

THEORETICAL CONSIDERATIONS ON THE INDIRECT DETERMINATION OF ANIONS

DETERMINATION OF SULPHATE WITH BARIUM CHLORANILATE

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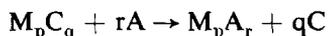
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Summary—Some anions (sulphate) may be determined by their reaction with a slightly dissociated or slightly soluble compound (barium chloranilate), another anion (chloranilate ion) being liberated and its extinction measured. An equation is given in this paper for the relationship between the concentration of sulphate and the extinction. For low concentrations the equation is non-linear. A calibration curve, prepared under standardised conditions, agrees well with theory. It shows a precision of about 5% at 20 μg of sulphate. At higher levels the precision is slightly better. It is proved that many interferences of foreign ions may be explained quantitatively by consideration of the activity coefficients. The scope of this method is discussed.

INTRODUCTION

FOR the quantitative determination of anions with organic reagents, indirect methods often have to be used. Many of them are based on reactions of the following type (charges have been omitted for simplicity):



where A is the anion to be determined. C may represent any anion which can be easily determined, for example, by spectrophotometry. $M_p C_q$ and $M_p A_r$ are slightly soluble or slightly dissociated compounds. Several applications¹⁻⁹ of this principle have been described for the case when C represents the bivalent anion of $C_6H_2Cl_2O_4$ (H_2C), 2,5-dichloro-3,6-dihydroxybenzoquinone (chloranilic acid). In this paper the use of salts of this reagent will be discussed, but similar results may be expected for some other reagents.

The dissociation constants of H_2C are given by Schwarzenbach and Suter:¹⁰ $pK_1 = 0.85$ and $pK_2 = 3.18$. Other authors give slightly different values.^{11,12} The differences may arise from differences in ionic strength. The anion C is violet and has a strong absorption at 332 $m\mu$; ϵ is about 27.5×10^3 litre. mol^{-1} . cm^{-1} . Salts of the acid have been used for the determination of sulphate,^{1,3,4,6,8} fluoride,^{5,7} chloride,^{2,3} phosphate¹³ and other ions.

It seems to be generally assumed that a linear relationship exists between the concentration of A and the extinction E. In the first part of the present paper a more exact relationship between these quantities is given for the case when $p = q = r = 1$ and MC and MA are slightly soluble salts. In the second part of the paper the interference by foreign compounds (sodium chloride, potassium nitrate), not reacting *chemically* with M, C and A, is calculated from activity considerations. In the third part some results are given of experiments in which $M = Ba^{2+}$ and $A = SO_4^{2-}$, *i.e.*, in the case of the determination of sulphate with barium chloranilate.

THEORETICAL DISCUSSION

Relationship between extinction and unknown concentration

The symbol $[X]_i$ is used for the moles of component X, present in phase i, not calculated for 1 litre of solution but for 1 litre of the complete system: solid compounds (MA and MC) plus liquid. This notation simplifies the calculations, because the difference between total volume and volume of the liquid alone is neglected. The difference is so small, however, that the error made may certainly be neglected. The index t indicates the total amount of a substance present.

Furthermore, it should be noted that s_1 and s_2 have been defined in equations (6) and (8) as the products of the ionic concentrations, not of the ionic activities. The influence of this difference will be discussed in the section on the causes of error.

We define:

$$x = [C]_{\text{sol}} + [\text{HC}]_{\text{sol}} + [\text{H}_2\text{C}]_{\text{sol}} \quad (1)$$

$$y = [A]_{\text{sol}} + [\text{HA}]_{\text{sol}} + [\text{H}_2\text{A}]_{\text{sol}} + [A]_{\text{MA}} \quad (2)$$

$$A' = [A]_{\text{sol}} + [\text{HA}]_{\text{sol}} + [\text{H}_2\text{A}]_{\text{sol}} \quad (3)$$

$$\alpha = \frac{[C]_{\text{sol}}}{x} \quad (4)$$

$$\beta = \frac{[A]_{\text{sol}}}{A'} \quad (5)$$

s_1 and s_2 are the "solubility products" of MC and MA, respectively, ϵ is the molar extinction coefficient of C, and d is the path length of the light in the spectrophotometer cell.

From these definitions we see that, if no A is added and there is only a saturated solution of MC:

$$[M]_{\text{sol}} \cdot [C]_{\text{sol}} = s_1 \quad (6)$$

and because $x = [M]_{\text{sol}}$, substitution of equation (4) gives $\alpha x^2 = s_1$ and

$$x = \sqrt{\frac{s_1}{\alpha}} \quad (7)$$

If so much A is added that the solution is saturated with respect to MA, but no solid MA is formed, it is seen from

$$[M]_{\text{sol}} \cdot [A]_{\text{sol}} = s_2 \quad (8)$$

that

$$[A]_{\text{sol}} = \frac{s_2}{[M]_{\text{sol}}}$$

Combination with equations (2), (4), (5), (6) and (7) gives:

$$y = \frac{s_2}{\beta} \cdot \sqrt{\frac{\alpha}{s_1}} \quad (9)$$

This value gives the amount of y which is at least necessary to give an extinction larger than the blank.

If solid MC and MA are both present, equations (10)–(14) are valid:

$$[C]_t = x + [C]_{MC} \quad (10)$$

$$[M]_t = [M]_{sol} + [M]_{MC} + [M]_{MA} \quad (11)$$

$$[M]_{MC} = [C]_{MC} \quad (12)$$

$$[A]_{MA} = [M]_{MA} \quad (13)$$

$$[M]_t = [C]_t \quad (14)$$

Substitution of equations (10) and (11) in (12) and subtraction of (14) gives:

$$x = [M]_{sol} + [M]_{MA} \quad (15)$$

From equations (2), (3), (5) and (13) we find:

$$[M]_{MA} = y - \frac{[A]_{sol}}{\beta} \quad (16)$$

and from (4), (6), (8) and (16):

$$[M]_{MA} = y - \frac{s_2}{s_1} \cdot \frac{\alpha}{\beta} \cdot x \quad (17)$$

From equations (4), (6) and (15) we see:

$$[M]_{MA} = x - \frac{s_1}{\alpha x} \quad (18)$$

Combination of (17) and (18) gives:

$$x = y - \frac{s_2}{s_1} \cdot \frac{\alpha}{\beta} \cdot x + \frac{s_1}{\alpha x} \quad (19)$$

After rearrangements we find the quadratic equation:

$$x^2 \left\{ 1 + \frac{s_2}{s_1} \cdot \frac{\alpha}{\beta} \right\} - yx - \frac{s_1}{\alpha} = 0 \quad (20)$$

Solution of this equation gives:

$$x = \frac{y + \sqrt{y^2 + \frac{4 \cdot s_1}{\alpha} + \frac{4 \cdot s_2}{\beta}}}{2 + 2 \cdot \frac{s_2}{s_1} \cdot \frac{\alpha}{\beta}} \quad (21)$$

For many practical cases $\frac{s_2}{\beta} \ll \frac{s_1}{\alpha}$, *i.e.*, the apparent (conditional) solubility constant of MA is much smaller than that of MC. Therefore in those cases equation (21) simplifies to:

$$x = \frac{y + \sqrt{y^2 + \frac{4 \cdot s_1}{\alpha}}}{2} \quad (22)$$

The extinction measured, however, is caused by one of C, HC or H₂C, and not by their sum x. Therefore, the relation between x and this specimen should be used. In this paper the extinction of C is measured, and equation (4) gives the relation required.

From Beer's law:

$$E = \varepsilon \cdot c \cdot d \quad (23)$$

and from equations (4) and (22) it now follows that

$$E = \frac{\varepsilon \cdot d \cdot \alpha}{2} \left(y + \sqrt{y^2 + \frac{4 \cdot s_1}{\alpha}} \right) \quad (24)$$

where E is written for the extinction from C. We assume that the contribution of HC and H₂C to the extinction may be neglected.

It is necessary at this point to stress the fact that the values of α and s_1 may vary with the experimental conditions. The variation of α is caused especially by the pH and also by the dissociation constants, which vary with the composition (including ionic strength) of the solution. The variation of s_1 is caused especially by the composition of the solution. For these reasons the indices b and s are used below, b indicating the blank and the calibration solution, which generally will have the same over-all composition, and s indicating the sample solution.

In this way we find for the difference between the extinction of the sample solution and the blank, the value

$$\Delta E_s = \frac{\varepsilon \cdot d \cdot \alpha_s}{2} \left(y + \sqrt{y^2 + \frac{4s_{1,s}}{\alpha_s}} \right) - \frac{\varepsilon \cdot d \cdot \alpha_b}{2} \sqrt{\frac{4s_{1,b}}{\alpha_b}} \quad (25)$$

The difference between the extinction of the calibration solution and the blank solution is given by:

$$\Delta E_b = \frac{\varepsilon \cdot d \cdot \alpha_b}{2} \left(y + \sqrt{y^2 + \frac{4s_{1,b}}{\alpha_b}} \right) - \frac{\varepsilon \cdot d \cdot \alpha_b}{2} \sqrt{\frac{4s_{1,b}}{\alpha_b}} \quad (26)$$

The equations are simplified if $\alpha_s = \alpha_b = 1$.

This was the case in our experiments. The relative error:

$$F = \frac{\Delta E_s - \Delta E_b}{\Delta E_s}$$

is now given by:

$$F = \frac{\sqrt{y^2 + 4s_{1,s}} - \sqrt{y^2 + 4s_{1,b}}}{y + \sqrt{y^2 + 4s_{1,s}}} \quad (27)$$

Causes of error

The main causes of error are:

- (a) Errors caused by foreign compounds reacting chemically with one of the components of the solutions or absorbing at the wavelength used. They are not discussed in this paper.
- (b) Photometric errors. They are discussed briefly in the discussion on the scope of the method
- (c) Errors caused by different conditions and compositions in calibration and sample solutions. They are discussed below.

Errors from different conditions. It is clear that α is a function of the dissociation constants and of the pH. In the case when H₂C is chloranilic acid, with $pK_1 = 0.85$ and $pK_2 = 3.18$, a pH above about 5 is necessary to ensure that small differences in pH do not give large differences in α . Regarding β , a lower pH value may be used if $A = SO_4^{2-}$. In non-aqueous media the calculation of the desirable pH region is

complicated by the fact that K values are not generally known in those media, and that pH values measured in the conventional way may be seriously in error because the diffusion potential between reference electrode and sample solution is often unknown. Fortunately, it is possible to find conditions, which have not to be kept rigorously constant, without danger for changes in α and β .

More serious, however, is the variation of s_1 with the experimental conditions. This is now treated in some detail.

If the symbol s is used for the product of *ionic concentrations* in the saturated solution, a for activities, c for concentrations, f for activity coefficients and ω for ionic strength, we see that

$$s_\omega = c_C \cdot c_M = \frac{a_C \cdot a_M}{f_C \cdot f_M} \quad (28)$$

It should be noted that for calculations of ω , concentrations have to be expressed in moles/kg of solvent and not moles/litre of solution.

Now

$$s_{\omega=0} = a_C \cdot a_M \quad (29)$$

and combination of equations (28) and (29) gives:

$$s_\omega = s_{\omega=0} \cdot \frac{1}{f_C \cdot f_M} \quad (30)$$

The values of f_C and f_M are approximately equal if both ions have the same charge. Writing $f = f_C = f_M$, we find:

$$s_\omega = s_{\omega=0} \cdot \frac{1}{f^2} \quad (31)$$

The values of f are found approximately from:¹⁴

$$-\log f = \frac{z^2 A \sqrt{\omega}}{1 + \delta b \sqrt{\omega}} \quad (32)$$

In this equation b is the ionic radius of M^{2+} and C^{2-} ; z is their charge. The values of A and δ depend on factors of which only the dielectric constant of the medium is important to us. The exact value of b is not known, but at low values of ω , $\delta b \sqrt{\omega} \ll 1$, and therefore the exact value is not very important. We used $b = 5 \times 10^{-8}$. Values of A and δ were calculated for some cases of practical importance: (1) water, (2) water-ethanol mixture containing 50 ml of 95.5% ethanol in a 100-ml total volume (*i.e.*, 43% ethanol), and (3) the same but 75 ml of 95.5% ethanol in 100 ml (*i.e.*, 69% ethanol). For water $D = 80$, and for the mixtures $D = 54$ and 40, respectively.¹⁵ Inserting these values and $z = 2$ or -2 in the formulae for A and δ found in the literature,¹⁴ we find:

$$\text{for water:} \quad -\log f = \frac{2.00 \sqrt{\omega}}{1 + 1.64 \sqrt{\omega}} \quad (33a)$$

$$\text{for 43\% ethanol:} \quad -\log f = \frac{3.65 \sqrt{\omega}}{1 + 2.00 \sqrt{\omega}} \quad (33b)$$

$$\text{for 69\% ethanol:} \quad -\log f = \frac{5.65 \sqrt{\omega}}{1 + 2.34 \sqrt{\omega}} \quad (33c)$$

Table I gives some values of f for various values of ω . It is clear that for low values of ω , the value of f is chiefly determined by the numerator. Therefore about the same value of f is found in water and in 69% ethanol if $(2.00 \sqrt{\omega})_{\text{water}} = (5.65 \sqrt{\omega})_{69\% \text{ ethanol}}$, i.e., the ionic strength in water may be eight times as high as in the mixture to give the same effect. From this we may conclude that in this respect water is a more favourable solvent than the mixtures.

More generally, the relative influence of ionic strength in various media may be approximated by the fact that A is proportional to $D^{3/2}$.

TABLE I.—VALUES OF f FOR BIVALENT IONS

Ionic strength (ω)	Activity coefficient (f)		
	Water	43% Ethanol	69% Ethanol
10^{-5}	0.986	0.974	0.960
1.1×10^{-5}	0.985	0.973	0.958
10^{-4}	0.956	0.921	0.881
1.1×10^{-4}	0.954	0.917	0.875
10^{-3}	0.871	0.779	0.682
1.1×10^{-3}	0.865	0.770	0.670
10^{-2}	0.673	0.496	0.348
1.1×10^{-2}	0.662	0.482	0.334
10^{-1}	0.383	0.196	0.094
1.1×10^{-1}	0.371	0.187	0.088

CONCLUSIONS FROM THEORETICAL DISCUSSION

Calibration curve

A calibration curve was calculated from equation (26). The values used were $y = 10^{-6}$ to 3×10^{-5} , $s_1 = 6 \times 10^{-11}$, $\epsilon = 27.5 \times 10^3$, $d = 4$ and $\alpha = \beta = 1$. In Table II the results are given and compared with those obtained, assuming every ion of A^{2-} liberates one ion of C^{2-} . The table shows that the extinction values, calculated in the first way, are much lower, and that the deviation from linearity is large.

TABLE II.—RELATIONSHIP BETWEEN SULPHATE CONCENTRATION (y) AND EXTINCTION (E)

y	E^a	E^b
10^{-6}	0.055	0.110
3×10^{-6}	0.180	0.330
10^{-5}	0.710	1.10
3×10^{-5}	2.65	3.30

^a Calculated from equation (26).

^b Assuming 1 SO_4^{2-} gives 1 C^{2-} .

Consequences of variation of s_1 with ω

The error F was calculated from equation (27) for the case when $\omega = 0.01$, both in blank and calibration solution, and $\omega = 0.011$, 0.013 and 0.020 in the sample solution (69% ethanol). It was found from experiments that when $\omega = 0.01$, $s_1 = 6 \times 10^{-11}$. From this value and equations (31) and (33c) the values 6.5×10^{-11} , 7.6×10^{-11} and 11.9×10^{-11} were calculated for the solubility product at $\omega = 0.011$,

0.013 and 0.020. Table III shows that at $\omega = 0.01$, the ionic strength of the sample solution should not differ more than about 10 or 20% from the ionic strength of the blank and calibration solutions.

TABLE III.—ERROR (F) RESULTING FROM A DIFFERENCE IN IONIC STRENGTH (ω) BETWEEN BLANK AND SAMPLE SOLUTION AT VARIOUS SULPHATE CONCENTRATIONS (y)

y	ω_b	ω_s	F, %
10^{-6}	0.010	0.011	4
10^{-6}	0.010	0.013	11
10^{-6}	0.010	0.020	28
3×10^{-6}	0.010	0.011	3
3×10^{-6}	0.010	0.013	9
3×10^{-6}	0.010	0.020	25
10^{-5}	0.010	0.011	2
10^{-5}	0.010	0.013	6
10^{-5}	0.010	0.020	16

EXPERIMENTAL

Barium chloranilate was prepared by slowly adding, at room temperature, with stirring, a slight excess of H_2C in 4 litres of water to 250 ml of 0.04M barium chloride solution. A fine purple precipitate is formed. After standing overnight the liquid is decanted, and the BaC is filtered by suction through a porcelain filter. After washing with ethanol and ether, the product is dried at 100°. Some water is retained unless the product is dried for some considerable time. A less satisfactory brown product was obtained when the directions of Bertolacini and Barney¹ were followed, *i.e.* when a large excess of barium chloride was added to the H_2C solution.

For preparation of the calibration curve, the sample, containing very little free hydrogen ion, is transferred to a 100-ml calibrated flask. Five ml of 10% urotropine solution, 10 ml of 0.1M sodium chloride solution and 75 ml of 95.5% ethanol are added exactly, followed by water to just below the calibration mark. This causes a rise in temperature of about 5°. The flask is placed in a thermostat bath at 20° for 10 min, the volume adjusted with water, 50 mg of BaC added and the flask again placed in the thermostat bath for at least 1 hr with occasional shaking. The suspension is filtered through a G4 filter (Fig. 1) by application of gentle pressure. Part of the filtrate is collected in a spectrophotometer cell and sucked from it with a polythene tube. This filling and suction procedure is repeated twice. In this way the cell is cleaned and filled with the required solution without risk that any liquid touches the outside of the walls, and that change of the absorption results from complete purification of the walls. The blank and calibration solution were measured in the same cells. As reference an approximately $10^{-4}M$ potassium dichromate solution in 0.02M sulphuric acid was used.

RESULTS

Some extinction measurements were made of aqueous solutions of chloranilic acid at various pH. The results at pH 3–9 agreed with the values of pK_2 given in the literature and gave a value of 28×10^3 for ϵ . At pH < 3 the extinction was slightly higher than expected, probably because of the extinction of H_2C or HC^- . The difference was so small, however, that no interference from H_2C and HC^- may be expected at the pH used for the measurements.

In 69% ethanol the value for ϵ was 27.5×10^3 . No measurement of the dissociation constant was made in this solvent, for the reason given above, but it was found that at an apparent pH of 6–6.5 (measured with the glass electrode), prepared with urotropine, small changes in pH did not influence the results. The solubility product of BaC was calculated from measurements of C^{2-} with the assumption that BaC is completely dissociated.

In 69% ethanol in 0.01M (0.0115 molal) solution of sodium chloride the value

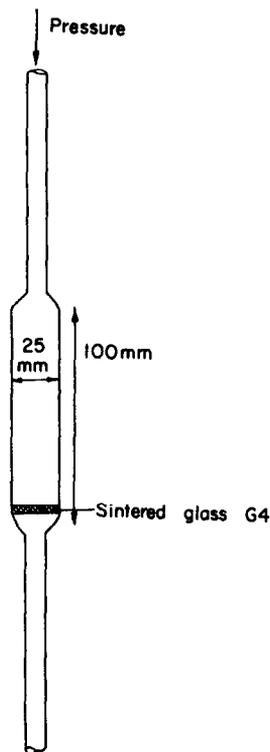


FIG. 1.—Filtration apparatus.

found was $s_1 = 6 \times 10^{-11}$. In 43% ethanol and $\omega = 0.01$ the value was about 16×10^{-10} (20°). The large difference of these values makes it necessary for the ethanol concentration to be controlled rigorously.

The validity of equations (31) and (33c) was tested by measuring the extinction of saturated solutions of BaC to which different monovalent salts were added. The agreement of the results with theory is good (Table IV). Some experiments showed that slightly different results were found if sodium chloride was replaced by potassium nitrate in the same concentrations (the values in the presence of potassium nitrate were corrected for nitrate extinction, $\epsilon = 0.6$). This proves that not only the ionic strength but also the type of ion present influences the results.

A calibration curve was prepared for quantities of sulphate ranging from 18 to 108 μg in 69% ethanol and $\omega = 0.0115$ in sodium chloride. The agreement with the theoretical curve is satisfactory. For s_2 the value 3×10^{-16} was used. It has been calculated from the value 4×10^{-17} , found by interpolation from the data given in the literature¹⁶ and correction of this value for $\omega = 0.0115$. The agreement with theory is very bad if it is assumed that one C^{2-} is liberated for each SO_4^{2-} added. (Fig. 2). In later experiments the curve was extended up to 400 μg of sulphate. The theoretical curve was also followed closely in this region.

For large values of y the difference between both curves corresponds to a difference in concentration of $\sqrt{s_1} = 7.7 \times 10^{-6}$ moles/litre, *i.e.*, with 74 μg of sulphate/100 ml.

TABLE IV.—RELATIONSHIP BETWEEN IONIC STRENGTH AND EXTINCTION OF SOLUTIONS OF BARIUM CHLORANILATE IN 69% ETHANOL

Ionic strength	Salt	Extinction	
		Calculated	Found
1.71×10^{-4}	NaCl	0.086	0.075
3.42×10^{-4}	NaCl	0.095	0.088
8.55×10^{-4}	NaCl	0.106	0.096
1.71×10^{-3}	NaCl	0.122	0.108
5.88×10^{-3}	NaNO ₃	0.177	0.174
8.55×10^{-3}	NaCl	0.203	0.220
1.22×10^{-2}	NaNO ₃	0.242	0.267
1.72×10^{-2}	NaNO ₃	0.280	0.339
2.57×10^{-2}	NaCl	0.358	0.395

Therefore, a calibration curve constructed for high sulphate concentrations extrapolated to low sulphate concentrations suggests zero extinction for 47 μg of sulphate/100 ml.

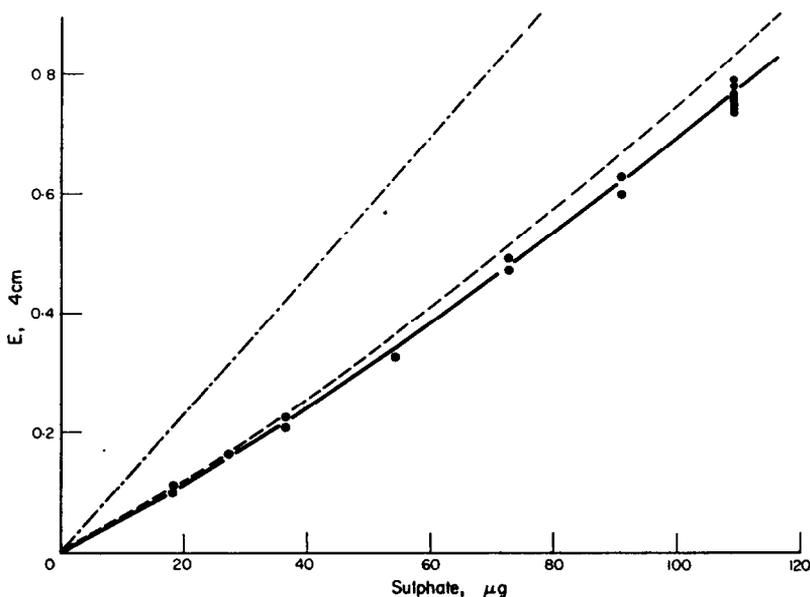


FIG. 2.—Calibration curve at 332 $m\mu$ in 100 ml of final solution (69% ethanol):

- experimental,
- calculated from equation (26),
- · - · calculated by assuming 1 SO_4^{2-} gives 1 C^{2-} .

SCOPE OF METHOD

The sensitivity of a colorimetric method may be limited by two factors: chemical and instrumental. The latter factor is caused by the fact that at low extinction readings the percentage error is greatly increased. Assuming the Ringbom curve to be valid and accepting a value of 0.2% for the standard deviation in the transmission measurements, the percentage error in E from the instrument is 1% at $E = 0.10$, 2% at $E = 0.05$, 4.5% at $E = 0.02$ and 9% at $E = 0.01$.

The chemical error probably arises largely from the uncertainty in the blank (salt concentration).

The total error is found by quadratic addition of both errors. In the present example it seems that the instrumental error is of minor importance, but if the chemical error is reduced, the instrumental one may become the limiting factor.

One way to achieve this reduction seems to be a decrease in the value of the blank itself, which, probably, will give improvement in the reproducibility. In our experiments this was performed by the addition of ethanol, but the blank remained too large.

A disadvantage, however, of this change in the procedure will be that with constant sample volume the final volume will be increased considerably.

In any case, it is necessary that the ionic composition is controlled between narrow limits. It seems, therefore, that the practical application of the procedure will be limited to those problems in which good control of the ionic composition of the sample is possible.

The chloranilic acid method has also been used with other metal salts of the same anion. In some cases the solubility is less and it is an important consequence that it makes the control of the ionic composition less stringent. For the solubility product of the lead salt in 69% ethanol we found 2.5×10^{-12} . Unfortunately, however, the solubility of lead sulphate in this medium is too large to make this favourable aspect useful for the determination of sulphate. Similar unfavourable results were obtained with 50% dioxan and 50% methylcellosolve solutions.

This consequence that a less soluble product (or a stronger complex) is required, may be a disadvantage of the use of a less soluble metal chloranilate.

Another possibility for increasing the sensitivity seems to be the replacement of the chloranilate ion by another ion giving less soluble salts. The value of ϵ , though theoretically limited,¹⁷ may also be higher than in our case.

Zusammenfassung—Die Bestimmung von einigen Anionen (z.B. das Sulfat) kann durchgeführt werden durch die Reaktion mit einer wenig dissoziierte oder wenig lösliche Verbindung (z.B. Bariumchloranilat). Von dieser Reaktion wird ein anderes Anion (z.B. Chloranilation) freigesetzt, dessen Extinktion gemessen wird. In dieser Arbeit ist eine Gleichung abgeleitet worden für die Beziehung zwischen der Sulfat-konzentration und der Extinktion. Für niedrige Konzentrationen ist die Beziehung nicht linear. Eine Eichkurve wurde hergestellt und zeigte gute Übereinstimmung mit der Theorie. Die Genauigkeit war ungefähr 5% bei 20 μg Sulfat, etwas besser bei grösseren Mengen. Es wird nachgewiesen dass viele Störungen erklärt werden können durch Berücksichtigung der Aktivitätskoeffizient. Die Möglichkeiten dieses Verfahrens werden erörtert.

Résumé—La détermination de certains anions (par exemple le sulfate) peut être exécutée à l'aide de la réaction avec une substance peu dissociée ou peu soluble (par exemple le chloranilate de baryum). Par cette réaction un autre anion (l'ion de chloranilate) est libéré et son extinction est mesuré. Dans notre publication une équation est dérivée, exprimant la relation entre la concentration de sulfate et l'extinction mesuré. A concentrations basses la relation n'est pas linéaire. Une courbe d'étalonnage est en bon rapport avec la théorie. Elle montre une précision de 5%, quand 20 μg de sulfate sont déterminés. Avec des quantités plus élevées, la précision est meilleure. Nous avons démontré que beaucoup d'erreurs sont explicables, considérant les coefficients d'activité. Les possibilités de cette méthode sont discutées.

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