Silber-chlorid-Elektroden wurde in Isopropanol, Methyläthylketon und einer Mischung gleicher Volumina der beiden Lösungsmittel gemessen; sie liegt in der Gegend von 1 mV. Änderungen im Elektrodenpotential auf Grund von Wasserzusatz und Zugabe von Trägerelektrolyt wurden untersucht. Die Glaselektrode sprach reversibel auf Änderungen der Wasserstoffionenaktivität in Puffern aus Pikrinsäure-Tetraäthylammoniumpikrat und Überchlorsäure-Diisopropylamin an. Die Autoprotolysenkonstanten bei 25° wurden berechnet: $2 \cdot 10^{-19}$ in Isopropanol, $2 \cdot 10^{-26}$ im Keton und $8 \cdot 10^{-19}$ in der Mischung.

Résumé—On a mesuré la stabilité des électrodes de verre et d'argent/chlorure d'argent dans l'isopropanol, la méthyléthylcétone et leur mélange à volumes égaux, et trouvé qu'elle était de l'ordre de 1 mV. On a étudié les changements de potentiel de l'électrode dûs à l'addition d'eau et à l'addition d'électrolyte support. L'électrode de verre répond réversiblement aux variations d'activité de l'ion hydrogène en tampons acide picrique-picrate de tétraéthylammonium et acide perchlorique-diisopropylamine. On a calculé que les constantes d'autopyrolyse à 25° sont 2×10^{-19} en isopropanol, 2×10^{-26} dans la cétone et 8×10^{-19} dans le mélange.

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ANALYTICAL APPLICATIONS OF TERNARY COMPLEXES—II*

SPECTROPHOTOMETRIC DETERMINATION OF COPPER AS ROSE BENGAL BISPHENANTHROLINIUM COPPER(II)

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(*Received* 22 *November* 1965. *Accepted* 11 *January* 1966)

Summary—A ternary complex system, [(Cu.phen$_2$)Rose Bengal], is proposed for the determination of traces of copper ion. The reaction is rendered specific for copper amongst 56 cations and most anions by extraction of bis(2,9-dimethyl-1,10-phenanthrolinium) copper(I) from an EDTA medium. Because of the high molar absorptivity, 62,500, solutions containing 0·002 ppm of copper may be analysed without difficulty. The colour system is stable for a period of days.

In 1964, Dagnall and West described an extremely sensitive spectrophotometric procedure for the determination of trace amounts of silver(I) which was based on the formation of a ternary complex with 1,10-phenanthroline and Bromopyrogallol Red (BPR).[1] Although the reaction was unselective it was made virtually specific for silver by use of EDTA plus, in some instances, hydrogen peroxide and fluoride ion. An extractive system for selective separation of the ternary complex into nitrobenzene was also described.[2]

Further investigation of this type of ternary complex system indicates that the selectivity of reaction could be improved considerably by using an anionic dyestuff other than BPR which does not contain *vic.* hydroxyl groups. It has already been demonstrated that complex formation in the above system occurs through co-ordination of the central cation with the nitrogen atoms of the phenanthroline to form a co-ordinately bonded phenanthrolinium cation carrying the same charge as the central ion. This ion then associates with BPR to form a well defined ternary complex system. Since the *vic.* hydroxyl groups play no co-ordinative part in binding the cation, it is apparent that their presence detracts from the inherent selectivity of this reaction because BPR may undergo colour reactions with many ions other than silver in this way. Furthermore, BPR is subject to oxidation, particularly in alkaline media, and its solutions are, therefore, somewhat unstable. Yet again, the strongly hydrophylic sulphonic acid group in BPR renders extraction of complexes into water-immiscible solvents rather difficult. The mechanism of the colour reaction in the bis(silver diphenanthrolinium)-BPR complex is also a factor of considerable interest because one does not normally associate such marked changes in absorption spectra with ion association systems of this nature. This aspect will be considered in a subsequent communication, but the present paper is concerned with the effect of using non-chelating anionic dyes in these ternary systems with a view to improving their basic selectivity. It also describes in detail the determination of one particular ion, *viz.* copper(II), by means of one of these systems.

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* Part I: R. M. Dagnall and T. S. West, *Talanta*, 1964, **11**, 1533.

Selection of anionic counter ion

As a result of an examination of a range of anionic dyestuffs for this purpose it was concluded that those which were most advantageous were the carboxylic acid members of the fluorescein series, particularly those substituted with bromine and iodine. Because it was apparent that only those cations which form phenanthrolinium complexes would be expected to yield ternary systems, attention was concentrated on these, *viz.* cadmium, cobalt(II), copper(II), manganese(II), nickel, lead and zinc.

The well known trisphenanthrolinium iron(II) complex does not form a ternary complex because of the high value of the third formation constant, which is due to orbital stabilisation. This stability precludes the formation of a $\{[\mathrm{Fe(II)phen}_2]^{2+}\mathrm{RBE}^{2-}\}$ body. This aspect of the work will be dealt with in a subsequent communication dealing with the theoretical aspects of these ternary systems.

With these dyestuffs, it was found that strongly absorbing ternary complexes were formed in all instances and that all except that with silver could be extracted into chloroform, ethyl acetate, *etc.*, whereas the dyestuffs were not extracted appreciably in alkaline solution in the absence of these metal ions. The silver complexes could only be extracted into nitrobenzene, as observed in the first paper in this series. A significant feature of these fluorescein-based ternary systems is the much smaller separation that occurs between the absorption bands of the free dyestuff and the ternary complex relative to those obtained with BPR as counter anion. This factor is important in considering the mechanism of colour formation, and demands extractability of the ternary complexes for satisfactory analytical use. If these were not extractable from the excess of anionic dye, the sensitivity of determination based on an average 20–40 mμ bathochromic band separation of complex and reagents would inevitably be unsatisfactory.

Table I shows the results of a preliminary study of the sensitivity of some of the ternary complexes obtained with 1,10-phenanthroline and tetrachloro(P) tetraiodo(R) fluorescein, by comparing the molar absorptivities obtained in chloroform, ethyl acetate and nitrobenzene extracts with the values quoted[3] for the corresponding dithizone complexes of the same metals. These data do not necessarily represent the maximum values of the molar absorptivities because they are measured under the conditions found to be most suitable for the copper(II) complex which is the subject of this communication. However, the table shows that these ternary complexes are, on the whole, capable of yielding greater sensitivity than dithizone, which is one of

TABLE I.—TENTATIVE SENSITIVITIES OF TERNARY ION-ASSOCIATION SYSTEMS

Ion determined	Molar absorptivity	
	Ternary complex	Dithizone
Cd	92,000 (E.A.)	85,000
Co	92,000 (E.A.)	59,000
Cu(II)	78,000 (E.A.)	45,000
Mn	65,000 (E.A.)	32,000
Ni	50,000 ($CHCl_3$)	34,000
Pb	70,000 (N.B.)	72,000
Zn	95,000 (E.A.)	94,000

E.A. = Ethyl Acetate. N.B. = Nitrobenzene.

the most sensitive of all spectrophotometric reagents. Further, the stability of the colour system is very much superior to that of dithizone systems.

The copper(II) phenanthroline system

Rose Bengal (Extra), C.I. 45440 [tetrachloro(P) tetraiodo(R)fluorescein], (RBE), provided the most sensitive counter ion for the copper(II)phenanthrolinium cation, but it is not readily available in a pure state and it was found to be difficult to purify it to theoretical composition. As a result, we have used the closely related substance Erythrosin, C.I. 45430 [tetraiodo(R) fluorescein] to study the nature of the complexes involved because, as a foodstuff additive, it is easily obtained in a state of known purity. RBE itself was used in developing the analytical method because of its slightly higher sensitivity. The optimum conditions of reaction were the same for Erythrosin and RBE.

Figure 1 shows the absorption spectra of the copper-1,10-phenanthroline-Erythrosin complex in aqueous solution and following extraction into chloroform. A phosphate buffer at pH 9 was used to obtain a constant pH and chloroform was selected because it is denser than water and may also be used to extract the copper(I) Neo-cuproine complex. It will be seen that, whereas a mixture of 1,10-phenanthroline and Erythrosin in the absence of copper(II) shows maximum absorption at 525 mμ, the ternary complex absorbs at 545 mμ in aqueous solution and in chloroform. In the latter medium, however, the molar absorptivity of the complex is several times greater.

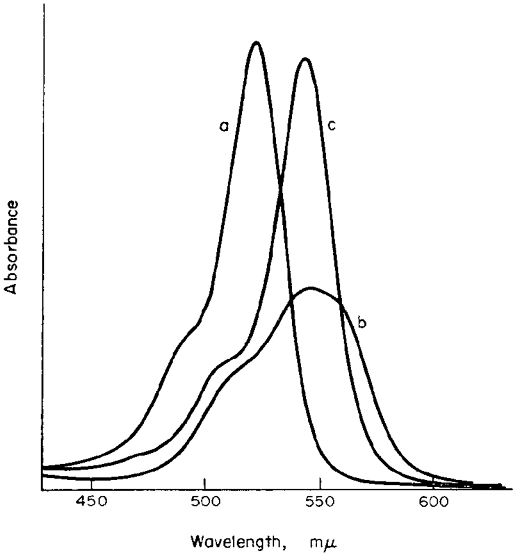

Fig. 1.—Absorption spectra of ternary system:

(a) 3 ml of $10^{-4}M$ Erythrosin plus 3 ml of $10^{-3}M$ 1,10-phenanthroline and 1 ml of phosphate pH 9 buffer diluted to 25 ml with distilled water.

(b) As (a) but plus 5 ml of $10^{-4}M$ copper.

(c) As (b) but after extraction into 25 ml of chloroform.

Spectra measured against a distilled water blank in 1-cm cuvettes.

Figure 2 shows the response to pH of (i) the reagent system (curve *b*), in the absence of copper(II) (ii) the ternary complex (curve *a*) with copper(II) following extraction into chloroform and (iii) the combined reagent/complex system (curve *c*). Best results are obtained at pH 7–9 but the higher value was selected for further studies as a matter of convenience. A disodium hydrogen phosphate buffer was found to be most suitable; there was no apparent deleterious effect of the phosphate ion on the colour response of the copper.

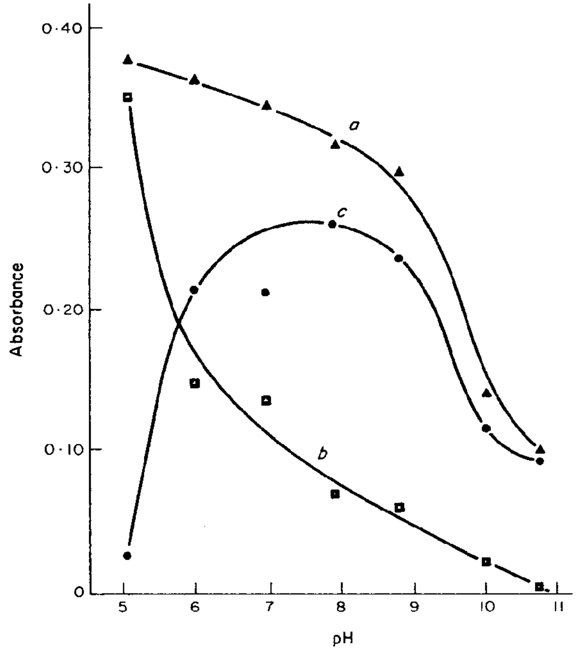

FIG. 2.—Effect of pH on ternary system:

(a) 1 ml of $10^{-5}M$ copper, 1 ml of $10^{-2}M$ 1,10-phenanthroline and 20 ml of $10^{-4}M$ Erythrosin adjusted to the required pH with acetic acid and ammonia and extracted into 25 ml of chloroform.

(b) As (a) but containing no copper.

(c) Resultant curve of (a) compared with (b).

Absorbance measured at 545 mμ in 1-cm cuvettes.

As with the previously described $[Ag(phen)_2]_2BPR$ system,[1] it was found that the present complex also precipitated from aqueous solution after several hours, particularly when its concentration was greater than $10^{-4}F$. Chloroform extracts were quite stable over a period of 4 days standing exposed to normal laboratory conditions of illumination. Irradiation by bright sunlight caused a slow fading, however. The time necessary for maximum colour to develop after extraction was found to be 30 min and the order of addition of reagents to the copper solution did not appear to be critical in any way. To obtain the maximum colour response it was found necessary to maintain a minimum five-fold molar excess of phenanthroline and a two-fold excess of Erythrosin over copper(II). In subsequent experiments leading to the development of an analytical procedure a minimum ten-fold excess of Erythrosin or RBE and a hundred-fold minimum excess of phenanthroline were employed.

Composition of the complex

The ternary complex between silver, 1,10-phenanthroline and BPR was shown by the usual optical procedures to have the empirical formula $\{[Ag(phen)_2{}^+]_2BPR^{2-}\}$. Because Erythrosin carries two negative charges and copper has a co-ordination number of four or six, a similar but somewhat simpler structure was expected for the present system. Job and mole-ratio plots carried out as described by Dagnall and West[1] for the ternary silver system revealed the structure to be $\{[Cu(phen)_2{}^{2+}]Ery^{2-}\}$ (Figs. 3 and 4). Figure 5 shows the results of a Harvey-Manning slope ratio plot obtained by varying one constituent at a time whilst maintaining a constant large excess of the other two. The reacting ratios of copper(II) to Erythrosin and of copper(II) to phenanthroline balance well at 1:1 and 1:2 but the value of the Erythrosin to phenanthroline ratio is more indeterminate being close to 2:3. Nevertheless, the situation is complicated by the extraction procedure and taken in conjuction with the more definite evidence of the Job and mole ratio plots the complex appears to be as formulated.

The molar absorptivity of the RBE complex following extraction into ethyl acetate is 78,000, whilst in chloroform it is 62,500. The conditions most favourable to the formation of the copper complex do not necessarily favour the other ions mentioned in Table I, the ternary complexes of which will be reported on in subsequent communications. In these experiments also, the complexes were partitioned into equal volumes of the organic solvent. Obviously a concentration effect and, therefore, a greater analytical sensitivity, could be obtained by using a small volume ratio of organic solvent to aqueous phase, but this would not, of course, alter the molar absorptivity.

Development of analytical method

An attempt was made to use the extraction of copper(I) as its Neo-cuproine (2,9-dimethyl-1,10-phenanthroline) complex to separate copper from the other ions likely to interfere. The extraction of copper(I) Neo-cuproine is reported in the literature to give a specific colour reaction for copper(I) in the presence of some 56 metals and numerous anions except cyanide.[4,5,6] Morrison and Freiser[7] suggest that it may be used as a specific extractant for copper(I), but in the present experiments when Neo-cuproine was employed to try to separate copper from the other ions likely to interfere in the proposed method, *viz.* those in Table I, it was found that cadmium, cobalt, nickel, and zinc were also extracted. However, when EDTA was used as a masking agent in conjunction with the Neo-cuproine only copper(I) was extracted. In fact, silver was also found to form a Neo-cuproine complex, but this is not extracted into chloroform and will only interfere if present in such large amounts as to consume sufficient Neo-cuproine.

In the recommended analytical procedure copper(II) is first reduced and extracted into chloroform as its copper(I) Neo-cuproine complex from aqueous solution containing EDTA and citrate at pH 4–6. This gives a quantitative and specific extraction of copper from all other cations we have examined. The copper extract is then equilibrated with a pH 9 phosphate buffer containing 1,10-phenanthroline and RBE and

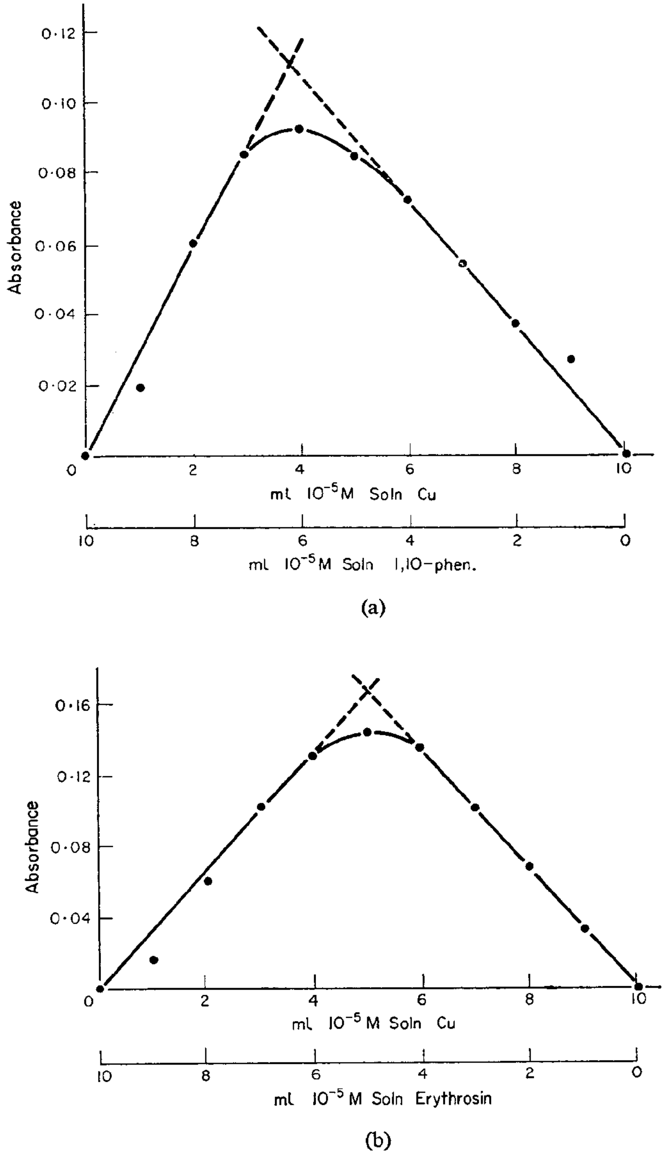

Fig. 3.—Job's plots.

(a) Variation of copper and 1,10-phenanthroline. 0–10 ml of $10^{-5}M$ copper and 10–0 ml of $10^{-5}M$ 1,10-phenanthroline added to 5 ml of $10^{-4}M$ Erythrosin, 1 ml of phosphate pH 9 buffer, and sufficient distilled water to give a constant volume, and extracted into 25 ml of chloroform.

(b) Variation of copper and Erythrosin. 0–10 ml of $10^{-5}M$ Erythrosin and 10–0 ml of $10^{-5}M$ copper added to 1 ml of $10^{-3}M$ 1,10-phenanthroline, 1 ml of phosphate pH 9 buffer and sufficient distilled water to give a constant volume, and extracted into 25 ml of chloroform.

Absorbances measured at 545 mμ in 1-cm cuvettes.

the absorbance of the Cu(Phen)$_2$-RBE complex in the chloroform layer is measured after 30 min at 570 mμ. Oxidation by air proved as efficient as by sodium persulphate and more satisfactory because the RBE was not attacked.

In fact, the copper(I) Neo-cuproine complex can also form a good ion-association complex with Erythrosin in the chloroform layer at pH 9, but the absorbance of this complex is only half of that for the copper(II)—1,10-phenanthroline system. This we presume is because of the difference in charge on the central ion of the complex whereby two copper(I) Neo-cuproine complexes are required for association with one Erythrosin molecule. Fortunately the copper(II)-phenanthroline complex is more

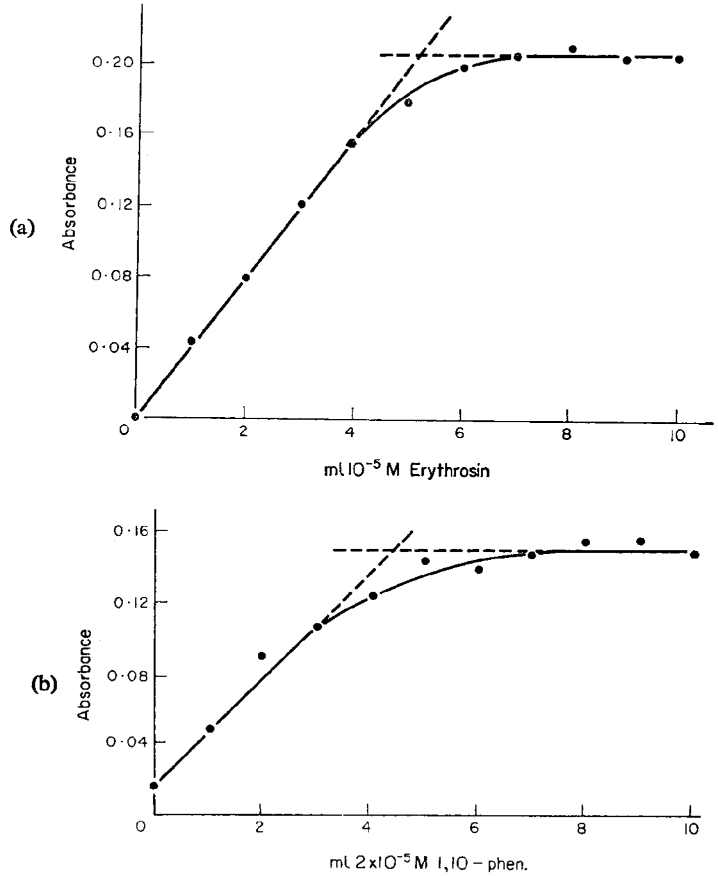

FIG. 4.—Mole ratio plots:

(a) Variation of Erythrosin against constant copper. 0–10 ml of $10^{-5}M$ Erythrosin added to 5 ml of $10^{-5}M$ copper, 1 ml of $10^{-3}M$ 1,10-phenanthroline, 1 ml of phosphate buffer, pH 9, and sufficient distilled water to give a constant volume and extracted into 25 ml of chloroform.

(b) Variation of 1,10-phenanthroline against constant copper. 0–10 ml of $2 \times 10^{-5}M$ 1,10 phen. added to 5 ml of $10^{-5}M$ copper, 5 ml of $10^{-5}M$, Erythrosin, 1 ml of phosphate buffer pH 9 and sufficient distilled water to make up to constant volume, and extracted into 25 ml of chloroform.

Absorbances measured at 545 mμ in 1-cm cuvettes.

stable at pH 9 and is formed quantitatively when the Neo-cuproine complex is treated with excess of 1,10-phenanthroline.

Because the order of addition of reagents is not critical, we used a composite solution containing EDTA, sodium nitrate, sodium citrate and hydroxylamine hydrochloride pre-adjusted to pH 4–6 and a separate Neo-cuproine solution for the initial extraction of the copper(I) complex. Similarly a composite solution containing 1,10-phenanthroline and RBE, and a separate pH 9 phosphate buffer solution were used to convert the Cu(I) Neo-cuproine complex into the Cu(Phen)$_2$.RBE system.

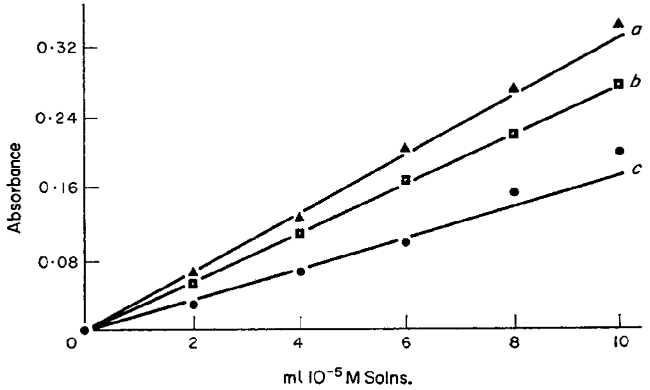

FIG. 5.—Slope ratio plot:

(a) 2–10 ml of $10^{-5}M$ copper added to 5 ml of $10^{-4}M$ Erythrosin, 1 ml of $10^{-3}M$ 1,10-phenanthroline, 1 ml of phosphate pH 9 buffer and sufficient distilled water to give a constant volume, and extracted into 25 ml of chloroform.

(b) As (a) but with 2–10 ml of $10^{-5}M$ Erythrosin and 5 ml of $10^{-4}M$ copper, and 1 ml of $10^{-3}M$ 1,10-phenanthroline.

(c) As (a) but with 2–10 ml of $10^{-5}M$ 1,10-phenanthroline, 5 ml of $10^{-4}M$ copper, and 5 ml of $10^{-4}M$ Erythrosin.

Absorbances measured at 545 mμ in 1-cm cuvettes.

The calibration curve with RBE was found to be linear for 1–6 μg of copper and probably beyond, by the procedure described below; also its extension passes through the origin. Under these conditions in a 1-cm cuvette, at 570 mμ, 1·27 μg of copper gave an absorbance of 0·050, while 6·35 μg gave 0·254 absorbance unit following extraction into an original 25 ml of chloroform. Extraction of the 1·27 μg of copper from 500 ml of solution into 25 ml of chloroform gave exactly similar results, *i.e.*, with test solution at the 0·0024-ppm level. Smaller amounts are best determined using 4-cm cuvettes.

EXPERIMENTAL

Reagents

All reagents are of analytical grade unless otherwise stated.

Copper sulphate solution, $10^{-5}M$

Composite solution A, 0.1*M* sodium nitrate, 0·01*M* EDTA, 30% sodium citrate, and 1% hydroxylamine hydrochloride. Dissolve 8·5 g of sodium nitrate, 3·7 g of EDTA, 300 g of sodium citrate, and 10 g of hydroxylamine hydrochloride in distilled water, adjust the pH to 4–6 with aqueous ammonia and dilute to 1 l.

Neo-cuproine (2,9-dimethyl-1,10-phenanthroline) solution in ethanol, 0·1 % *w/v*

Composite solution B, $10^{-3}M$ 1,10-phenanthroline and *ca.* $10^{-4}M$ Rose Bengal Extra solutions. Dissolve 0·20 g of 1,10-phenanthroline and *ca.* 0·20 g of Rose Bengal Extra distilled water and dilute to 1 l.

Phosphate buffer, pH 9. Dissolve 20 g of disodium hydrogen phosphate in distilled water and dilute to 100 ml. (A 2 ml aliquot of this solution diluted to 20 ml gives pH 9–9·2.)

Apparatus

Spectrophotometer. Unicam SP 600 spectrophotometer with 1-cm glass cuvettes.

Procedure

Calibration curve Pipette 2–10 ml of $10^{-5}M$ copper sulphate solution, 10 ml of the composite solution A, and 1 ml of a 0·1 % Neo-cuproine solution into 100-ml separating funnels. Add distilled water to make the volume to 25 ml. Finally add 25 ml of chloroform and shake for 1 min. Allow the phases to separate and run off the chloroform extracts into another series of 100-ml separating funnels. Pipette into these 10 ml of the composite solution B and 2 ml of the phosphate buffer, add about 10 ml of distilled water and shake for 1 min. Allow the passes to separate and after 30 min run off the chloroform extracts into 1-cm cuvettes. Measure the absorbance at 570 mμ against a blank carried through the same procedure, but containing no copper.

Determinations. Proceed as above, taking an aliquot containing 1–6 μg of copper(II) in $\leqslant$500 ml of nearly neutral solution.

Acknowledgements—We are grateful to the British Welding Research Association for the award of a research grant to one of us (B.W.B.). We also wish to thank Messrs. Procter and Gamble for a grant for the purchase of the Unicam SP 600 spectrophotometer and Mr. H. C. Stagg of I.C.I. Dyestuffs Division for the gift of a sample of Erythrosin.

Zusammenfassung—Ein ternäres Komplexsystem, [(Cu. phen$_2$) Rose Bengal], wird zur Bestimmung von Kupferspuren vorgeschlagen. Die Reaktion wird durch Extraktion von Bis(2,9-dimethyl-1,10-phenanthrolinium)kupfer(I) aus EDTA-Medium neben 56 Kationen und den meisten Anionen für Kupfer spezifisch. Wegen des hohen molaren Extinktionskoeffizienten 62500 können Lösungen mit 0,002 ppm ohne Schwierigkeit analysiert werden. Das Farbsystem ist über mehrere Tage stabil.

Résumé—On propose un système ternaire complexe [(Cu-phen)$_2$ Rose Bengale] pour le dosage de traces d'ion cuivre. Par extraction du bis (2,9-diméthyl 1,10-phénanthrolinium) cuivre (I) à partir d'un milieu EDTA, on rend la réaction spécifique du cuivre parmi 56 cations et la plupart des anions. Le coefficient d'extinction moléculaire étant élevé, 62500, on analyse sans difficulté des solutions contenant 0,002 ppm. Le système coloré est stable pendant plusieurs jours.

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Talanta, 1966, Vol. 13, pp. 763 to 764. Pergamon Press Ltd. Printed in Northern Ireland

SHORT COMMUNICATIONS

Jodometrische Selenbestimmung nach vorausgegangener Extraktionstrennung mit Diisopropylketon

(*Eingegangen am* 29. *November* 1965; *Angenommen am* 14. *Januar* 1966)

In früheren Arbeiten[1–3] wurde aufgezeigt, daß Selen(IV) in salzsaurem Medium sich schnell mit einer Reihe von aliphatischen gesättigten Monoketonen unter Bildung chloroformlöslicher Organoselenverbindungen umsetzt. Diese Tatsache ermöglicht die spezifische Trennung des Selens von den übrigen Elementen.

In der vorliegenden Arbeit wird eine neuentwickelte Methode zur Selenbestimmung in Industriezwischenprodukten wie Schlämmen, Zusammenbackungen, Preßkuchen u.a. mit Selengehalten von 0,5 bis 10 Gew.% beschreiben.

Danach wird das Probegut mit einem geeigneten Lösungsmittel aufgeschlossen, die Lösung mit 7,5*N* HCl behandelt und Diisopropylketon zugesetzt.* Die anfallende organische Selenverbindung wird mit Chloroform extrahiert. Nach Abtrennung der organischen Phase und Zusatz von etwas Salpetersäure erhitzt man das Reaktionsgemisch auf dem Wasserbad, wobei Chloroform verdunstet und die Organoselenverbindung zersetzt wird. Anschließend wird die überschüssige Salpetersäure durch Carbamid zerstört und der vorbehandelten Lösung Kaliumjodid zugesetzt. Das in einer dem Selen äquivalenten Menge abgeschiedene Jod wird dann mit Thiosulfatlösung und Stärke als Indikator titriert.

EXPERIMENTELLER TEIL

Reagenzien

Selen-Standardlösung. Selendioxyd (3,5125 g) wird im 500-ml-Meßkolben in Wasser gelöst. Die Lösung enthält 5000 μg Se in 1 ml.

Diisopropylketon p.a.

Salz-, Schwefel- und Salpetersäure p.a.

Kaliumjodid p.a.

Carbamid p.a.

0,02N-*Natriumthiosulfatlösung*.

0,5 %*ige Stärkelösung*.

Analysenvorschrift

Man übergießt 0,1 bis 0,5 g des Probegutes mit 5–8 ml konz. Salpetersäure und läßt etwa 1 Stde. in der Kälte stehen. Die Lösung wird auf die Hälfte des ursprünglichen Volumens eingedampft. Nach Zugabe von 2 ml konz. Schwefelsäure wird abermals bis zum Eintritt der Säurezersetzung erhitzt. Man kühlt den Rückstand ab, setzt einige ml Wasser und konz. Salzsäure hinzu und filtriert in einen 50-ml-Meßkolben ab. Man setzt soviel Salzsäure hinzu, daß ihre Konzentration im Endvolumen 7,4*N* wird. Man bringt 10 ml der Lösung in ein Scheidetrichter, gibt noch 0,4 ml Diisopropylketon hinzu, schüttelt 1–2 Min. um und läßt dann das Gemisch etwa 20 Min. stehen. Extrahiert wird zweimal je 3 Min. lang mit je 10 ml Chloroform. Die organische Phase wird in einem 50-ml-Meßkolben gesammelt. Nach Zugabe von 2 ml Wasser und 0,5 ml konz. Salpetersäure erhitzt man auf dem siedenden Wasserbad 10–15 Min. Der Rückstand wird abfiltriert, mit Wasser auf 100–150 ml verdünnt und in einen Erlenmeyerkolben mit Schliff gebracht. Man bringt die Lösung zum Sieden und setzt dann 1,5 g Carbamid hinzu. Nach Abkühlen und Ansäuern mit 15 ml konz. Salzsäure werden

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* Bei der Ausarbeitung der Methode wurden zahlreiche aliphatische Monoketone wie Aceton, Methyläthyl-, Diäthyl-, Methylisobutylketon u.a. erprobt. Die mit Diisopropylketon erzielten Ergebnisse ließen sich am besten reproduzieren. Der störende Einfluß der Zerfallsprodukte dieses Ketons auf die anschließende jodometrische Bestimmung dürfte hier am geringsten sein.

2 g KJ zugesetzt. Das abgeschiedene Jod wird mit 0,02N Thiosulfatlösung in Gegenwart von 3 ml Stärkelösung titriert. Kurz vor Erreichen des Äquivalenzpunktes wird der Kolben durch einen Schliffstöpsel verschlossen und die Lösung kräftig geschüttelt. Das elementare Selen flockt aus und erleichtert somit das Ablesen des Äquivalentpunktes.

Zur Bestimmung des Natriumthiosulfat-Titers werden in einem Erlenmeyerkolben 20 ml Selen-Standardlösung mit Salpeter- und Schwefelsäure nach obiger Vorschrift behandelt. Der Rückstand wird in einen 50-ml-Meßkolben gebracht und mit 7,5N HCl verdünnt. Man extrahiert 3 ml der Lösung mit Diisopropylketon und Chloroform und bestimmt dann im Extrakt den Selengehalt wie beschrieben. Der Titer der Thiosulphatlösung wird in mg Selen je ml der Lösung angegeben.

Fehlergrenzen

Zur Bestimmung der Reproduzierbarkeit der Methode wurden Analysenbefunde für aufbereitete Schlämme statistisch ausgewertet.

$$\text{Bei } n = 10, \quad \bar{x} = 8{,}33\%, \quad s = 0{,}025\%$$

Variationskoeffizient: $VK = 100\, s/\bar{x} = 0{,}30$ Rel%

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Summary—The possibility is indicated of determining selenium in industrial intermediate products, such as slurries, agglomerates and briquettes, containing from 0·5 to 10% of selenium. Selenium(IV) in a strongly acidic medium forms a chloroform-soluble organo-selenium compound with isopropyl ketone, and this product can be decomposed by heating with nitric acid. This can be followed by an iodometric determination of the selenium, undisturbed by other elements. The reproducibility of the method, expressed as the coefficient of variation, is 0·3% for 8% of selenium.

Zusammenfassung—Es wird auf die Möglichkeit zur Selenbestimmung in Industriezwischenprodukten wie Schlämmen, Zusammenbackungen, Preßkuchen u.a. mit Selengehalten von 0,5 bis 10 Gew.% hingewiesen. Selen(IV) bildet mit Diisopropylketon in stark salzsaurem Medium (7,5N HCl) eine chloroformlösliche Organoselenverbindung, die sich bei Erhitzen mit Salpetersäure zersetzt. Anschließend wird eine jodometrische Selenbestimmung vorgenommen, die von anderen Elementen nicht gestört wird. Die Reproduzierbarkeit der Methode, durch den Variationskoeffizienten ausgedrückt, beträgt 0,30 Rel-% bei Se-Gehalten um 8 Gew.%.

Résumé—On montre la possibilité de dosage du sélénium dans les produits industriels intermédiares tels que pâtes, agglomérats et briquettes contenant de 0,5 à 10% de sélénium. En milieu fortement acide, le sélénium(IV) forme avec l'isopropylcétone un composé organo-sélénié soluble en chloroforme, et ce produit peut être décomposé par chauffage avec l'eau régale Cette opération peut être suivie d'un dosage iodométrique du sélénium, non perturbé par d'autres éléments. La reproductibilité de la méthode, exprimée par le coefficient de variation, est de 0,3% pour 8% de sélénium.

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Talanta, 1966, Vol. 13, pp. 765 to 766. Pergamon Press Ltd. Printed in Northern Ireland

Adsorption indicators in the titrations of hexacyanoferrate(II) and oxalate with thorium ions

(*Received* 9 *July* 1965. *Accepted* 16 *November* 1965)

THERE are a number of available titrimetric methods for the determination of thorium. Willard and Winter[1] titrated fluoride with thorium nitrate in presence of 50% ethanol using a lake of zirconium and Alizarin Red S as indicator, and this method has been studied by a number of workers.[2-5] An indirect method[6] in which thorium is precipitated as thorium oxalate, and the oxalate determined by permanganate has been proposed. EDTA has also been successfully used.[7,8] The titrations of thorium against hexacyanoferrate(II) and oxalate ions have not been previously described.

Mehrotra and Tandon[9] have recently discussed the mechanism of the action of adsorption indicators, and laid down the essential requirements for the successful application of adsorption indicators to precipitation titrations. The successful applications of Alizarin Red S, Pyrocatechol Violet and Xylenol Orange to the precipitation titrations of hexacyanoferrate(II) and oxalate against thorium ions lends further support to the theory.

The dyes are not adsorbed by the precipitates of thorium hexacyanoferrate(II) and oxalate, whilst the hexacyanoferrate(II) and oxalate ions remain in excess in the supernatant solution. When the equivalence point is just passed the dyes are adsorbed on to the surface of the precipitates with a simultaneous change of colour which is quite sharp and reversible. Hence it is possible to titrate both hexacyanoferrate(II) and oxalate ions separately against thorium ions in weakly acidic solutions.

These titrations when carried out in pure solutions are comparable in accuracy to the titration of thorium with EDTA; but, in common with most precipitation titrations, the method is not suitable in presence of ions which form slightly soluble compounds either with the cation or anion of the main precipitate or which react with the dye. Nevertheless, the proposed method is of value in that it demonstrates the utility of adsorption indicators for the determination of thorium, oxalate and hexacyanoferrate(II) ions.

EXPERIMENTAL

Reagents

Potassium hexacyanoferrate(II) solution. Prepare and standardise by standard methods.[6,10,11] Stabilise[12,13] by addition of 3 ml. of $1M$ KOH/l.

Sodium oxalate solution. Prepare and standardise by standard methods.[6,10,11]

Thorium nitrate solution. Prepare and standardise by standard methods.[6,10,11] Add 3–4 ml of $0{\cdot}1M$ acid/l. of solution.

Indicators. 0·2% w/v of Alizarin Red S, Pyrocatechol Violet and Xylenol Orange.

Procedure

The pH of the solution to be titrated [(oxalate or hexacyanoferrate(II)] was adjusted to the required value by the addition of $0{\cdot}1M$ or $0{\cdot}01M$ acid or alkali (Table I). One drop of the indicator (either Alizarin Red S or Xylenol Orange or Pyrocatechol Violet) for every 10 ml of the solution was added. The solution was then titrated with a solution of thorium nitrate of corresponding strength. During the addition of the titrant a white suspension was produced and as the equivalence point approached, the titrant was added slowly with constant shaking. At the end-point, which occurs just after the equivalence point, the dye is transferred from the supernatant solution to the precipitate with a sudden

TABLE I.—SUMMARY OF CONDITIONS FOR SUCCESSFUL APPLICATION OF INDICATORS

Indicator	Transition at the end-point	Conditions
Alizarin Red S.	Yellowish white suspension → Pink suspension	Applicable in the pH range 2·5–4
Xylenol Orange	Yellowish white suspension → Pink suspension	Applicable in the pH range 2·5–4
Pyrocatechol Violet	Yellowish white suspension → bluish violet suspension	Applicable in the pH range 3–5

change of colour. The precipitate turned pink in case of Alizarin Red S and Xylenol Orange and bluish violet in case of Pyrocatechol Violet. The change of colour was quite sharp and reversible. Coagulation did not occur even in 0·02*M* solutions. Solutions of oxalate and hexacyanoferrate(II) can be titrated up to a dilution of *M*/500 within an experimental error of 0·3%. The colour change at the end-point and the conditions in which the indicators are applicable in the titration of oxalate and hexacyanoferrate(II) with thorium ions are described in Table I.

A study of interferences has shown that the above titrations can be carried out even in the presence of appreciable quantities of chloride, bromide, iodide, acetate and nitrates of alkali metals. The ions that interfere are those which form either a slightly soluble compound with the cation or anion of the main precipitate or react with the dye either to form a complex or to oxidise it. These interfering ions include silver, lead, zinc, cadmium, copper, nickel, cobalt, hexacyanoferrate(III), phosphate, chromate, iodate and fluoride.

Acknowledgement—The author's thank are due to Prof. R. C. Mehrotra, Head of the Chemistry Department, for providing laboratory facilities and encouragement.

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Summary—Alizarin Red S, Pyrocatechol Violet and Xylenol Orange are shown to be effective adsorption indicators for the titrations of hexacyanoferrate(II) and oxalate with Thorium(IV) solution. The action of the indicators can be explained by the theory of surface compound formation.

Zusammenfassung—Es wird gezeigt, daß Alizarinrot S, Brenzcatechinviolett und Xylenolorange bei der Titration von Hexacyanoferrat(II) und Oxalat mit Thorium(IV)-Lösung brauchbare Adsorptionsindikatoren darstellen. Die Wirkung der Indikatoren kann durch die Theorie der Bildung einer Oberflächenverbindung erklärt werden.

Résumé—On montre que le rouge d'alizarine S, le violet de pyrocatéchol et le xylénol orangé sont des indicateurs d'adsorption efficaces pour les dosages et l'hexacyanoferrate(II) et l'oxalate au moyen d'une solution de thorium(IV). On peut expliquer l'action des indicateurs par la théorie de la.formation de composé de surface.

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Talanta, 1966, Vol. 13, pp. 767 to 769. Pergamon Press Ltd. Printed in Northern Ireland

Quantitative infrared analysis of 2,4-tolylene diamine and 2,4-tolylene diurea mixtures

(*Received* 25 *October* 1965. *Accepted* 6 *January* 1966)

THE importance of aromatic derivatives of isocyanate and urea has increased in the past few years, because these substances are used for the processing of polyurethane foam. For process control it is essential to have a rapid method for the simultaneous determination of 2,4-tolylene diamine and 2,4-tolylene diurea. Infrared spectrophotometry seems the most suitable technique. Existing quantitative methods[1,2] used liquid solvent techniques, but in our special case a potassium bromide disk technique was preferred. For the determination of 2,4-tolylene diamine we chose the sharp intense absorption peak at 855 cm^{-1}, originating from the wagging vibration of the amine group. The absorption of 2,4-tolylene diurea is negligible at this wave number. The diurea was determined at 1360 cm^{-1} where a band that is characteristic of urea appears and absorption by 2,4-tolylene diamine is sufficiently low. The base-line method can be used advantageously for the determination.

TABLE I.—CHARACTERISTIC ABSORPTION BANDS OF 2,4-TOLYLENE DIAMINE

Wavenumber, *cm*$^{-1}$	Origin
804	Out-of-plane bending
855	NH_2 wagging
1230	C—N stretching
1320	Symmetric C—H deformation
1470	Asymmetric C—H deformation
1470	Aromatic C—C stretching
1525	Aromatic C—C stretching
1590	Aromatic C—C stretching
2860	CH_3 group, C—H stretching
2930	CH_3 group, C—H stretching
3005	Aromatic C—H stretching
3050	Aromatic C—H stretching
3215	NH group, stretching
3310	NH group, stretching
3360	NH group, stretching
3390	NH group, stretching
3460	NH group, stretching

TABLE II.—CHARACTERISTIC ABSORPTION BANDS OF 2,4-TOLYLENE DIUREA

Wavenumber, *cm*$^{-1}$	Origin
795	Aromatic out-of-plane bending
1360	Urea band
1370	C—H deformation
1460	Aromatic C—C stretching
1460	C—H deformation
1510	Aromatic C—C stretching
1540	Secondary amine, band II
1560	Secondary amine, band II
1600	Aromatic C—C stretching vibration
1610	Primary amide, band II
1630	Primary amide, band II
1660–80	Amide, bands I
2855	C—H stretching
2920	C—H stretching
3030	Aromatic C—H stretching

TABLE III.—RESULTS FOR 2,4-TOLYLENE DIAMINE

Taken, *mg*	Found, *mg*	Relative error, %	Coefficient of variation, % (6 results)
30	24	−20	11
100	119	+19	11
142	125	−12	11
170	152	−10	10
240	260	+8	5
309	309	0	5

TABLE IV.—RESULTS FOR 2,4-TOLYLENE DIUREA

Taken, *mg*	Found, *mg*	Relative error, %	Coefficient of variation, % (6 results)
119	118	−1	6
297	303	+2	4
386	361	−6	3
475	492	+4	2
653	662	+1	3
831	823	−1	3

Procedure

Prepare the disk by mixing thoroughly 2 mg of the dry sample (accurately weighed) with 1 g of potassium bromide (prepared specially for infrared work) in a vibration mill. Press the mixture to a disk under a pressure of 200 atm. Prepare a reference disk from pure potassium bromide in a similar way. Prepare two-component mixtures containing 0–100, 20–80, 40–60, 50–50, 60–40, 80–20 and 100–0% of 2,4-tolylene diamine and 2,4-tolylene diurea and press them into disks with potassium bromide as described, and use them to obtain the calibration curve. Scan the spectrum from 400 to 4000 cm^{-1} and identify the components by their characteristic absorption bands, which are summarised in Tables I and II.

We obtained the following equations for the calibration curves (E denotes the absorbance, and c the concentration in %), using a Zeiss UR10 spectrophotometer:

for 2,4-tolylene diamine at 855 cm^{-1},

$$E = (0{\cdot}04 \pm 0{\cdot}01) + (0{\cdot}0035 \pm 0{\cdot}0003)c;$$

for 2,4-tolylene diurea at 1360 cm^{-1},

$$E = (-0{\cdot}06 \pm 0{\cdot}01) + (0{\cdot}0089 \pm 0{\cdot}0002)c.$$

The accuracy and precision of the results can be judged from Tables III and IV. The steeper slope of the calibration curve for 2,4-tolylene diurea makes the results for this substance reasonably precise and accurate, whereas those for 2,4-tolylene diamine are not very satisfactory.

If sufficiently dry samples can be taken, one analysis can be completed within an hour.

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Summary—A rapid method is described for the simultaneous determination of 2,4-tolylene diamine and 2,4-tolylene diurea by infrared spectroscopy. The method is satisfactory for the diurea determination but gives rather large errors in the diamine determination.

Zusammenfassung—Eine schnelle infrarotspektroskopische Methode zur gleichzeitigen Bestimmung von 2,4-Toluylendiamin und 2,4-Toluylendiharnstoff wird beschrieben. Die Methode ist bei der Diharnstoffbestimmung zufriedenstellend, gibt aber bei der Diaminbestimmung relativ große Fehler.

Résumé—On décrit une méthode rapide de dosage simultané de la 2,4-toluylène diamine et de la 2,4-toluylène diurée par spectroscopie infra-rouge. La méthode est satisfaisante pour le dosage de la diurée mais donne des erreurs relativement importantes pour le dosage de la diamine.

REFERENCES

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[2] S. Tanaka and O. Kinoshata, *Bunseki Kagaku*, 1960, **9**, 621.

Talanta, 1966, Vol. 13, p. 771. Pergamon Press Ltd. Printed in Northern Ireland

LETTER TO THE EDITOR

Some uses of ascorbic acid in the analytical chemistry of iron

SIR,

We have observed some advantages in the use of L-ascorbic acid in the analytical chemistry of iron.

First, in the determination of copper at the 1-ppm level in calcium carbonate by cathode ray polarography[1] (in hydrochloric acid solution), iron in quantities above 200 ppm seriously affects the wave form preceding the copper wave. If about 50 mg of L-ascorbic acid are added to the mercury in the polarographic cell before addition of 5 ml of the sample solution, up to 1000 ppm of iron can be tolerated, and oxygen is more rapidly removed from the solution.

Secondly, in the determination of iron in "Pharmaceutical Grade" calcium carbonate by the 1,10-phenanthroline procedure,[2] under certain conditions hydroxylamine hydrochloride does not completely reduce the iron(III). We have confirmed Wilkinson's suggestion,[3] that under the conditions of the determination in the presence of soluble silica (*i.e.*, sodium silicate) iron(III) is not completely reduced to iron(II) by hydroxylamine hydrochloride. If L-ascorbic acid is used as reducant as proposed by Wilkinson,[4] quantitative reduction occurs. We recommend addition of 10 mg of L-ascorbic acid instead of the 1 ml of 10% w/v hydroxylamine hydrochloride solution previously recommended.[2] The same method of reduction can be used in any colorimetric procedure for the determination of iron(II).

We thank the Directors of John and E. Sturge Limited for permission to publish this letter.

John and E. Sturge Limited
Lifford Chemical Works
Kings Norton
Birmingham 30
England.

M. L. RICHARDSON
P. E. LUTON

3 *January* 1966

REFERENCES

[1] M. L. Richardson, *Analysis of Calcareous Materials*, S.C.I. Monograph No. 18, 1963, p. 245.
[2] *Idem, ibid.*, p. 172.
[3] N. T. Wilkinson, *ibid.*, p. 178.
[4] *Idem*, personal communication.

Talanta, 1966, Vol. 13, p. i. Pergamon Press Ltd. Printed in Northern Ireland

NOTICES

CANADA

Wednesday–Friday 22–24 *June* 1966: **Nineteenth Annual Summer Symposium** on **Separation Techniques:** *Division of Analytical Chemistry of American Chemical Society* and *Analytical Chemistry*. University of Alberta, Edmonton, Canada.

The 27 papers to be presented cover both theoretical and practical aspects of chromatographic separations and include such topics as comparative studies of band spreading in liquid and gas chromatography, new developments in liquid chromatographic techniques, and reports on applications.

UNITED STATES OF AMERICA

Monday–Thursday 10–13 *October* 1966: **80th Annual Meeting of Association of Official Analytical Chemists** to be held at Marriott Motor Hotel, Twin Bridges, Washington, D.C. For further information contact L. G. ENSMINGER, Association of Analytical Chemists, Box 540, Benjamin Franklin Station, Washington, D.C., 20044, U.S.A.

Talanta, 1966, Vol. 13, pp. iii to iv. Pergamon Press Ltd. Printed in Northern Ireland

PAPERS RECEIVED

Flavin enzymes: Molecular orbital calculations: W. R. Carper, M. Q. Freeland and F. R. Duke. (2 *February* 1966)

Titrimetric determination of some organic acids by xenon trioxide oxidation: Bruno Jaselskis and R. H. Kruger. (6 *January* 1966)

Polarographische Bestimmung von Azid-Ionen in Gegenwart von Stickstoffverbindungen aller übrigen Wertigkeitsstufen: Richard Schrader und Gehard Pretzschner. (20. *Januar* 1966)

Polarographische Bestimmung von Barium, Strontium und Cäsium: Hans Th. Christensen. (7 *February* 1966)

Bestimmung von Barium mittels einer stationären Quecksilberelektrode und inverser Polarographie: Hans Th. Christensen. (7 *February* 1966)

Purity determinations by differential thermal analysis: P. B. Bowman and L. B. Rogers. (16 *February* 1966)

Phase titrations—VI: New applications and the phase titration of homologous alcohols: D. W. Rogers, D. L. Thompson and I. D. Chawla. (17 *February* 1966)

Study of the cerium(IV)-picrate system in acetonitrile: Byron Kratochvil, Marie Tipler and Bruce McKay. (17 *February* 1966)

Flame conductivity as a new analytical method for determination of heavy alkali and alkaline earth metals, especially barium: Věnceslav Patrovský. (17 *February* 1966)

Die Trennung niederer aliphatischer Amine durch Gasverteilungschromatographie: S. Häntzsch. (21 *February* 1966)

Present state of complexometry—III: Determination of bivalent metals: Rudolf Přibil. (22 *February* 1966)

Multi-spot paper chromatograms of sodium orthophosphate: Marjorie A. Rommel and Roy A. Keller. (23 *February* 1966)

A method for simultaneous detection of hydrogen fluoride and fluorine: James G. Knowles and John H. Holloway. (24 *February* 1966)

Isotopenverdünnungsanalyse mit stabilen Isotopen—II: Monomeren-Bestimmung im Polycaproamid mit ε-Caprolactam-[^{15}N]: P. Krumbiegel, M. Scholz, H. Hübner und A. Schmidt. (24 *February* 1966)

A comparison of the X-ray crystallography of undecafluorocyclohexane with that of dodecafluorocyclohexane: W. D. Jensen and F. Wm. Cagle, Jr. (25 *February* 1966)

An improved procedure for determining tellerium with Bismuthiol II: K. L. Cheng and B. L. Goydish. (1 *March* 1966)

Crystalline Calmagite and a study of sulphonation effects on azo-dye metal-ion indicators: Frederick Lindstrom and Robert Isaac. (1 *March* 1966)

Extractive photometric determination of barium and strontium using dimethylsulphonazo DAL: Břetislav Buděšínský and Dana Vrzalová. (2 *March* 1966)

Determination of molecular weights of air-sensitive compounds: P. G. Perkins and M. E. Twentyman. (2 *March* 1966)

Coulometric titration of carbon dioxide on the microscale: D. C. White. (7 *March* 1966)

Stoichiometry of the reaction between iron(II) and chromium(VI): U. Mwiali Krishna and G. Gopala Rao. (9 *March* 1966)

Chromatography of traces of metals, with automatic scanning of thin layers by multiscaling using a gamma-ray spectrometer: R. A. A. Muzzarelli. (10 *March* 1966)

Studies on Calcichrome as a spectrophotometric reagent—VI: A new spectrophotometric method for determination of magnesium with Calcichrome: Hajime Ishii and Hisahiko Einaga. (11 *March* 1966)

Determination of traces of tin in beer by activation analysis: J. F. W. Tertoolen and Miss C. Buijze. (11 *March* 1966)

Studies of the spectra of copper dimethylglyoximate, nickel dimethylglyoximate and nickel ethylmethylglyoximate in various solvents: John E. Caton, Jr. and Charles V. Banks. (11 *March* 1966)

Precipitation of beryllium from homogeneous solution in presence of sulphate by the urea hydrolysis technique: T. P. Prasad and M. N. Sastri. (11 *March* 1966)

Vanadium compounds in reductimetric titrations—IV: Titrimetric determination of vanadium(IV), vanadium(V) and their binary mixtures with vanadium(II) sulphate: K. L. Chawla and J. P. Tandon. (16 *March* 1966)

Determination of phosphorus in organic compounds on the centimilligram scale: A. J. Christopher and T. R. F. W. Fennell. (16 *March* 1966)

Amperometric determination method of thioacetamide—II: Maria Pryszcsewska. (17 *March* 1966)

Talanta, 1966, Vol. 13, pp. v to vi. Pergamon Press Ltd. Printed in Northern Ireland

PUBLICATIONS RECEIVED

Electroanalytical Chemistry, Vol. 1: Edited by A. J. BARD. Marcel Dekker, New York, 1965. 280 pp., approx. $10.00.

A. C. polarography and related techniques: theory and practice, D. Smith; Applications of chronopotentiometry to problems in analytical chemistry, D. G. Davis; The electrical double layer, adsorption and electrode reactions, D. M. Mohilner; Photochemistry and electrochemistry, T. Kuwana.

Advances in Chromatography, Vols. 1 & 2: Edited by J. C. GIDDINGS and R. A. KELLER. Marcel Dekker, New York, 1965. Vol. 1—375 pp. Vol. 2—400 pp., approx. $13.75 per Volume.

Volume 1, *General Chromatography.* Ion exchange chromatography, F. G. Helfferich; Chromatography and electrophoresis on paper and thin layers. A teachers' guide, I. Smith; The stationary phase in paper chromatography, G. H. Stewart; The techniques of laminer chromatography, E. V. Truter. *Gas Chromatography.* Capillary columns trials, tribulations and triumphs, D. H. Desty; Qualitative and quantitative aspects of the separation of steroids, E. C. Horning and W. J. A. Vanden den Heuvel; Inorganic gas chromatography, R. S. Juvet. Jr.; Lightly loaded columns, B. L. Karger and W. D. Cooke; Gas chromatographic characterization of organic substances in the retention index system, E. Kovats; Interactions of the solute with the liquid phase, D. E. Martire; Flame ionization detectors, J. C. Sternberg.

Volume 2. The gas chromatography of carbohydrates, J. W. Belly; High speed analysis with packed columns, D. D. Dedford; Ion mobilities in electrochromatography, J. T. Edward; Relation between chromatographic behavior and chemical structure, J. Green; Adsorption chromatography, C. H. Giles; The use of packed capillary columns in gas chromatography, I. Halsz; Ion-exchage chromatography of amino acids: recent advances in analytical determinations, P. B. Hamilton; Gas chromatography, J. Janek; Ionization detectors, A. Karmen; Advances in programmed temperature gas chromatography, L. Mikkelsen; Horizons in technique of thin layer chromatography, A. Niederweiser; Geology: an inviting field to chromatographers, A. S. Ritchie.

Chromatographic Science, Vol. 1—Dynamics of Chromatography, Edited by J. C. GIDDINGS and R. A. KELLER. Marcel Dekker, New York, 1965. Part I—320 pp., $9.95.

Part I. General Principles and Theory. Introduction. Dynamics of zone spreading. Nonequilibrium and the mass transfer terms. Kinetic and diffusion processes in chromatography. Packing structure and the dynamics of flow.

Part II. Gas Chromatography. Introduction. Elementary theory. Packed columns. Capillary columns. Gas solid chromatography. Optimum parameters. High speed analysis. Programmed temperature methods. Preparative seals.

Part III. Liquid Chromatography. Introduction. Elementary theory. Optimum separations. Paper and thin layer chromatography. Ion exchange chromatography. Electrophoresis—electrochematography.

Atomic Absorption Spectroscopy: J. W. ROBINSON, Marcel Dekker, New York, 1965. 96 pp., approx. $4.50.

Introduction: Advantages of atomic absorption, disadvantages of atomic absorption. Equipment: radiation source, hollow cathode, continuous radiation sources, flame sources, time resolved spark, modulation, atomizers, flame atomizers, hollow cathode atomizer, electrical discharge, thermal atomizers, monochromator, Detectors, optical systems, power supply.

Analytical parameters: Choice of absorption wavelength, atomizers, flame atomizer, flame atom population profile, sample feed rate, flame energy oxide formation, flame composition, cations, anions, solvents, solvent emission, solvent absorption, solvent effect on atom popuation, optimum operating conditions sample feed rate, sample viscosity, organic solvents, flame adapters, spectral slit width, dispersion, excitation interferences, radiation interferences, chemical interferences, matrix effects.

Analytical Applications: Sensitivity limits, quantitative analysis, recommended procedures (aluminum through zirconium), commercial equipment, installation.

The determination of the oscillator strength by atomic absorption spectroscopy: Vidales equipment for Cu 3247°A, atomic absorption in the vacuum ultra violet, references, glossary.

Microchemical Techniques—Plenary lectures presented at the International Symposium on Microchemical Techniques, 1965: International Union of Pure and Applied Chemistry and American Microchemical Society. Butterworths, London, 1965. 102 pp. 40*s*.

Microchemistry—the present and the future, P. J. Elving; Identification and determination of unusual functional groups, E. Sawicki; Recent microtechniques in forensic science, P. L. Kirk; The status and future of chemical microscopy, M. Kuhnert-Brandstätter; Organic microanalysis in Japan—past and future, T. Mitsui; Microtechniques in the modern laboratory of clinical chemistry, S. Natelson; Photometric titrations, H. Flaschka; Techniques in organic microsynthesis, V. Horak.

Titrimetric Organic Analysis, Part II: Indirect Methods: M. R. F. ASHWORTH (*Chemical Analysis*, Vol. XV). Interscience, New York, 1965. Pp. xix + 1023. 245*s*.

Indirect Titration Procedures. Reagents used in Indirect Titration of Organic Compounds. Index to Functional Groups and Compound Classes. Index to Individual Compounds Determined by Direct and Indirect Titration.

Submicro Methods of Organic Analysis: RONALD BELCHER. Elsevier, Amsterdam, 1966. Pp. x + 174. 55*s*.

Introduction; The Balance; General Apparatus; Determination of Nitrogen; Determination of Carbon and Hydrogen; Determination of Chlorine; Determination of Bromine and Iodine; Determination of Fluorine; Determination of Sulphur; Determination of Phosphorus and Arsenic; Determination of Carboxyl Groups; Determination of Organic Bases in Non-aqueous Media; Determination of Alkoxyl and N-methyl Groups; Determination of Acetyl Group; Determination of Carbonyl Group; Determination of Olefinic Unsaturation; Oxidation with Periodates; Determination of Nitro and Nitroso Groups; Determination of Thiol Groups; Cryoscopic Determination of Molecular Weight; Index.

Talanta, 1966, Vol. 13, p. vii. Pergamon Press Ltd. Printed in Northern Ireland

PUBLISHER'S ANNOUNCEMENT

REPRINTS OF REVIEW PAPERS

Reprints of the following reviews published in Talanta are available from Journals Department Pergamon Press Ltd., Headington Hill Hall, Oxford, England, at 7s. or $1 per copy, on a cash with order basis only:

"**Precipitation of Metal Chelates from Homogeneous Solution**" by F. H. Firsching.

"**Recent Developments in the Ring Oven Technique**" by H. Weisz.

"**Adsorption Indicators in Precipitation Titrations**" by R. C. Mehrotra and K. N. Tandon.

"**Radiometric Titrations**" by T. Braun and J. Tölgyessy.

"**Recent Uses of Liquid Ion Exchangers in Inorganic Analysis**" by H. Green.

"**Applications of Nuclear and Electron Magnetic Resonance in Analytical Chemistry**" by B. D. Flockhart and R. C. Pink.

"**A Critical Evaluation of Colorimetric Methods for Determination of Noble Metals—III: Palladium and Platinum**" by F. E. Beamish.

"**A Critical Evaluation of Colorimetric Methods for Determination of the Noble Metals—III: Rhodium, Iridium, Ruthenium, Osmium and Gold**" by F. E. Beamish.

"**Present State of Complexometry—I: Determination of Quadrivalent and Tervalent Metals**" by Rudolf Přibil.

"**Some Recent Developments in Radioactivation Analysis: A Review of Improvements in the Analytical Technique**" by F. Girardi.

"**Separation of Transplutonium Elements**" by J. Starý.

"**Differential Spectrophotometry**" by G. Svehla.

Single copies of the **Heyrovský Honour Issue of Talanta,** December 1965, may be obtained from Journals Dept., Pergamon Press Ltd., Headington Hill Hall, Oxford, England, at £2 or $6.50 per copy on a cash with order basis only.

SUMMARIES FOR CARD INDEXES

Differential Spectrophotometry: G. Svehla, *Talanta*, 1966, **13**, 641 (Department of Chemistry, University of Aberdeen, Scotland.)

Summary—The principles of various methods of differential spectrophotometry are briefly discussed. Practical problems connected with the measurements are presented and analytical applications so far available are reviewed.

Reaction of 4-(2-thiazolylazo)resorcinol with copper(II), lead(II), zinc(II), cadmium(II) and bismuth(III): M. Hniličková and L. Sommer, *Talanta*, 1966, **13**, 667 (Institut für analytische Chemie der Purkyně-Universität, Brno, Tschechoslowakei.)

Summary—A spectrophotometric investigation of the complex formation of 4-(2-thiazolylazo)resorcinol with copper(II), lead(II), zinc(II), cadmium(II) and bismuth(III) shows that protonated and normal 1:1 chelates predominate, although 1:2 chelates are also formed in part. The equilibria which are present and the stability, optical properties and applicability of the chelates in the spectrophotometric determination of these metals have been studied. The reagent is particularly suitable for the determination of copper and bismuth.

Photometric determination of niobium with azo-dyestuffs: I. P. Alimarin and S. B. Savvin, *Talanta*, 1966, **13**, 689 (V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, U.S.S.R. Academy of Sciences, Moscow V-334, U.S.S.R.)

Summary—The azo-dyestuffs, which contain the analytically functional O,O'-dioxyazo group and are widely employed as photometric reagents for niobium, are reviewed. Two new groups of reagents are described: mono-azo-dyestuffs based on R-salt and 2,7-bisazo dyestuffs based on chromotropic acid. The reaction with niobium is sensitive ($\varepsilon = 20,000$ to 40,000), selective and takes place in strongly acidic solution ($0{\cdot}5$–$6M$ hydrochloric or nitric acid). It is possible to extract with butanol the diphenylguanidine salt of the corresponding niobium complex and to measure the absorbance of the extract.

Quantitative gas chromatographic determination of the constituents of technical divinylbenzene: E. Blasius and H. Lohde, *Talanta*, 1966, **13**, 701 (Institut für Analytische Chemie und Radiochemie der Universität des Saarlandes, 66 Saarbrücken 15, Bundesrepublik Deutschland)

Summary—A new arrangement has been developed to separate *m*- and *p*-isomers of divinyl- and cthylvinylbenzene from technical divinylbenzene by preparative gas chromatography. Using the pure constituents so isolated, it was possible to ascertain correction factors, calibration curves and methods of quantitative analysis. The described method is more exact and requires less time than those previously known. A new liquid phase (Bentone 34 and Siliconoil DC 550) has also been investigated for the complete gas chromatographic analysis of the isomers.

ОБЗОР ДИФФЕРЕНЦИАЛЬНОЙ СПЕКТРОФОТОМЕТРИИ:

G. Svehla, *Talanta*, 1966, **13**, 641.

Резюме—Коротко рассмотрены принципы различных методов дифференциальной спектрофотометрии. Приведены практические проблемы в связи с определением и обсуждены применения в анализе опубликованные до сих пор.

РЕАКЦИЯ 4-(2-ТИАЗОЛИЛАЗО)РЕЗОРЦИНА С МЕДЬЮ(II), СВИНЦОМ(II), ЦИНКОМ(II), КАДМИЕМ(II) И ВИСМУТОМ(III):

M. Hniličková and L. Sommer, *Talanta*, 1966, **13**, 667.

Резюме—Спектрофотометрическое исследование образования комплексов 4-(2-тиазолилазо)резорцина с медью(II), свинцом (II), цинком(II), кадмием(II) и висмутом(III) показало преобладание протонованных и нормальных 1 : 1 хелатов, хотя 1 : 2 хелаты тоже образуются. Изучены равновесия и постоянность, оптические свойства и применимость хелатов в спектрофотометрическом определении этих металлов. Реагент особенно применимый Δля определения меди и висмута.

ФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ НИОБИЯ ИСПОЛЬЗОВАНИЕМ АЗОКРАСИТЕЛЕЙ:

I. P. Alimarin and S. B. Savvin, *Talanta*, 1966, **13**, 689.

Резюме—Приведен обзор азокрасителей содержащих аналитическую функциональную группу O,O′-диоксиазо, которые широко применяются в качестве фотометрических реагентов для ниобия. Описаны две новых группы реагентов: моноазокрасители основывающиеся на соли R и 2,7-бисазокрасители основывающиеся на хромотроповой кислоте. Реакция с ниобием чувствительна (= 20,000–40,000), и избирательна, она происходит в сильнокислом растворе (0,5–6M соляная или азотная кислоты). Можно экстрагировать бутанолом дифенилгуанидиновую соль соответствующих комплексов ниобия и измерять светопоглощение экстракта.

КОЛИЧЕСТВЕННОЕ ОПРЕДЕЛЕНИЕ КОМПОНЕНТОВ ТЕХНИЧЕСКОГО ДИВИНИЛБЕНЗОЛА МЕТОДОМ ГАЗОВОЙ ХРОМАТОГРАФИИ:

E. Blasius and H. Lohde, *Talanta*, 1966, **13**, 701.

Резюме—Разработана новая птоцедура для разделения м- и п-изомеров дивинил- и этилвинилбензола в техническом дивинилбензоле методом препаративной газовой хроматографии. Пользуясь чистыми компонентами выделенными этим образом, удалось определить поправочные коефициенты, стандартные кривы и разработать методы для количественного анализа. Описанный метод быстрее и более точный чем до сих пор знакомые методы. Тоже была исследована новая житкая фаза (Бэнтон 34 и силиконовое масло ДЦ 550) для полного анализа изомеров методом газовой хроматографии.

Structures of the uranyl 8-hydroxyquinolates: R. J. Magee and I. Woodward, *Talanta*, 1966, **13**, 709 (Department of Chemistry, Queen's University, Belfast 9, N. Ireland.)

Summary—An X-ray investigation of the two uranyl 8-hydroxyquinolates

$$UO_2\cdot(C_9H_6NO)_2\cdot C_9H_6NOH \text{ (dark red)}$$

and

$$[UO_2\cdot(C_9H_6NO)_2]_2\cdot C_9H_6NOH \text{ (orange)},$$

has been carried out on the untreated compounds and after recrystallising them from chloroform. The unsolvated compound $UO_2\cdot(C_9H_6NO)_2$ and the residue remaining after dissolving the orange compound in chloroform have also been examined. The investigation shows that the crystals obtained from the red and orange compounds, respectively, after dissolving in chloroform and recrystallising, are identical. The untreated red and orange compounds are different, the latter showing evidence of existing as a polymer, whereas the former is crystalline. On the basis of the results obtained, a structure for the orange compound is proposed.

Stability of hypobromite solutions: H. L. Polak, G. Feenstra and J. Slagman, *Talanta*, 1966, **13**, 715 (Laboratory of Analytical Chemistry, University of Amsterdam, Amsterdam-C, Netherlands.)

Summary—The stability of hypobromite solutions is governed by such factors as the concentration of hypobromite and hydroxide, light, temperature, and the presence of foreign substances. From a review of the literature it is concluded that it is impossible to obtain perfectly stable solutions. The preparation of more or less stable hypobromite solutions is described, and the dependence of the stability on various factors is determined.

Some new heterocyclic compounds as analytical reagents: F. H. Pollard, G. Nickless and R. G. Anderson, *Talanta*, 1966, **13**, 725 (Department of Inorganic Chemistry, The University, Bristol, U.K.)

Summary—A survey of the metal-complexing reactions, as determined by reactions on chromatography paper, of 44 compounds with a substituted or modified 4-(2-pyridylazo)-resorcinol (PAR) or 1-(2-pyridylazo)-2-naphthol (PAN) structure is reported.

Electron microscope investigation of the thermal aging of barium sulphate precipitates: É. Buzágh-Gere, F. Paulik and L. Erdey, *Talanta*, 1966, **13**, 731 (Institute for General Chemistry, Technical University, Budapest, Hungary.)

Summary—Barium sulphate precipitates, formed by four different analytical methods, dried and ignited at different temperatures, have been examined with an electron microscope. The study of the dissolution of precipitates has been found useful for the investigation of thermal aging. On heating the precipitates, diffusion, which takes place at temperatures depending on structure, permits structural changes such as reordering to take place. Consequently, the structure of the ignited precipitates approaches the ideal arrangement.

СТРОЕНИЕ 8-ОКСИХИНОЛИНАТОВ УРАНИЛА:

R. J. Magee and I. Woodward, *Talanta*, 1966, **13**, 709.

Резюме—Авторы изучали помощю рентгеновских лучей два 8-оксихинолината уранила, $UO_2 \cdot (C_9H_6NO)_2 \cdot C_9H_6NOH$) темнокрасный) и $[UO_2 \cdot (C_9H_6NO)_2]_2 \cdot C_9H_6NOH$ (оранжевый), в твердом состоянии, так же и после растворения и рекристаллизации из хлороформа. Тоже исследованы несольватированное соединение $UO_2 \cdot (C_9H_6NO)_2$ и остаток после растворения оранжевого соединения в хлороформе. Результаты исследования показивают что кристаллы полученные из красного и оранжевого соединений после растворения и рекристаллизации идентичные. Необработанные красные и оранжевые соединения различаются, последнее указывает на полимерное строение, первое находится в кристаллической форме. На основании полученных результатов предложено строение для оранжевого соединения.

УСТОЙЧИВОСТЬ РАСТВОРОВ ГИПОБРОМИТА:

H. L. Polak, G. Feenstra and J. Slagman Talanta, 1966, 13, 715.

Резюме—Устойчивость растворов гипобромита зависит от таких факторов как концентрация гипобромита и гидроокиси, свет, температура и присутствие посторонных веществ. На основании литературного обзора сделан вывод что невозможно получить совершенно устойчивые растворы. Описано приготовление более или менее устойчивых растворов гипобромита и определена зависимость устойчивости от различных факторов.

НЕКОТОРЫЕ НОВЫЕ ГЕТЕРОЦИКЛИЧЕСКИЕ СОЕДИНЕНИЯ В КАЧЕСТВЕ АНАЛИТИЧЕСКИХ РЕАГЕНТОВ:

F. H. Pollard, G. Nickless and R. G. Anderson, *Talanta*, 1966, **13**, 725.

Резюме—Приведен обзор изученных на хроматографической бумаге комплексообразующих реакций 44 соединений, содержающих замещенное или измененное строение 4-(2-пиридилазо)-резорцина (ПАР) или 1-(2-пиридилазо)-2-нафтола (ПАН).

ИЗУЧЕНИЕ ТЕПЛОВОГО СТАРЕНИЯ ОСАДКОВ СУЛЬФАТА БАРИЯ С ИСПОЛЬЗОВАНИЕМ ЭЛЕКТРОННОГО МИКРОСКОПА:

E. Buzágh-Gere, F. Paulik and L. Erdey, *Talanta*, 1966, **13**, 731.

Резюме—Осадки сульфата бария, образованные в четырех различных методах, сушились и жарились при различных температурах и изучались электронным микроскопом. Изучение растворения осадков оказалось полезным в исследовании теплового старения. При нагревании осадков диффузия, появляющаяся при повышенных температурах в зависимости от строения, позволяет перемены в строении—перегруппировки. Последственно, строение жареных осадков приближается идеальном порядке.

Hydroxamic acids as colorimetric reagents: Virginia C. Bass and John H. Yoe, *Talanta*, 1966, **13**, 735 (Pratt Trace Analysis Laboratory, Department of Chemistry, University of Virginia, Charlottesville, Va., U.S.A.)

Summary—Thirty-three hydroxamic acids and three *N*-substituted hydroxamic acids or structurally similar compounds have been studied as possible colorimetric reagents for metal ions. They were tested with 78 ions under varying conditions of acidity and basicity. Aliphatic, substituted aliphatic, aromatic, substituted aromatic, and heterocyclic hydroxamic acids were represented in the compounds studied. An attempt was made to correlate the activity towards metal ions with variations in the molecular structure of the hydroxamic acids. The studies with *C*-substituted hydroxamic acids indicate that the preferential formation of a colour or a precipitate depends on pH, the solvent, and reagent concentration, and is not a function of the presence or absence of a substituent on the nitrogen atom. A number of the compounds offer promise of being useful colorimetric reagents under proper reaction conditions.

Behaviour of glass and silver/silver chloride electrodes in some non-aqueous media: Karin Norberg, *Talanta*, 1966, **13**, 745 (Department of Analytical Chemistry, University of Lund, Lund, Sweden.)

Summary—The stability of glass electrodes and silver/silver chloride electrodes in isopropanol, methyl ethyl ketone and a mixture of equal volumes of these has been measured, and found to be of the order of 1 mV. Changes in the electrode potential due to addition of water and to addition of supporting electrolyte have been investigated. The glass electrode responded reversibly to hydrogen ion activity changes in buffers of picric acid-tetraethylammonium picrate, and perchloric acid-di-isopropylamine. The autoprotolysis constants at 25° were calculated to be 2×10^{-19} in isopropanol, 2×10^{-26} in the ketone and 8×10^{-19} in the mixture.

Analytical applications of ternary complexes—II: Spectrophotometric determination of copper as Rose Bengal bisphenanthrolinium copper(II): B. W. Bailey, R. M. Dagnall and T. S. West, *Talanta*, 1966, **13**, 753 (Chemistry Department, Imperial College, London S.W.7, U.K.)

Summary—A ternary complex system, $[(Cu.phen_2)Rose Bengal]$, is proposed for the determination of traces of copper ion. The reaction is rendered specific for copper amongst 56 cations and most anions by extraction of bis(2,9-dimethyl-1,10-phenanthrolinium) copper(I) from an EDTA medium. Because of the high molar absorptivity, 62,500, solutions containing 0·002 ppm of copper may be analysed without difficulty. The colour system is stable for a period of days.

ГИДРОКСАМОВЫЕ КИСЛОТЫ В КАЧЕСТВЕ КОЛОРИМЕТРИЧЕСКИХ РЕАГЕНТОВ:

VIRGINIA C. BASS and JOHN H. YOE, *Talanta*, 1966, **13**, 735.

Резюме—Изучена применимость тридцать три гидроксамовых кислот и три N-замещенных гидроксамовых кислот или соединений подобного строения в качестве колориметрических реагентов для ионов металлов. Эти соединения испытаны с 78 ионами при различной степени кислотности и щелочности. В исследованных соединениях были представлены алифатические, замещенные алифатические, ароматические, замещенные ароматические и гетероциклические гидроксамовые кислоты. Сделан опыт чтобы привести в соотношение активность к ионам металлов и перемены в молекулярном строении гидроксамовых кислот. Изучение C-замещенных гидроксамовых кислот оказало что образование окраски или осадка зависит от pH, растворителя и концентрации реагента, а не зависит от присутствия или отсутствия заместителя на атоме азота. Число этих соединений моглы бы быть полезные колориметрические реагенты в соответствующих условиях.

ПОВЕДЕНИЕ СТЕКЛЯННЫХ ЭЛЕКТРОДОВ И ЭЛЕКТРОДОВ СЕРЕБРО/ХЛОРИД СЕРЕБРА В НЕКОТОРЫХ НЕВОДНЫХ СРЕДАХ:

KARIN NORBERG, *Talanta*, 1966, **13**, 745.

Резюме—Определена устойчивость стеклянных электродов и электродов серебро/хлорид серебра в изопропиловом спирте, метилэтилкетоне и их смеси одинаковых объемов и нашлось что она величины 1 мв. Исследованы перемены напряжения при добавлении воды и электролита носителя. Стеклянный электрод дал реверсивный ответ на перемены активности водородного иона в буферных растворах пикриновая кислота—пикрат тетраэтиламмония и хлорная кислота—диизопропиламин. Вычислены постоянные автопиролиза при 25°: 2×10^{-19} в изопропиловом спирте, 2×10^{-26} в кетоне и 8×10^{-19} в смеси.

АНАЛИТИЧЕСКИЕ ПРИМЕНЕНИЯ ТРЕТИЧНЫХ КОМПЛЕКСОВ—II: СПЕКТРОФОТОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МЕДИ В ФОРМЕ БЕНГАЛЬСКАЯ-РОЗАБИСФЕНАНТОЛИНИЙ-МЕДИ(II):

B. W. BAILEY, R. M. DAGNALL and T. S. WEST, *Talanta*, 1966, **13**, 753.

Резюме—Третичный комплекс [(Cu.phen$_2$) Rose Bengale] предложен для определения следов иона меди. Экстрагированием бис(2,9-диметил-1,10-фенантолиний) меди(I) из раствора ЭДТА реакция становится специфической для меди между 56 катионов и большинства анионов. Вследствые высокого молярного поглощения (62,500) можно удобно анализировать растворы содержающие 0,002 мкг/мл. Окраска устойчива через несколько дней.

Iodometric determination of selenium after extractive separation with isopropyl ketone: L. Futekov and N. Jordanov, *Talanta*, 1966, **13**, 763. (Institut für allgemeine und anorganische Chemie der Bulgarischen Akademie der Wissenschaften in Sofia, Bulgarien.)

Summary—The possibility is indicated of determining selenium in industrial intermediate products, such as slurries, agglomerates and briquettes, containing from 0·5 to 10% of selenium. Selenium(IV) in a strongly acidic medium forms a chloroform-soluble organo-selenium compound with isopropyl ketone, and this product can be decomposed by heating with nitric acid. This can be followed by an iodometric determination of the selenium, undisturbed by other elements. The reproducibility of the method, expressed as the coefficient of variation, is 0·3% for 8% of selenium.

Adsorption indicators in the titrations of hexacyanoferrate(II) and oxalate with thorium ions: P. S. Dubey and K. N. Tandon, *Talanta*, 1966, **13**, 765 (Chemical Laboratories, University of Rajasthan, Jaipur, India.)

Summary—Alizarin Red S, Pyrocatechol Violet and Xylenol Orange are shown to be effective adsorption indicators for the titrations of hexacyanoferrate(II) and oxalate with thorium(IV) solution. The action of the indicators can be explained by the theory of surface compound formation.

Quantitative infrared analysis of 2,4-tolylene diamine and 2,4-tolylene diurea mixtures: K. Eröss, G. Svehla, L. Erdey and É. Vázsonyi, *Talanta*, 1966, **13**, 767 (Institute for General Chemistry, Technical University, Budapest XI, Hungary.)

Summary—A rapid method is described for the simultaneous determination of 2,4-tolylene diamine and 2,4-tolylene diurea by infrared spectroscopy. The method is satisfactory for the diurea determination but gives rather large errors in the diamine determination.

ИОДОМЕТРИЧЕСКОЕ ОПРЕДЕЛЕНИЕ СЕЛЕНА ПОСЛЕ ВЫДЕЛЕНИЯ ЭКСТРАГИРОВАНИЕМ ИЗОПРОПИЛКЕТОНОМ:

L. FUTEKOV and N. JORDANOV, *Talanta*, 1966, **13**, 763.

Резюме—Указана возможность определения селена в промышленных промежуточных продуктах, как на пример в шламмах, агломератах и брикетах, содержающих 0,5–10% селена. Селен(IV) в сильнокислой среде образует органоселеновое соединение с изопропилкетоном, растворимое в хлороформе, которое разлагается нагреванием с царской водкой. Последовательно, селен определяется иодометрически, без мешания других злементов. Точность метода, выражена козфициентом вариации, равна 0,3% для 8% селена.

ИСПОЛЬЗОВАНИЕ АДСОРБЦИОННЫХ ИНДИКАТОРОВ В ТИТРОВАНИИ ГЕКСАЦИАНОФЕРРАТА(II) И ОКСАЛАТА С ТОРИЕМ:

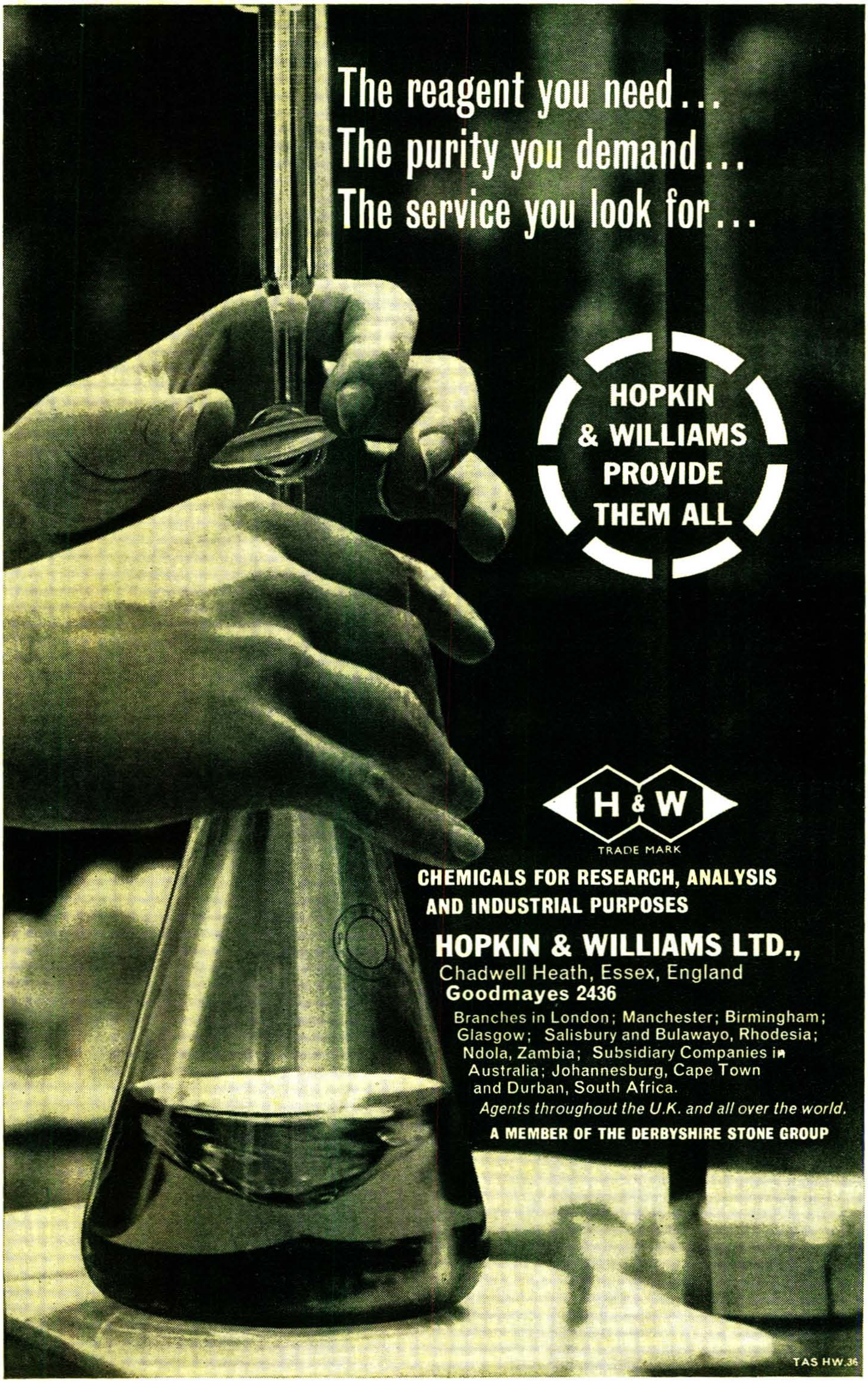
P. S. DUBEY and K. N. TANDON, *Talanta*, 1966, **13**, 765.

Резюме—Ализаринкрасный S, пирокатехинфиолетовый и ксиленолоранжевый оказались как зффективные адсорбционные индикаторы в титровании гексацианоферрата(II) и оксалата с раствором тория(IV). Действие индикатора обясняется теорией образования поверхностных соединений.

КОЛИЧЕСТВЕННОЕ ОПРЕДЕЛЕНИЕ 2,4-ТОЛУИЛЕНДИАМИНА И 2,4-ТОЛУИЛЕНДИМОЧЕВИНЫ МЕТОДОМ ИНФРАКРАСНОЙ СПЕКТРОСКОПИИ:

K. ERÖSS, G. SVEHLA, L. ERDEY and É. VÁZSONYI, *Talanta*, 1966, **13**, 767.

Резюме—Описан быстрый метод для одновременного определения 2,4-толуилендиамина и 2,4-толуилендимочевины методом инфракрасной спектроскопии. Методом можно пользоваться для определения димочевины, но большие ошибки являются при определении диамина.



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PRINTED IN NORTHERN IRELAND AT THE UNIVERSITIES PRESS, BELFAST