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ESTIMATION OF EFFICIENCY FOR BUBBLER-TYPE GAS ABSORBERS

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Summary—The behaviour of bubbler-type absorbers is discussed, and used to predict an estimate of absorption efficiency for such absorbers and to indicate the factors which have the greatest effect on efficiency.

GAS analysis methods involving the selective collection of one or more components of a gaseous mixture in a liquid absorbent are subject to error if the absorption efficiency is unknown and may even be limited in feasibility if the efficiency is too low. It is important to be able to predict (or estimate) the efficiency of an absorption system and to control the factors which significantly affect efficiency. While performance data for laboratory-scale absorbers have been reported in the literature, they are not universally applicable and must be interpreted for any situation which is not identical with the original experiment.

The purpose of this paper is to present sufficient generalised information to serve as a basis for predicting the performance and understanding the behavior of bubbler-type absorbers. Bubblers were chosen for discussion because they are the simplest and most commonly used class of absorbers. Much of the general discussion which follows applies to all absorbers, but the design equations were developed for specific application to the case of bubbles rising through liquid.

An extensive general discussion of analytical absorbers is given by Jacobs[1] and performance data (also presented by Jacobs) are given[2] in the American Public Health Association Yearbook, 1939–40. It will be assumed here that these or other sources may be consulted for details of absorber construction and operating procedure. While there are many variations in design, bubbler-type absorbers generally involve the dispersion of gas into the bottom of a reservoir of liquid and withdrawal of the gas above the level of the "aerated" column of liquid.

Dispersion of the gas is obtained either by introduction of a gas jet from a submerged orifice or by introduction of gas through a sintered-glass plate or similar porous medium. Effective gas bubble size is practically independent of orifice (or pore) size when the bubble population is high[3]. This observation is attributed to the coalescence of small bubbles in the vicinity of the dispersion plate. While the bubble diameters are statistically distributed, the distributions measured by Houghton *et al.*[3] are fairly narrow and the average diameters range from 0.35 to 0.45 cm over a wide range of gas velocity.

Because the extent of absorption depends on both the residence time of a bubble in the aerated column of liquid and the bubble velocity relative to the liquid, it is important to have information on these quantities. Fig. 1 is a plot of bubble (air)

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residence time per centimetre of non-aerated liquid (water) depth above the gas entrance versus superficial gas velocity (cm³/min per cm² of absorber cross-sectional area) with absorber diameter as a parameter. The curve for 80 mm diameter is from the data of Houghton on gas hold-up and that for 22 mm is from the author's data on hold-up in a midget impinger.
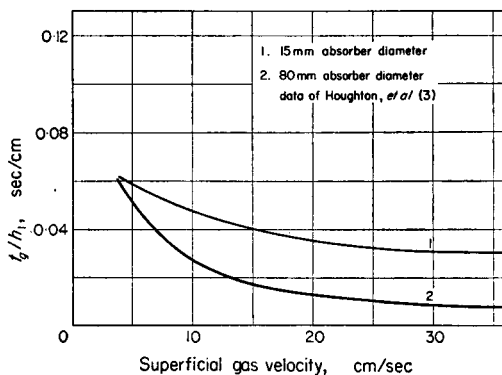
FIG. 1.

The residence time is practically independent of the method of gas dispersion so long as the superficial gas velocity is high enough to provide many bubbles. This would not be true for bubbles rising singly with a large distance between bubbles. It can be seen that so far as residence time and bubble diameter are concerned, there appears to be no value in using a fine fritted disc as compared with a coarse one. Although there is no information on the point, it would probably be unwise to use extremely large nozzles for dispersion. The midget impinger nozzle, for example, was about 1 mm, which would provide a gas jet velocity of 6,000 cm/sec at the point of maximum absorption efficiency.

The velocity of rise of single bubbles[4] is approximately constant at 24 cm/sec for diameters greater than 0.2 cm. While the average velocity relative to the absorber walls is lower than this where bubble population is high, we will approximate the velocity relative to the liquid as being equal to the velocity of rise of a single bubble.

DEFINITIONS OF SYMBOLS

A　= Designation of transferring component.
a　= Bubble radius, *cm*.
B　= Designation of reactant in liquid.
C　= Concentration of A in liquid, *mol/cm³*.
C_a　= Average concentration of A in liquid at any instant, *mol/cm³*.
C_0　= Initial average concentration of A in liquid, *mol/cm³*.
C_{Ai}　= Concentration of A in the liquid interface, *mol/cm³*.
D　= Diffusivity coefficient for A, *cm²/sec*.
D_g　= Gas phase diffusivity, *cm²/sec*.
D_f　= Fictitious gas phase diffusivity for cases of mixed resistance.
D_{T_1}　= Diffusivity of A in water at T_1.
D_{T_2}　= Diffusivity of A in water at T_2.

F　= Overall instantaneous collection efficiency $= f\left(\dfrac{p_1 - HC_a}{p_1}\right) = f\left(\dfrac{p_1 - p_e}{p_1}\right).$

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f = Fractional instantaneous approach to equilibrium $= \dfrac{p_1 - p_2}{p_1 - HC_a} =$ equilibrium collection efficiency.

f_g = Equilibrium collection efficiency for gas phase controlling.

f_L = Equilibrium collection efficiency for liquid phase controlling.

f_L' = Equilibrium collection efficiency during period of movement of one bubble diameter relative to liquid.

G = Gas flow rate, $cm^3/sec.$

H = Henry's Law Constant, $\dfrac{atm}{mol/cm^3}$.

k_g = Mass transfer coefficient for gas phase, $mols/cm^2\text{-}sec\text{-}atm.$

k_{OG} = Overall gas-phase mass transfer coefficient based on driving force equal to average partial pressure of A in the gas minus the partial pressure in equilibrium with average liquid concentration, $C_a.$

k_L = Liquid-phase mass transfer coefficient, $mols/cm^2\text{-}sec\text{-}mol/cm^3$ based on driving force = $C_{A_i} - C_a.$

N = Diffusion rate, $mol/sec\text{-}cm^2.$

n = Total number of bubble diameters of relative motion during bubble residence time.

P = Total pressure, $atm.$

p_1 = Partial pressure of A in inlet gas, $atm.$

p_2 = Partial pressure of A in outlet gas, $atm.$

p_e = Partial pressure of A in equilibrium with liquid concentration, C_a, $atm.$

q = Concentration (average) of B in liquid for one mole of B reacting with one mole of A, $mol/cm^3.$

R = Gas law constant $= 82.057,$ $\dfrac{atm\text{-}cm^3.}{mol\text{-}°K.}$

T = Absolute temperature, $°K.$

t_a = Total time of absorption, $sec.$

t_g = Residence time of a gas bubble, $sec.$

t_L = Time of exposure of fresh liquid surface to gas bubble.

u_b = Bubble velocity relative to liquid, $cm/sec.$

u_g = Superficial gas velocity, $cm^3/min\text{-}cm^2.$

V_L = Volume of liquid in absorber, $cm^3.$

x = Distance in direction of diffusion, $cm.$

π = 3.1416.

ρ_g' = Molar density of gas, $mol/cm^3.$

μ_{T_1} = Viscosity of water at T_1, $centipoises.$

μ_{T_2} = Viscosity of water at $T_2.$

Mass transfer

The fundamental process in an absorber involves the tendency toward equilibrium between the gas and the liquid in contact with it. This may involve the transfer of several components between the phases, but it will be assumed here that the liquid is non-volatile and that if there is more than one component in the gas phase, they may be considered independently. Thus we are concerned with the transfer of one component, A, from the gas to the liquid.

Because each bubble is in contact with the liquid for a limited time, equilibrium will not be attained and the degree of approach to equilibrium will be determined by the rate of transfer of A. Mass transfer rate in a bubbler can best be considered quantitatively in terms of unsteady-state diffusion rather than the "two-film" theory because of the generally small effects of turbulence in either fluid phase. However,

a simpler qualitative description can be given in terms of steady-state diffusion, where for a one-dimensional case:

$$N = -D \frac{\partial c}{\partial x} \frac{\text{(mols)}}{\text{(sec–cm}^2)} \tag{1}$$

Equation (1) states that the rate of diffusion depends on the diffusivity and the concentration gradient, $\partial c/\partial x$.

Although, in general, the rate of mass transfer is determined by the concentration gradients and diffusivities of both phases, there are two limiting cases in which the rate is controlled by either the liquid or the gas phase. To illustrate, consider the purely physical absorption (i.e., a reversible equilibrium process such as the solution of oxygen in water) of A from a bubble rising through a liquid. If A is extremely soluble in the liquid just at the interface, a low gas-phase concentration would be in equilibrium with a high liquid-phase concentration. Consequently, a high concentration gradient would exist between the liquid at the interface and the bulk of the liquid. Because the rate of diffusion from the gas must equal the rate of diffusion into the liquid, there must be a fixed ratio of gas concentration gradient to liquid concentration gradient. In order to maintain this ratio the interfacial gas concentration must be quite small and indeed, it approaches the concentration in equilibrium with the bulk of the liquid. In this limiting case the concentration gradient in the gas phase becomes practically identical with that which would exist if there were no liquid phase concentration gradient.

The other limiting case, liquid phase controlling, occurs when a gas of very low solubility is being absorbed. The maximum possible liquid-phase concentration gradient will be so small that the gas-phase concentration gradient must be small if the transfer rates in the two phases are to be equal. Here the liquid-phase concentration gradient may be approximated as that which would exist if there were no concentration gradient in the gas.

Gas phase controlling

The rate of mass transfer from a bubble, if gas-phase resistance controls, is represented in Fig. 2, a graph of fractional approach to equilibrium, f_g, versus a
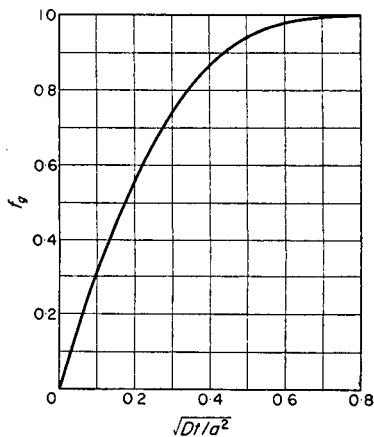
FIG. 2.

dimensionless time group, $\sqrt{Dt_g/a^2}$. This figure represents the solution of the equations for unsteady-state diffusion from a sphere which is initially at a uniform concentration and which is in contact with liquid of constant, uniform composition as given by Crank[5]. Physically, this corresponds to a bubble contacting liquid whose composition does not change appreciably during the period of contact (for this bubble) and under conditions such that gas-phase resistance is controlling.

One must distinguish between overall collection efficiency, F, which represents simply the fraction of A absorbed, and equilibrium collection efficiency, f, which represents the fractional absorption of that portion of A which would be absorbed if equilibrium were attained. It will be recognised that if the reaction products are such that there is an appreciable equilibrium vapour pressure above the liquid, the amount of A which can be removed from the gas will decrease as the concentration of the liquid increases. Thus, while the first bubbles of gas might transfer 99% of their A-content to fresh liquid (barren of A-reaction products), later bubbles might contact liquid so concentrated that they could not possibly transfer more than, say, 50% of the A-content even though they would still attain 99% of this equilibrium limit.

Liquid phase controlling

If liquid-phase resistance is controlling, the fractional approach to equilibrium is given by:

$$f_L' = \left(\frac{2D}{\pi a u_b}\right)^{1/2}\left(\frac{6RT}{H}\right) \tag{2}$$

and

$$(1 - f_L) = (1 - f_L')^n \tag{3}$$

These relationships were derived on the basis of Higbie's Penetration Theory, which states that the rate of diffusion from a sphere is given by the rate of diffusion into a semi-infinite medium which is originally at a uniform concentration, C_0, over a period of time, t_L, which may be approximated as the time required for the bubble to rise one diameter, $2a/u_b$. The fraction f_L' is equal to the change in concentration of the gas divided by the maximum change possible (for gas in equilibrium with liquid at C_0) which occurs during the time the bubble rises one diameter. The total fractional approach to equilibrium, f_L, is given for a bubble rising through n diameters, where n equals the number of diameters of relative movement per second, $u_b/2a$ times the residence time. The velocity relative to the liquid, u_b, may be taken as 24 cm/sec for this purpose and for bubble diameters of 3.5–4.5 mm.

Although the distinction between gas phase controlling and liquid phase controlling has been given above in comparative qualitative terms, it can now be given quantitatively. The basic relationship is based on the two-film concept of mass transfer, which is discussed in any text-book of chemical engineering, and describes the relationship between a mass transfer coefficient, k_g, based on the actual gradient in the gas phase (which requires that interfacial concentrations be known), and an overall coefficient, k_{OG}, based on the gradient for the assumption of gas-phase controlling (which requires knowledge of bulk concentrations only):

$$\frac{k_g}{k_{OG}} = 1 + H\frac{k_g}{k_L} \tag{4}$$

If the ratio, k_g/k_{OG}, is unity, then the gas phase controls. Liquid-phase resistance is important if the ratio is significantly greater than one and may be said to control if the ratio is greater than 10. We may evaluate the ratio by using the following expressions for gas-phase coefficient, k_g, and liquid-phase coefficient, k_L. The expression for k_g is an approximate representation of the relationship given in Fig. 2 and the expression for k_L results from penetration theory.

$$k_g = \frac{7.6(D_g)^{0.7}}{3RT(t_g)^{0.3}(a)^{0.4}} \tag{5}$$

$$k_L = 2\sqrt{\frac{D_L u_b}{2\pi a}} \tag{6}$$

We can estimate the ratio k_g/k_L for average conditions where a gas is being absorbed from air into an aqueous solution at room temperature. The bubble radius, a, is taken as 0.2 cm and the velocity of rise, u_b, as 24 cm/sec. Representative diffusivities are gas diffusivity, $D_g = 0.1$ cm²/sec and liquid diffusivity = 1.5×10^{-5} cm²/sec. Upon making the substitutions it is seen that $k_g/k_L = 1.87 \times 10^{-3}$ for "average" conditions. Thus we may say that gas-phase resistance controls [i.e. $-(k_g/k_{OG}) < 1.1$] if H is less than 54 $\frac{(atm)}{(mol/cm^3)}$ and that liquid phase controls [$(k_g/k_{OG}) > 10$] if H is greater than 4,800 $\frac{(atm)}{(mol/cc)}$.

Intermediate cases may be approximated by considering the absorption to be gas-phase controlled and by using a fictitious diffusivity, D_f, such that:

$$\frac{k_g}{k_{OG}} = \left(\frac{D_g}{D_f}\right)^{0.7} \tag{7}$$

or

$$D_f = D_g \left(\frac{k_{OG}}{k_g}\right)^{1.43}$$

Chemically reactive solutions

Examples of the prediction of absorption efficiencies for each of the three cases discussed above are given later in this paper. Before turning to them we must consider two more matters of general importance. The first of these is the consideration of absorption by a chemically reactive solution, which probably includes the majority of applications in gas analysis. In the ideal situation one might picture the liquid-phase reaction as being extremely rapid and the reaction products such that the vapour pressure of A in equilibrium with the liquid interface is negligible. Where this is approximately true, the absorption is gas-phase controlled, and the absorption will be substantially complete in the contact time attained in most laboratory absorbers.

Even though the reaction products might be non-volatile, however, there is still no assurance that liquid-phase resistance will be negligible. It is necessary that the reacting substance, B, diffuses through the liquid towards the interface and reacts at a high enough rate to match the rate of diffusion of A into the liquid. If B diffuses

too slowly or if the reaction is too slow, the reaction zone may be displaced a consider-able distance into the liquid with the result that the equilibrium pressure of A above the liquid interface will rise.

The magnitude of the effect of reactant diffusion rate is illustrated mathematically in the solution[6] for the case wherein the second order reaction between A and B, yielding a non-volatile product, is infinitely rapid and the diffusivities of A and B are equal:

$$k_L = \left(1 + \frac{q}{C_{Ai}}\right) 2\sqrt{\frac{D_L u_b}{2\pi a}} \qquad (8)$$

It can be seen that if the ratio of the average concentration of B to the concentra-tion of A at the liquid interface, q/C_{Ai} is small, the liquid-phase transfer coefficient, k_L, is the same as that for physical absorption. This bears out the qualitative observation that the concentration of B must be high relative to the concentration of A in order for liquid-phase resistance to be substantially eliminated. If the absorption can be described as liquid-phase controlled at zero concentration of B, then the effect of B on the fractional approach to equilibrium per bubble diameter of rise is given by:

$$f_L' = \left(1 + \frac{q}{C_{Ai}}\right) \left(\frac{2D}{\pi a u_b}\right)^{1/2} \left(\frac{6RT}{H}\right) \qquad (9)$$

If the absorption is to be considered as overall gas-phase controlled, then the ratio k_g/k_L in equation (4) should be divided by $[1 + (q/C_{Ai})]$.

Liquid flow pattern

The final matter of general importance is the effect of liquid flow pattern in the absorber. In the previous discussion it has been assumed that the liquid is completely mixed so that the liquid composition encountered by any one bubble at the bottom of the absorber is the same as that encountered at the top by the same bubble. In other words, the rate of change of liquid-phase composition was assumed small with respect to the residence time of any one bubble because the amount of liquid associated with the bubble is large.

It is possible to have a definite circulatory liquid flow pattern set up so that some small fraction of the liquid travels up with a bubble and experiences little mixing with the bulk of the liquid during its upward travel. The result will be that the liquid contacting the bubble at the top of the absorber is more concentrated in A than the bulk of the liquid. Where the absorption process is purely physical, the minimum concentration of A in the gas leaving the absorber will be limited to that in equilibrium with the liquid last contacting the bubble. In the case of absorption with a reactive solution there may be no adverse effect if the concentration of the reactant is not appreciably depleted.

While it is not now possible to quantitatively characterise the co-current movement of liquid with the gas, evidence of its existence has been observed. The discussion of the absorption of ammonia in water, given later, points out the probable effect of co-current flow at low gas flow rates. Study of the absorption of carbon dioxide in water in an absorber in which the bubbles travel up in a helical path formed in a glass liner is at present being conducted by the authors and has shown that there is pro-nounced co-current flow in this apparatus.

Where co-current flow does exist in physical absorption, it can be shown mathematically that, for the same residence time, the approach to equilibrium, f, will be greater than for the case of complete mixing of the liquid phase. However, the shifting of the equilibrium limit will more than compensate for the increase of f in causing overall collection efficiency, F, to decrease.

EXAMPLES

Some examples of gas absorption in bubblers for which experimental data are available will now be considered in order to illustrate both the application of the design principles and the order of accuracy which can be attained. It must be emphasised that the predicted efficiencies can only be interpreted as approximations and that for precise work the efficiency must be determined for the particular system.

Liquid phase controlling

The absorption of carbon dioxide by aqueous solutions of sodium hydroxide, sodium carbonate and ammonia in nozzle-type bubblers has been reported by Mochalova and Kishinevskii[7]. Their data for absorption in pure water (extrapolated to 0% Na_2CO_3) will be compared with predictions based on liquid-phase resistance controlling. The apparatus used consisted of a 0.5-cm diameter tube pointed downward with the end of the tube submerged 1.7 cm below the liquid level in a 5-cm diameter cylinder. Measured absorption efficiencies were 7.61% at 5°C and 7.39% at 45°C. The total gas rate was cited as 0.6 litres per minute (we assume this to be at standard conditions), which corresponds to a superficial gas velocity of 0.51 (cm/sec).

Solubility data[8] were converted to values of H equal to $1.57 \times 10^4 \left(\dfrac{atm}{mol/cm^3}\right)$ at 5° and $4.57 \times 10^4 \left(\dfrac{atm}{mol/cm^3}\right)$ at 45°. Applying the criterion of equation (4) indicates that liquid phase controls, since H is greater than 4.8×10^3. Thus the absorption efficiency should be predicted with equations (2) and (3). Diffusivities for carbon dioxide in water of 1.14×10^{-5} (cm²/sec) at 5°C and 3.19×10^{-5} (cm²/sec) at 45°C were estimated from the International Critical Tables value of 1.8×10^{-5} (cm²/sec) at 20°C by means of the following relationship[9] for dilute aqueous solutions:

$$D_{T_1} = D_{T_2} \left(\frac{\mu_{T_2}}{\mu_{T_1}}\right) \tag{10}$$

The viscosities μ_{T_2} and μ_{T_1} are those of water at the temperatures T_2 and T_1. If the liquid viscosity is much different from that of water, equation (10) will not apply and another relationship[9] must be used.

Because the orifice size is relatively large (5 mm) and the gas rate is low, we would expect that the bubbles would emerge singly as reported. Thus, the velocity of rise, u_b would be about 24 (cm/sec) for an assumed bubble radius, a, of 0.2 cm. Substitution of these values into equation (2) leads to values for f_L' of 0.0107 at 5° and 0.007 at 45°. At the low superficial gas velocity used there is no significant difference between aerated and non-aerated liquid heights, so the value of n is 4.25 bubble diameters for a submergence of 1.7 cm.

The efficiencies, f_L, are then computed to be 4.5% at 5°C and 3.0% at 45°C. If

we take into account the fact that, because the orifice is pointed downward the bubble path will be a curve rather than a straight line, we might reasonably expect (as confirmed by observation) the path to be a few bubble diameters longer. If n is taken as 7.0, the values of f_L will be 7.3% at 5°C and 4.8% at 45°C. This approximation to the experimental values of 7.61% and 7.39% is about as good as can be expected considering all of the estimations involved in the calculations and the extremely small contact time.

Chemical reaction and gas phase controlling

Air contaminant absorption efficiencies for several models of bubblers have been determined by Roberts and McKee[10]. Collection of sulphur dioxide in disodium tetrachloromercurate and of chlorine in 0.1N sodium hydroxide were reported as "... substantially complete regardless of the type of sampler or the flow rate used ...". For the absorption of 1 ppm (by volume) of ammonia from air in distilled water the efficiencies were lower and were dependent on air flow rate (see Fig. 3).

1. Predicted for midget sampler, $D_f = 0.0848$
2. Predicted for midget sampler, $D_f = 0.0475$
3. Experimental for midget impinger, (from Roberts and McKee, reference 10)
4. Experimental for midget bubbler, (from Roberts and McKee, reference 10)

Superficial gas velocity, cm/sec
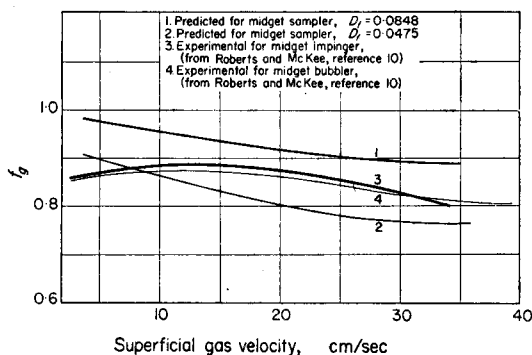
FIG. 3.

If we assume that the concentrations of sulphur dioxide and chlorine (data were not given) were of the same order as that of ammonia,* we may consider these two cases as being gas-phase controlled because the ratio (q/C_{Ai}) would be very high. Considering the case of chlorine absorption, for example, we find a value of $H = 1.33 \times 10^4 \left(\dfrac{\text{atm}}{\text{mols/cm}^3} \right)$ for un-ionised chlorine solubility[6] and approximately half that for total chlorine solubility. Employing the criterion of equation (4), this value of H indicates liquid-phase controlling if there is no chemical reaction. The effect of chemical reaction (assuming a second order, rapid reaction) can be estimated by means of equation (8) if we assume that C_{Ai} is in equilibrium with a gas-phase interface with chlorine concentration of 1 ppm ($p_1 = 1 \times 10^{-6}$ atm). Computation yields $C_{Ai} = 0.75 \times 10^{-10}$ mols/cm³ and we have $q = 1 \times 10^{-4}$ equiv./cm³. Putting C_{Ai} in terms of equivalents, since one mole of chlorine reacts with two equivalents of sodium hydroxide, we compute $q/C_{Ai} = 0.67 \times 10^6$.

For purposes of estimation we take $k_g/k_L = 1.65 \times 10^{-3}$ for the case of no reaction and obtain $k_g/k_L = 2.46 \times 10^{-9}$ for this case of chemical reaction. The group $H(k_g/k_L)$ can now be computed to be 3.3×10^{-5} and substitution in equation (8)

* Communication with Dr. McKee verified this assumption.

indicates that this is a case of gas-phase resistance controlling. One notes that, since gas phase is controlling, the concentration gradient in the gas would cause the partial pressure of chlorine at the interface, and consequently C_{Ai}, to be lower than that assumed (the average partial pressure, p_1), and thus the ratio, q/C_{Ai}, would be larger. It can be seen, then, that to base the computation on C_{Ai}, as given by the maximum gas-phase composition, will yield a conservative result.

The next step is to compute fractional approach to equilibrium based on gas-phase controlling. Diffusivities in air at 20°C were computed from values at 0°C by the method recommended in Reid and Sherwood[9] as 0.14 cm²/sec for sulphur dioxide, 0.143 cm²/sec for chlorine and 0.228 cm²/sec for ammonia. Assuming a bubble radius of 0.2 cm, a liquid volume of 10 cm³,* and a bubbler cross-sectional area of 3.6 cm² (for a standard Midget Impinger), we compute the un-aerated liquid height to be 2.78 cm and can proceed to find residence time and f_g. At a superficial gas velocity of 15 cm/sec, Fig. 1 indicates a residence time of 0.04 seconds per centimetre of un-aerated height or 0.11 sec for 2.78 cm of liquid. By use of Fig. 2 the efficiencies are computed to be 0.984 for sulphur dioxide and chlorine, and 0.998 for ammonia.

Resistance in both phases

These predictions of f_g may be assumed to be equivalent to F if the testing time was so short that the liquid concentration did not rise appreciably. The predictions for sulphur dioxide and chlorine bear out the statement[10] that absorption was substantially complete. The prediction for ammonia is far from agreement with the experimental results shown in Fig. 3, in spite of the fact that $H = 13.5 \dfrac{\text{atm}}{\text{mol/cm}^3}$ (for dilute solutions[6]), and one would expect gas phase to be controlling from the criterion of equation (4).

We find that this same characteristic of ammonia absorption in water has been observed in large, industrial equipment[6] and that ratios of k_g/k_{OG} ranging from 2 to 3 have been determined experimentally. The existence of this additional resistance has been attributed to the possibility of a slow reaction between dissolved ammonia and ionised ammonia. There is also the possibility that the rate of accommodation at the interface is low. If we employ the extremes of the ratio, as given above, the corresponding values for D_f are 2.69 and 4.8 (see equation (7)). The predicted curves of efficiency versus flow rate are shown in Fig. 3.

While it is clear that the prediction covers too large a range of efficiencies to be useful in precise work, the "bracketing" of the experimental values at higher velocities is good confirmation of the mechanistic approach. The deviation of the slopes at low gas velocities is believed, by us, to be largely due to co-current flow, and to some extent to inaccuracy of bubble residence times as computed from gas hold-up. A definite circulatory liquid flow pattern can be observed at low gas flow rates and we believe that this results in a significant increase of ammonia concentration in the small volume of liquid which accompanies the bubbles.

CONCLUSIONS

The design methods presented above may be used to predict an estimate of absorption efficiency for a bubbler-type absorber and to point out which factors have the

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* Communication with Dr. McKee verified this assumption.

most important effect on efficiency. A recommended procedure for predicting efficiency is given below. It should be emphasised that this procedure is based on conservative approximations. High values for both bubble diameter and bubble velocity are used and the beneficial effect of circulation within bubbles is neglected. The approximate method for treating cases of mixed resistance is presented because of its simplicity although a rigorous solution for this case is given by Crank[5]. In any case, the prediction cannot be relied on for precise results and the specific system must be calibrated experimentally.

Recommended procedure

I. Determine whether the system is gas- or liquid-phase controlled or intermediate by means of the criterion of equation (4). For high concentration, either an average value of H may have to be estimated or the absorption process may have to be considered over incremental ranges of concentration in which H is approximately constant.

II. If the system involves purely physical absorption, evaluate the fractional approach to equilibrium by means of Fig. 2 for gas-phase controlling and equations (2) and (3) for liquid-phase controlling. For intermediate resistance use the relationship of Fig. 2 with a fictitious diffusivity given by equations (4) and (7). The ratio of k_g/k_L may be either estimated as the "average" value of 1.86×10^{-3} or it may be computed by means of equations (5) and (6).

If the absorption is to be carried on for a long time so that the liquid concentration builds up enough to impose an equilibrium limit on efficiency, the total amount of collection can be determined by integrating the relationship between the instantaneous rate of increase of liquid concentration and the liquid concentration. For an initial liquid phase concentration of zero and constant inlet gas concentration, the result is:

$$\ln \left(1 - \frac{HC_o}{p_1}\right) = -f \left(\frac{HG\,\rho_a'}{V_L P}\right) t_a \qquad (11)$$

III. If the system involves chemical reaction in the liquid phase and there is negligible equilibrium pressure of the transferring component above the reaction products, the maximum collection efficiency corresponds to the case of gas-phase controlling. The effect of reactant concentration for a second order reaction may be estimated by dividing k_g/k_L in equation (4) by $(1 + (q/C_{Ai}))$. Other reaction mechanisms are discussed by Crank[5].

In cases where an appreciable equilibrium pressure results from the reaction, the overall collection efficiency must be computed from the fractional approach to equilibrium as in the case of physical absorption.

IV. Having used the methods described above to design an appropriate absorption system, the performance of the system should be determined experimentally. The preferable method is to sample a gas mixture of known composition. If this is not possible, use two or more absorbers in series.

Zusammenfassung—Die Eigenschaften von Absorber des Gasblasentyps werden diskutiert. Es wird versucht auf Grund der Eigenschaften vorauszusagen wie gross die Absorptionsfähigkeit solcher Absorber ist und die Faktoren herauszuarbeiten, die den grössten Einfluss auf die Leistungsfähigkeit haben.

Résumé—Les auteurs discutent le comportement d'absorbeurs du type barboteur et utilisent les résultats obtenus pour prévoir une estimation du pouvoir d'absorption de tels absorbeurs et pour indiquer les facteurs qui influent le plus sur ce pouvoir d'absorption.

REFERENCES

[1] M. B. Jacobs, *The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents*, Interscience Publishers, Inc., New York, 2nd Ed., 1949.
[2] *American Public Health Association Yearbook*, 1939–40.

[3] G. Houghton, A. M. McLean and P. D. Ritchie, *Chem. Eng. Sci.*, 1957, **7**, 44.

[4] F. H. Garner, and D. Hammerton, *Chem. Eng. Sci.*, 1954, **3**, 1.

[5] J. Crank, *The Mathematics of Diffusion*, Oxford Univ. Press, London, 1st Ed., 1956.

[6] T. K. Sherwood and R. L. Pigford, *Absorption and Extraction*, McGraw-Hill Book Co., New York, 2nd Ed., 1952.

[7] L. A. Mochalova and M. Kishinevskii, *J. Appl. Chem.*, 1958, **31**, 525.

[8] *Handbook of Chemistry and Physics*, Chemical Rubber Publishing Co., 39th Ed., 1957.

[9] R. C. Reid, and T. K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill Book Co., New York, 1st Ed. 1958.

[10] L. R. Roberts and H. C. McKee, *J. Air Pollution Control Assn.*, 1959, **9**, 51.

THE ANALYSIS OF BERYLLIUM AND BERYLLIUM OXIDE—II

THE DETERMINATION OF COPPER

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Summary—A method is described for the determination of copper in beryllium or beryllium oxide by extraction of the neocuproïne complex with methyl *iso*butyl ketone. The method is accurate to ±5% or ±2.5 micrograms of copper, whichever is greater. The accuracy and sensitivity could be improved by appropriate choice of sample size, volume of extract and/or cell length. Of the 68 elements investigated, only gold interferes in 10 mg amounts; in this case a slight loss of copper is caused by occlusion or co-precipitation.

INTRODUCTION

In a previous paper,[1] the authors discussed the necessity of obtaining accurate chemical methods for the analysis of beryllium and beryllium oxide. Certain desirable features of such methods were also discussed. In the present paper a method is presented which is, assuming no synergistic effects, specific for copper. No interference was caused by 10 mg amounts of 67 elements. The presence of 5 or 10 mg of gold resulted in an 8% loss of copper by occlusion or co-precipitation. The method is accurate to ±5% relative or ±2.5 micrograms of copper, whichever is greater. The accuracy and sensitivity could be improved by appropriate choice of sample size, volume of extract and/or cell length.

The method adopted is a modification of that presented by Gahler.[2] The sample is dissolved as previously described,[1] and citric acid is added to prevent precipitation of beryllium. The copper is reduced with hydroxylamine hydrochloride, and the pH is adjusted to 5.0 ± 0.1. Neocuproïne is added and the complex is extracted with methyl *iso*butyl ketone (4-methyl-2-pentanone). The absorbance of the organic extract, measured at 457 millimicrons, is a linear function of concentration, at least from 0 to 5 ppm, and is stable for at least 24 hours.

EXPERIMENTAL

Apparatus

Cary Model 14 Spectrophotometer and 1-cm cells.
International Clinical Centrifuge, 15-ml glass-stoppered centrifuge tubes.
Beckman H-2 pH meter.

Reagents

Standard copper solution: Remove the oxide film from high-purity copper metal shot by treating it with 3*M* nitric acid. Rinse and dry. Dissolve approximately 0.1 g in 12 ml of 4*M* nitric acid. Add 10 ml of perchloric acid and evaporate to fumes to expel nitric acid. Cool and dilute to 1 litre. Dilute this solution to obtain a solution containing 10 μg of copper per ml.

Hydroxylamine hydrochloride, 10% (w/v): Store in refrigerator.

Neocuproïne, (2:9-dimethyl-1:10-phenanthroline): 0.1% (w/v), in absolute ethanol. Store in refrigerator.

Citric acid, 50% (w/v).

Methyl isobutyl ketone, (4-methyl-2-pentanone): B.P. 114–116°.

Hydrochloric acid, (Sp. gr. 1.19).

Sulphuric acid, (Sp. gr. 1.84).

Sodium hydroxide, 50% (w/v).

Procedure

Dissolve a sample, containing about 50 μg of copper, according to the directions previously given[1] and transfer to a 400-ml beaker. Add sufficient acid to have present 5 ml of hydrochloric acid and 10 ml of sulphuric acid. Add 10 ml of 50% citric acid, 5 ml of 10% hydroxylamine hydrochloride, dilute to about 100 ml with water and cool in an ice-bath. Adjust the pH to 5.0 $\pm$ 0.1 with 50% sodium hydroxide, keeping the solution at room temperature with an ice-bath. Transfer to a 250-ml separatory funnel. Add 10 ml of 0.1% neocuproïne solution and allow to stand for 2 hours. Add exactly 10 ml of methyl isobutyl ketone. Stopper tightly and shake for 1 minute. Allow the layers to separate, and discard the aqueous phase. Centrifuge the organic layer and measure its absorbance in 1-cm cells at 457 millimicrons versus methyl isobutyl ketone in the reference cell. Determine the copper concentration by reference to a standard curve obtained by carrying known amounts of copper through the above procedure. A blank and standard should be carried through the entire procedure.

Extraction of the copper-neocuproïne complex

In attempting to apply Gahler's method[2] to the determination of copper in beryllium or beryllium oxide, it was found that chloroform was unsatisfactory as an extractant because of a tendency for emulsion formation. Also, in many cases a precipitate formed at the phase interface. Methyl isobutyl ketone was found to be a satisfactory extractant under these conditions. It has been reported[3] that methyl isobutyl ketone is soluble to the extent of 2% in water. However, its solubility is negligible in this medium of high salt content. Copper is quantitatively extracted according to the procedure described.

Measurement of the copper-neocuproïne complex

The absorption spectrum and molar absorptivity (8400) of the copper-neocuproïne complex are essentially the same as those observed when chloroform is used as the extractant. The absorbance is stable for at least 24 hours and is a linear function of concentration, at least from 0–5 ppm. In the presence of large amounts of beryllium, the copper-neocuproïne complex does not attain full colour development for 15 or 20 minutes. Chromium and hafnium are the only elements of the 68 tested which retard complete colour development. A minimum of 2 hours is required for complete colour development when 10-mg amounts of these elements are present. The addition of neocuproïne, up to three times the amount usually added, did not hasten colour development; it was hastened to some extent by the addition of five times the amount of hydroxylamine normally added.

The concentration of neocuproïne has little effect on the molar absorptivity, at least between 0.05 and 1.00 weight per cent.

Effect of other elements

In testing the effect of other elements on the determination of copper using the procedure described, a solution containing the appropriate amount of sodium sulphate and sodium chloride was added.

Luke and Campbell[4] reported that Gahler's method yielded satisfactory results in the presence of 50-μg quantities of 56 metal ions. It was thought that the effects of larger amounts of impurities needed investigation. No interference was observed by 10 mg of Al, Sb^{III}, As^{III}, Ba, Be, Bi, B, Br, Cd, Ca, Ce^{IV}, Cs, Cr^{III}, Cr^{VI}, Co, Dy, Er, Eu, F, Gd, Ga, Ge, Hf, Ho, In, I, Ir, Fe^{III}, La, Pb, Li, Lu, Mg, Mn^{II}, Mn^{VII}, Hg^{II}, Mo, Nd, Ni, Nb, Pd, P, Pt, K, Pr, Re, Rh, Rb, Sm, Sc, Se, Si, Na, Sr, Ta, Te, Tb, Tl^{I}, Th, Tm, Sn^{II}, Ti^{III}, W, U^{VI}, V^{V}, Yb, Y, Zn, or Zr. The presence of 5–10 mg of gold caused a loss of copper by occlusion or co-precipitation amounting to about 8% of the amount of copper

present (in this case 53.7 μg). Citric acid prevented lead sulphate from precipitating, and reduced the amount of precipitation of barium sulphate considerably. Slight precipitation occurred during the test with mercury.

Application of the method

A sample of beryllium oxide analysed using this procedure was found to contain 6.1 and 6.6 ppm copper. When 1 g of this oxide was "spiked" with 53.7 μg of copper, recoveries of 104% and 99% were obtained, indicating the applicability of the procedure to large amounts of beryllium.

Blank values corresponding to 5.0, 5.6, and 5.5 μg of copper were obtained with the amounts of reagents used during the analysis. Demineralised water was used throughout the procedure.

Results obtained when the method was applied to New Brunswick Laboratory standard samples of beryllium and beryllium oxide are shown in Table I.

TABLE I.—ANALYSIS OF NEW BRUNSWICK STANDARDS[a]

Sample No.	Cu found, *ppm*	Average	Nominal value
Be 85	23.2, 25.2	24.2	30
86	264, 264	264	300
87	207, 200	204	210
88	237, 241	239	250
BeO 72-1	35.9, 34.4	35.2	36.0
72-2	18.3, 20.1	19.2	18.0
72-3	7.0, 7.0	7.0	7·21
72-4	5.9, 3.9	4.9	3.60
72-5	1.8, 1.8	1.8	——

[a] Nominal values for beryllium metal are based on chemical analysis.

Zusammenfassung—Eine Methode zur Bestimmung von Kupfer in Beryllium oder Berylliumoxyd wird beschrieben, die auf der Extraktion des Kupfer-Neocuproinkomplexes mit Methyl-Isobutylketon beruht. Die Methode ist auf ±5% oder 2.5 ppm (Mikrogramm per Gramm) genau, abhängig davon welches der grössere Wert ist.

Résumé—Les auteurs décrivent une méthode de dosage du cuivre dans le béryllium ou l'oxyde de béryllium par extraction du complexe néocuproïne dans la méthylisobutylcétone. La méthode est précise à ±5% près (limite de sensibilité: 2,5 ppm). On pourrait augmenter la précision et la sensibilité par un choix approprié de la taille de l'échantillon, du volume du corps extrait, et/ou de la longueur de la cellule. Parmi les 68 éléments étudiés, seul l'or gêne pour une quantité de 10 mg; dans ce cas il y a une légère perte de cuivre causée par occlusion ou coprécipitation.

REFERENCES

[1] J. O. Hibbits, W. F. Davis, and M. R. Menke, *Talanta*, 1960, **4**, 61
[2] A. R. Gahler, *Analyt. Chem.*, 1954, **26**, 577.
[3] Report 5006/23, 1959, United Kingdom Atomic Energy Authority, Industrial Group Headquarters, Lancashire.
[4] C. L. Luke and M. E. Campbell, *Analyt. Chem.*, 1953, **25**, 1958.

THE ANALYSIS OF BERYLLIUM AND BERYLLIUM OXIDE—III

THE DETERMINATION OF MOLYBDENUM

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Summary—A method is described for the determination of molybdenum by extraction of its thiocyanate complex with methyl *iso*butyl ketone. The method is accurate to $\pm 4\%$ or ± 3 micrograms of molybdenum, whichever is greater. The accuracy and sensitivity can be improved by appropriate choice of sample size, volume of extract and/or cell length. Of 68 elements investigated, only rhenium, platinum, palladium, rhodium, vanadium, and tellurium interfere in 10-mg amounts. Of these, only rhenium interferes seriously.

INTRODUCTION

Previous papers[1,2] have discussed the determination of iron and copper in beryllium and beryllium oxide and the requirements for methods used for the analysis of these materials. In the present paper a method is presented which is almost specific for the determination of molybdenum. Of the 68 elements investigated, only rhenium, platinum, palladium, rhodium, vanadium, and tellurium interfere in 10-mg amounts. Of these, only rhenium interferes seriously.

The determination of molybdenum as the thiocyanate is treated extensively in the literature. The method which we have found most satisfactory is based on information supplied by Tombu[3]. Molybdenum thiocyanate, in a sulphuric-hydrochloric acid medium, is reduced with stannous chloride and extracted with methyl *iso*butyl ketone. The extraction is performed in the presence of iron in order to obtain maximum colour intensity. The extract is washed with a solution of oxalic acid in dilute hydrochloric acid; this removes cobalt and any zirconium which may have been extracted. A final wash with dilute hydrochloric acid eliminates any turbidity which may exist in the organic phase. After 2 hours, the absorbance of the extract is measured at 500 mμ. The method is accurate to $\pm 4\%$ or ± 3 micrograms of molybdenum, whichever is greater. The accuracy and sensitivity can be improved by appropriate choice of sample size, volume of extract and/or cell length.

EXPERIMENTAL

Apparatus

Cary Model 14 Spectrophotometer and 2-cm cells.
International Clinical Centrifuge, 15-ml glass-stoppered centrifuge tubes.

Reagents

Standard molybdenum solution. Dissolve 3 g of molybdenum trioxide in 200 ml of 10% sodium hydroxide and dilute to 2 litres with water. Store in a polyethylene container. Standardise this solution and dilute an aliquot to obtain a solution containing 25 μg of molybdenum per ml.

Citric acid, crystals.
Bromine water, saturated solution.
Sulphuric acid, sp. gr. 1.84 and 6*M*.
Potassium thiocyanate, 25% (w/v).
Stannous chloride, 25% (w/v), in 12*M* hydrochloric acid.
Oxalic acid, 2% (w/v), in 1.2*M* hydrochloric acid.
Hydrochloric acid, sp. gr. 1.19, 6*M* and 2.4*M*.
Iron solution. Dissolve 0.48 g ferric chloride hexahydrate in 33 ml of hydrochloric acid (sp. gr. 1.19) and dilute to 100 ml with distilled water.
Methyl isobutyl ketone (4-methyl-2-pentanone), B.P. 114–116°.

Procedure

Dissolve a sample of beryllium metal or beryllium oxide, containing up to 75 μg of molybdenum, according to the procedure described previously.[1] Transfer to a 250-ml separatory funnel and add 1 g of citric acid (to prevent possible precipitation of tungsten, which might occlude molybdenum). Add 1 ml of a solution containing 1 mg of iron per ml. Add water and hydrochloric or sulphuric acids until 5 ml of hydrochloric acid and 10 ml of sulphuric acid are contained in a final volume of 70 ml. Cool to room temperature. Add 2 ml of bromine water, 10 ml of 25% potassium thiocyanate solution and 5 ml of 25% stannous chloride solution. Mix and allow the solutions to stand at least 10 minutes. Add exactly 25 ml of methyl *iso*butyl ketone and shake for 1½ minutes. Allow the layers to separate and discard the aqueous phase. Add 35 ml of 2% oxalic acid solution and shake for 1 minute. Discard the acid wash. Add 35 ml of 2.4*M* hydrochloric acid, shake for 1 minute and discard the acid wash. Allow the organic phase to stand at least 2 hours in the tightly stoppered separatory funnel. Transfer to a centrifuge tube and centrifuge for 1 minute. Measure the absorbance of the extract in 2-cm cells at 500 mμ using methyl *iso*butyl ketone in the reference cell. Determine the molybdenum concentration by reference to a standard curve obtained by carrying known amounts of molybdenum through the above procedure. A blank and standard should be carried through the entire procedure.

Extraction of the molybdenum-thiocyanate complex

Molybdenum is quantitatively extracted using the procedure described. Minor variations in the amounts of hydrochloric or sulphuric acids have no significant effect.

Measurement of the molybdenum-thiocyanate complex

A comprehensive discussion of the molybdenum thiocyanate complexes and the difficulties in attaining maximum colour development has been given by Crouthamel and Johnson.[4] A number of workers have observed that the presence of small amounts of iron (or copper) increases the colour intensity. In this study, 1 mg of iron was added in order to obtain maximum colour formation.

The maximum absorbance of the molybdenum-thiocyanate complex occurs at 470 mμ. Interference from tungsten is minimised by measuring the absorbance at 500 mμ. Eighteen hours are required for maximum colour development. The colour increases by approximately 10% over that obtained in 2 hours. Solutions can be measured at any time after 2 hours provided the same time interval is used for establishment of the standard curve. The complex obeys Beer's law and has a molar absorptivity of approximately 10,000 at 500 mμ when extracted in the manner described.

Effect of other elements

No interference was obtained from 10 mg of Al, Sb^{III}, As^{III}, Ba, Be, Bi, B, Cd, Ca, Ce^{III}, Ce^{IV}, Cs, Cr^{III}, Cr^{VI}, Co, Cu, Dy, Er, Eu, Gd, Ga, Ge, Au, Hf, Ho, In, Ir, Fe^{II}, Fe^{III}, La, Pb, Li, Lu, Mg, Mn^{II}, Mn^{VII}, Hg^{II}, Nd, Ni, Nb, P (as phosphate), K, Pr, Rb, Sm, Sc, Se, Si, Na, Sr, Ta, Tb, Tl^{I}, Th, Tm, Sn^{II} Sn^{IV}, Ti^{III}, Ti^{IV}, W, U^{VI}, Yb, Y, Zn, or Zr, or 100 mg of F or Br. The effects of the few elements which did interfere at the 10-mg level are shown in Table I.

APPLICATION OF THE METHOD

When 1 g of beryllium oxide containing no detectable amount of molybdenum was "spiked" with 75 μg of this element, complete recovery (within $\pm 4\%$) of the

TABLE I.—EFFECT OF INTERFERING ELEMENTS ON THE
DETERMINATION OF 75 μg OF MOLYBDENUM

Element added	Amount	% Error
I (as iodide)	1 mg	<4
	10 mg	−12.5
	100 mg	−21.7
	100 mg	<4[a]
Te	5 mg	−50
	5 mg	<4[b]
	10 mg	−8[b]
V[V]	5 mg	<4
	10 mg	−8
Re[VII]	100 μg	+82[c]
Pt[IV]	100 μg	+5
	1 mg	+50
Pd[II]	100 μg	<4
	1 mg	+24
Rh[III]	100 μg	<4
	1 mg	+30

[a] Iodide was removed by the addition of 0.4 g of ferric ammonium sulphate, 2 ml of 9M sulphuric acid, a few drops of nitric acid, and boiling.
[b] Solution filtered before extraction.
[c] λ_{max} = 433 mμ.

"spike" was obtained. Results obtained when the method was applied to New Brunswick Laboratory standard samples of beryllium metal and beryllium oxide are shown in Table II.

TABLE II.—ANALYSIS OF NEW BRUNSWICK STANDARDS[a]

Sample No.	Mo found[b], ppm	Average	Nominal value[c]
Be 85	4.6, 5.1	4.8	5
86	25.8, 25.6	25.7	25
87	32.4, 32.4, 32.4	32.4	32
88	52.5, 50.4	51.5	51
BeO 72–1	18.8, 18.7, 18.8, 19.5	18.9	18.0
72–2	7.5, 7.5, 7.9, 7.9	7.7	6.5
72–3	3.9, 3.8, 4.2, 4.2	4.0	2.9
72–4	2.1, 1.9, 2.6, 2.6	2.3	1.8
72–5	0.1, 0.9, 0.9, 0.7	0.7	—

[a] Nominal values for beryllium metal are based on chemical analysis.
[b] Results should be accurate to within 1 ppm. Five-cm cells were used.
[c] Private communication with NBL.[6] Certificate values to be regarded as only tentative.

If there are no synergistic effects, high results are obtained with this procedure only when significant amounts of platinum, palladium, or rhodium, or small amounts of rhenium are present. Spectrographic analysis of all of the New Brunswick standards indicated less than 10 ppm of rhodium or palladium, and less than 20 ppm of platinum. Rhenium was not detected in the beryllium metal samples when these were analysed by the method of Hoffman and Lundell.[5] The rhenium content in each case was

estimated to be less than 2 ppm. It was also found that rhenium is volatilised during the dissolution of beryllium oxide with sulphuric acid. The rhenium content of the beryllium oxide samples is also estimated to be less than 2 ppm.

The method has also been applied to yttrium oxide with the results shown in Table III.

TABLE III.—APPLICATION OF THE METHOD TO YTTRIUM OXIDE

Sample	Mo added, μg	Mo found, μg
1.3 g Y_2O_3	75	75
1.3 g Y_2O_3 + 100 μg each of Zn, Ca, Mg, Sn^{II}, Al, Mn^{II}, V^V, Pb, Ba, Cd, B, Si, Li, K, Be, Dy, Ho, Tb, Yb, Co, Ni, Cr^{VI}, W, Nb, 200 μg Cu, 400 μg Ta, 1 mg Fe^{III}, 5 mg F, 4 mg Ti^{III}, 10 mg Zr	75	79

Zusammenfassung—Eine Methode zur Bestimmung von Molybdän wird beschrieben, basierend auf der Extraktion des Thiocyanat Komplexes mit Methyl-Isobutylketon. Die Methode ist auf ±4% oder 3 Mikrogramm per Gramm genau, abhängig davon was der grössere Wert ist. Genauigkeit und Empfindlichkeit der Methode können gesteigert werden durch geeignete Auswahl von Probenmenge, Extraktionvolum und/oder Zellänge. Von 68 untersuchten Elementen stören nur Rhenium, Platin, Palladium, Rhodium Vanadin und Tellur in Mengen bis zu 10 Milligrammen. Lediglich die durch Rhenium bewirkte Störung ist schwer.

Résumé—Les auteurs décrivent une méthode de dosage du molybdène par extraction du complexe thiocyanate dans la méthylisobutylcétone. La méthode est précise à ±4% près (limite de sensibilité: 3 p.p.m.). On peut augmenter la précision et la sensibilité par un choix approprié de la taille de l'échantillon, du volume du corps extrait, et/ou la longueur de la callule. Parmi les 68 éléments étudiés, seuls le rhénium, le platine, le palladium, le rhodium, le vanadium et le tellure gênent pour des quantités de 10 mg. Parmi ceux-ci, seul le rhénium gêne sérieusement.

REFERENCES

[1] J. O. Hibbits, W. F. Davis, and M. R. Menke, *Talanta* 1960, **4**, 61.
[2] *Ibid.*, 101.
[3] C. Tombu, Société Générale Metallurgique de Hoboken. Private Communication.
[4] C. E. Crouthamel and C. E. Johnson, *Analyt. Chem.* 1954, **26**, 1284.
[5] J. I. Hoffman and G. E. F. Lundell, *J. Res. Nat. Bur. Stand.* 1939, **23**, 497.
[6] C. J. Rodden, Atomic Energy Commission Laboratory, New Brunswick, New Jersey, U.S.A.

SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM IN URANIUM ALLOYS OF THE FISSION ELEMENTS*

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Summary—Alizarin-Red S has been used to determine zirconium spectrophotometrically in uranium alloys of the fission elements. Separation from interferences is effected by co-precipitating the zirconium with barium fluosilicate. Colour stability and improved precision have been realised through changes in the colour development procedure. Alloys containing from 1 to 0·01 % zirconium can be analysed by this method with coefficients of variation from 1.5 to 20.

INTRODUCTION

To re-establish the integrity of the fuel and remove certain undesirable fission elements, portions of the uranium core of the Experimental Breeder Reactor-II will be routinely melted down in oxide crucibles and recast. The process affords little or no separation of the fission elements zirconium to tellurium, and after a number of processing cycles an equilibrium alloy evolves which contains 1% or more of zirconium, molybdenum, and ruthenium, and lesser amounts of niobium, rhodium, and palladium. Since zirconium may impart certain undesirable metallurgical properties to these alloys, it has been necessary to seek process modifications which will afford significant zirconium removal in each process cycle. To make these studies, inactive uranium alloys containing from 0.01% to 1% zirconium, and the amounts of the other fission elements indicated, were used. Zirconium analyses were required which were precise enough to reveal small process-induced concentration changes at the higher level and sensitive enough to indicate within a factor of two or better the concentration at the lower level.

The success which other authors[1-3] had reported with Alizarin-Red S as a colorimetric reagent for zirconium led to its use in this work. The reported precision of replicate determinations was such that small changes in the higher zirconium alloys would be revealed and the sensitivity of the reagent such that sample sizes could be kept within reasonable limits, 0.1 g, even if the zirconium content were 0.01%. Alizarin-Red S (sodium alizarin sulphonate), like most other colorimetric reagents for zirconium, is rather unspecific, and separation from a number of the other alloying constituents had to be made.

Moore's solvent-extraction with TTA (thenoyltrifluoroacetone),[4] a cupferron extraction, an ion-exchange system developed by Krause and Nelson[5] and an extension of Hume's[6] barium fluozirconate precipitation of fission product zirconium were considered as possible separation methods. The TTA extraction was considered to be prohibitively slow for large numbers of samples. The cupferron extraction is not

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particularly selective and additional separations from one or more of the other fission elements would probably have been needed. Furthermore, both TTA and cupferron must be destroyed by wet ashing before the colour development can be carried out. The ion-exchange separation in hydrochloric-hydrofluoric acid mixtures is very straightforward, but reducing the large volume of eluant and freeing it of its fluoride content is not easily effected. Platinum, in the presence of even small amounts of hydrochloric acid, is attacked by perchloric acid, Pyrex and Vycor both contain prohibitive amounts of leachable zirconium. Even commercial quartz-ware contains 2 to 3 ppm zirconium and significant errors are introduced in low-level analyses when the large volumes of $0.5M$ hydrofluoric acid eluant are evaporated.

The precipitation of barium fluozirconate as a means of separating zirconium from other cations has been used by several workers. Hume[6] used it in the determination of fission-product zirconium as a method of purification but made no attempt to make the precipitation quantitative. Telford[7] showed that the precipitation is quantitative at the 100-mg level in separating zirconium from niobium before gravimetric determination. Milner and Barnett[8] found it to be quantitative at the milligram level providing the acidity is $3N$ or less. They also showed that the separation from niobium, tantalum, tungsten, uranium, molybdenum, lead, iron, copper, and tin was adequate for the titrimetric determination of zirconium with EDTA. In eliminating the yield determination in Hume's fission-product method the authors of this paper[9] had also shown that the precipitation was quantitative at the milligram level.

By co-precipitating barium fluozirconate with barium fluosilicate, satisfactory separation is made from the other fission elements and from the bulk of the uranium. The fluoride in the precipitate is removed by perchloric acid fuming; colour development can be carried out on an aqueous dilution without further manipulation.

A marked improvement in colour stability has been realised through changes in the method of acidity adjustment before colour development.

EXPERIMENTAL

Separations

Zirconium which had been tagged with [95]zirconium (65 d) was used to monitor the separation studies reported in this work. The daughter activity, [95]niobium, (35 d), was removed by extracting it into methyl *iso*butyl ketone from $8M$ hydrochloric acid. After three equal-volume extractions, less than 0.1% of the niobium remains in the aqueous phase while the zirconium loss is less than 20%. A well-type scintillation counter was used to assay the zirconium activity. Both precipitates and supernates were counted.

For uranium alloys of the fission elements which contain 0.5% or more zirconium, the precipitation of barium fluozirconate affords a satisfactory separation from interferences. In the absence of uranium and the other fission elements as little as 70 μg of zirconium can be quantitatively precipitated from 5 ml of solution. High fluoride and barium concentrations, $5M$ and $0.1M$, and low nitric acid concentration, $0.5N$ are essential for minimising the solubility of the salt. The effect of acidity on the precipitation of barium fluozirconate is shown in Table I. The nitric acid concentration selected for use is $0.5N$; this is low enough to insure the quantitative precipitation of the zirconium but high enough to prevent the precipitation of barium fluoride.

Unfortunately, uranium has a solubilising effect on the fluozirconate precipitate and complete zirconium recovery cannot be obtained when the uranium to zirconium weight-ratio is greater than 200. However, by co-precipitating barium fluozirconate with barium fluosilicate, zirconium can be quantitatively precipitated from solution even at the tracer level (Table II). Barium fluosilicate is not a particularly insoluble salt (the handbook value is 26 mg per 100 ml of water), but quantitative precipitation is apparently not a requisite for quantitative carrying of the zirconium. When separating the zirconium from larger volumes of solution, the standard addition of 6 mg of fluosilicic acid

TABLE I.—EFFECT OF NITRIC ACID CONCENTRATION ON THE PRECIPITATION OF FLUOZIRCONATE

Monitored with ^{95}Zr Activity

Vol = 3 ml	$Ba(NO_3)_2 = 0.1N$
^{95}Zr = 10^4 cpm	HF = 5N

Zirconium taken, μg	Nitric acid, N	Zirconium recovered, %
70	0.5	101
140		100
70	1.0	100
140		99
70	2.0	94
140		100
70	3.0	53
140		89

often does not initiate precipitation, and a further addition of fluosilicic acid produces only a relatively small amount. To repress the solubility the same conditions which minimise the solubility of barium fluozirconate, high fluoride and barium concentrations and low acidity are used. The precipitation is not easily initiated, particularly at room temperature, but vigorous stirring and heating will usually overcome this difficulty.

That zirconium in the amounts given in Table II is determinable with Alizarin-Red S after co-precipitation with barium fluosilicate is demonstrated by the results in Table III.

TABLE II.—CO-PRECIPITATION OF BARIUM FLUOZIRCONATE WITH BARIUM FLUOSILICATE

Monitored with ^{95}Zr Activity

Vol = 3 ml	H_2SiF_6 = 4 mg
^{95}Zr = 10^4 cpm	$Ba(NO_3)_2 = 0.1M$
HF = 5M	$HNO_3 = 0.5M$

Zirconium taken, μg	^{95}Zr recovered, %
Tracer	98
1	99
10	101
20	99
30	99
50	101
75	102
100	98

The effectiveness of the barium fluozirconate fluosilicate precipitation in separating zirconium from each of the other fission elements and uranium in the alloys is shown in Table IV. At the highest uranium : zirconium ratios, 10^4 : 1, the amount of uranium must be limited to about 150 mg to secure quantitative precipitation of the zirconium. Although the co-precipitation of uranyl fluoride is considerable at the 100-mg level, it does not constitute an interference since it neither reacts with the Alizarin-Red S nor absorbs at the zirconium-Alizarin-Red S wave length.

At ruthenium : zirconium and rhodium : zirconium ratios of 50 and more, some co-precipitation of these elements with barium fluorosilicate may also occur. For a particular sample this behaviour is reproducible, but for other samples, although very similar, the amount of co-precipitation may

TABLE III. DETERMINATION OF ZIRCONIUM WITH ALIZARIN-RED S
AFTER CO-PRECIPITATION WITH BARIUM FLUOSILICATE

Vol = 3 ml, HF = 5M, H$_2$SiF$_6$ = 4 mg, Ba(NO$_3$)$_2$ = 0.1M, HNO$_3$ = 0.5M

Zirconium taken,	Absorbance*	
μg	Direct	After pptn.
9.1	0.036	0.038
23.0	0.105	0.110
29.4	0.144	0.146
45.2	0.220	0.226

* 2-cm cells.

vary considerably. When it does occur it is always indicated by coloration, usually rose, of the precipitate. The ruthenium offers no problem as it is fumed off as the tetroxide in the subsequent perchloric acid fuming, but the rhodium interferes by absorbing at the wave length used for zirconium.

Colour development and stability

The perchloric acid fuming which is used to convert from the fluoride medium used for precipitation to one which is anionically satisfactory for colour development results in a 70% perchloric acid solution of unknown volume. Since the acidity at which the absorbance measurement is made must be controlled to ±5% and be in the range of 0.5N to 1.0N, practice has been to make the acidity adjustment by either fuming the sample to incipient dryness or by neutralising the diluted acid with alkali. The latter has been done by either adding alkali until the pH to be used in the colour development has been reached. or by a complete neutralisation and then adding a fixed amount of standard acid.

Each of these methods of acidity adjustment can easily result in irreversible zirconium hydrolysis. In fuming zirconium to incipient dryness, there is always grave danger that localised overheating will prevent some of the zirconium from redissolving in dilute acid. Zirconium which has been

TABLE IV. SEPARATION OF ZIRCONIUM FROM OTHER
FISSION ELEMENTS AND URANIUM BY THE BARIUM
FLUOZIRCONATE-FLUOSILICATE PRECIPITATION

2-cm cells

Interference	Foreign ion to zirconium weight ratio	Zirconium, μg	
		Taken	Found
None	—	61	61
Mo^{VI}	300	61	61
Ru^{III-IV} [a]	260	61	60
Rh^{III}	10	61	61
Pd^{II}	35	61	62
Nb^{V}	10	61	61
Ce^{III}	150	61	62
U^{VI}	1 × 10^{2}	61	61
	1 × 10^4 (600 mg)	61	15[b]
	1 × 10^4 (150 mg)	15	15[b]

[a] Removed in part by the HClO$_4$ fuming step.
[b] At uranium : zirconium weight ratios of 10^4, complete zirconium recovery can be realised only at the 150-milligram uranium level.

fumed to complete dryness cannot be resolubilised without treating the samples with fluoride and
re-fuming. Partial neutralisation of the acid with alkali will result in some zirconium hydrolysis
because of localised alkaline conditions no matter how carefully it is done, and complete neutralisation
and re-acidification will result in even more extensive hydrolysis.

By fuming the sample to about 1 ml of perchloric acid in a tared crucible and adding 70% acid
until there is a standard weight of acid in the crucible, the subsequent dilution to volume can be
made without danger of hydrolysis. (In this work, 2.30 g of perchloric acid were used. Diluted to
25 ml this gives an acidity of 0.60N.) That there is far less hydrolysis of zirconium when the acid
adjustment is made in this manner is shown by the colour stability of the Alizarin-Red S complex.
In contrast to colour stabilities of a few hours to a day reported by other authors[1-8] no decrease in
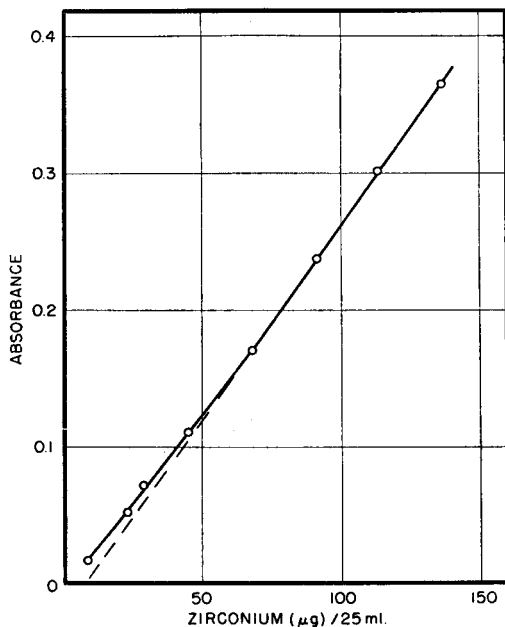
FIG. 1.   The absorbance of zirconium alizarin sulphonate vs micrograms of zirconium.

colour intensity was noted in a group of samples measured every day for more than a week. In the
routine application of the method several days often elapse between the final dilution to volume and
the absorbance measurement with no effect on the colour. Since colour development is rather slow,
the samples are allowed to stand over-night before the absorbances are measured.

Deviations from Beer's law

A plot of absorbance vs. concentration in the concentration range 0 to 150 $\mu g/25$ ml is shown in
Fig. 1. The dashed line, an extension of the linear portion of the curve above 75 μg, has been drawn
to help to emphasise the negative deviation from Beer's Law below 75 μg.

Reagents

Standard zirconium solution: dissolve 18 g of hafnium-free zirconium tetrachloride in 1 litre
of 3M hydrochloric acid. Standardise by precipitation with cupferron and ignition to the oxide.
Working dilutions, containing about 0.5 mg/ml, are prepared by making dilutions in 1M perchloric
acid.

Alizarin-Red S: 0.2%, in 0.1M perchloric acid	*Ammonium hydroxide*: 15M
Perchloric acid: 70%	*Nitric acid*: 16M
Fluosilicic acid: 0.2M	*Barium nitrate*: saturated

Equipment

Quartz crucibles must be used for fuming samples which contain fluoride as both Pyrex and Vycor contain appreciable amounts of zirconium. The quartz used in this work was found to contain 2 to 3 ppm zirconium. However, the fluoride content of the fluozirconate-fluosilicate precipitate is relatively low and detectable amounts of zirconium are not solubilised.

A Beckman Model B spectrophotometer was used for this work. The sensitivity was "3", and the shutter was in the open position.

Standard curve

Pipette duplicate aliquots of the working standard containing 25, 50, 75, 100, 150, 200, and 300 μg of zirconium into 25-ml volumetric flasks. Add 15 ml of water and 1.30 ml of 70% perchloric acid. Add 1.0 ml of the Alizarin-Red S reagent and dilute to volume with water. Measure the absorbance after 18 hours against a reagent blank at 520 mμ. Use 2-cm cells for those samples containing 75 μg or less.

Procedure for alloys

Dissolve the sample in a quartz flask using the special hydrochloric-nitric-hydrofluoric acid mixture and procedure described by Larsen[10]. Dilute to a known volume and pipette an aliquot of the sample containing 70–300 μg of zirconium into a 10-ml Lusteroid centrifuge tube. Dilute to 3 ml with water. Neutralise by the dropwise addition of 15N ammonium hydroxide until ammonium diuranate precipitates (yellow). Dissolve the precipitate by the dropwise addition of 16N nitric acid. Add 0.5 ml of 16N nitric acid, 1.0 ml of 27N hydrofluoric acid, (polyethylene pipettes), and four drops of 0.2M fluosilicic acid. Stir. Heat in a water bath (90° to 100°) for 1 minute. Add 1.5 ml of saturated barium nitrate solution and stir (the stirring rod must be platinum, quartz or polyethylene) until the barium fluosilicate precipitate begins to form (avoid excessive stirring). Continue heating for 1 minute. Centrifuge for 3 minutes. Remove the supernate by suction. Slurry the precipitate in 2 ml of water and transfer with two 1-ml water washes to a quartz crucible. Add 1 ml of 70% perchloric acid and evaporate to dryness. Tare the crucible to the nearest 0.01 g. Add 3 drops of 3N hydrofluoric acid, 1 ml of water and 2ml of 70% perchloric acid, and heat to fumes of perchloric acid. Re-fume twice after cooling and adding 1 ml of water. (The removal of fluoride by repeated water addition and fuming is superior to a single prolonged fuming.) When there is less than 2.3 g of perchloric acid in the crucible, cool, tare, and add 70% perchloric acid until the crucible contains 2.30 g of acid. Add 5 ml of water and warm gently on a hot plate. Transfer the solution with 10 to 15 ml of water to a 25-ml volumetric flask. Add 1.0 ml of the Alizarin-Red S reagent and dilute to volume with water. After 18 hours measure the absorbance of the sample against a reagent blank in 1-cm cells at 520 mμ.

RESULTS AND DISCUSSION

The reliability of the method was ascertained through the analysis of synthetic uranium solutions which contain percentage amounts of molybdenum, ruthenium, rhodium, and palladium and varying amounts of zirconium. The results are shown in Table V. In the range 0.3–1% the 2% coefficient of variation demonstrates that

TABLE V. ZIRCONIUM DETERMINATION IN SIMULATED ALLOY SOLUTIONS

Nominal alloy composition, % U, 95: Mo, 2.5: Ru, 1.5: Rh, 0.5: Pd, 0.3

Zirconium, %	Coeff. of variation.	Bias	Recovered activity, %	Number of Determinations
1.0	1.5	0	100	20
0.3	2	0	100	20
0.1	5	−1	99	5
0.03	11	+8	96	7
0.01	20	+10	94	6

the method will adequately reveal small changes in alloy composition; at 0.01% zirconium the accuracy and precision will adequately reveal changes in alloy composition within a factor of 2. The positive bias in the results at the lower zirconium concentrations is undoubtedly due to rhodium which is not completely separated.

Zusammenfassung—Alizarin S wurde zur spektrophotometrischen Bestimmung von Zirkonium in Uranlegierungen der Kernspaltelemente verwendet. Abtrennung von Störelementen wurde durch Mitfällung des Zirkonium mit Bariumfluosilikat erreicht. Verbesserung des Farbstabilität sowie der Reproduzierbarkeit der Methode wurden durch Änderungen in der Farbentwicklung erzielt. Legierungen mit 1–0.01% Zirkonium wurden analysiert.

Résumé—On a utilisé le rouge d'alizarine S pour doser par spectrophotométrie le zirconium dans les alliages d'uranium avec les éléments de fission. Le zirconium est séparé par coprécipitation avec le fluosilicate de barium. Une coloration stable et une meilleure précision ont été obtenues en modifiant le procédé de développement de la couleur. Des alliages contenant de 1 à 0,01 pour cent de zirconium peuvent etre analysés par cette méthode avec des coefficients de variation de 1,5 à 20.

REFERENCES

[1] H. G. King and W. H. Owens, U.S. Atomic Energy Comm. Report Y-917, October 1952.
[2] D. L. Manning and J. C. White, *Analyt. Chem.*, 1955, **27**, 1389.
[3] L. Silverman and D. W. Hawley, *ibid.*, 1956, **28**, 806.
[4] F. L. Moore, *ibid.*, 997.
[5] K. A. Krause and F. Nelson, Symposium on *Ion Exchange and Chromatography in Analytical Chemistry* ASTM Spec. Pub. No. 195 (1956).
[6] D. Hume, U.S. Atomic Energy Comm. Report CN-1312, 1945: see C. D. Coryell and N. Sugarman, *Radiochemical Studies of the Fission Products*, McGraw-Hill, New York, 1951, p. 1499.
[7] R. E. Telford, U.S. Atomic Energy Comm. Report MUC-J. W-686, 1945: see C. J. Rodden *Analytical Chemistry of the Manhattan Project*, McGraw-Hill, New York, 1950, p. 477.
[8] G. W. C. Milner and G. A. Barnett, *Analyt. Chim. Acta*, 1956, **14**, 414.
[9] R. P. Larsen and L. E. Ross, U.S. Atomic Energy Comm. Report ANL-5388, October, 1954, p. 84.
[10] R. P. Larsen, *Analyt. Chem.*, 1959, **31**, 545.

THE MINIMUM IGNITION TEMPERATURE OF ALUMINIUM OXIDE PRECIPITATES

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Summary—Although other workers have shown by thermogravimetric analysis of aluminium oxide precipitates that constant weight can sometimes be reached at temperatures below 700°, the results of the present investigation indicate that, at least where conventional ignition and weighing techniques are used, the safe minimum temperature for the ignition of aluminium oxide to constant weight is 1200°.

It is common practice among analytical chemists to use a temperature of about 1200° for the ignition of either hydrated aluminium oxide or basic aluminium salts to aluminium oxide[1]. Willard and Tang[2] also recommend this temperature for the ignition of basic aluminium sulphate or basic aluminium succinate precipitates obtained by the urea method. Duval[3] states that 611° is the minimum temperature required in the thermogravimetric ignition of basic aluminium succinate obtained by urea hydrolysis. Although Duval also states that 672° is the minimum temperature for aluminium precipitated with urea, it is not clear if it is basic aluminium sulphate which was ignited; Duval refers to the "urea/succinate" method in the one case but only to the "urea", *i.e.* not the "urea/sulphate", method in the other case. For aluminium precipitated with ammonium hydroxide in the presence of ammonium chloride, he recommends a minimum thermogravimetric temperature of 1031°. Duval quite correctly indicates that higher temperatures are often necessitated by ordinary ignition methods because crucibles must be cooled before weighing and this can expose the precipitate to atmospheric water vapour or other substances which may be absorbed by it.

This investigation was undertaken to determine whether ignition temperatures lower than those usually recommended can be used in the conventional ignition of aluminium oxide precipitates.

EXPERIMENTAL RESULTS

(a) *Conventional ignition*

Four solutions of aluminium chloride, each containing the equivalent of 0.2 g of Al_2O_3, were diluted to 400 ml; these solutions were at pH 2 to 3. A few drops of methyl red indicator and 5 g of ammonium chloride were added to each solution. The subsequent treatment of each solution was as follows:

Method A: Two g of potassium sulphate and 5 g of urea were added. The solution was heated to boiling. After precipitation began, in about 30 minutes, boiling was continued for about $1\frac{1}{2}$ hours more.

Method B: Five g of succinic acid and 5 g of urea were added and precipitation carried out as with solution *A*.

Method C: Five g of urea were added and precipitation carried out as in the previous cases. Though this is not a procedure recommended by Willard and Tang, because it precipitates aluminium in a gelatinous form, hydrous aluminium oxide was thus precipitated and ignited because of the uncertainty, previously stated, as to whether Duval used sulphate in his "urea" method.

Method D: Ammonium hydroxide (1 : 1) was added dropwise to the boiling solution until the indicator changed colour. Then, one additional drop of the hydroxide was added and the solution boiled for 1 minute more.

In all four cases, the precipitates were filtered on paper and washed with 1 % ammonium nitrate solution. The filter papers and precipitates were charred and allowed to ignite at 500° for 8 hours. The resulting residues were then further ignited in tared platinum crucibles for 1-hour periods at 650°, 800°, 950°, 1100°, and 1200°. After each ignition period, before being ignited at the next higher temperature, the covered crucibles were cooled in air for a minute, transferred to a desiccator containing phosphorus pentoxide, and weighed rapidly after 10 minutes. The final ignition at 1200° was repeated for a second hour. The results of this series of experiments are shown in Table I.

TABLE I.—EFFECT OF IGNITION TEMPERATURE ON THE WEIGHTS OF ALUMINIUM OXIDE PRECIPITATES OBTAINED BY DIFFERENT METHODS

Temperature[a]	Per cent excess weight over final reference value			
	Method A (urea-basic sulphate method)	Method B (urea-basic succinate method)	Method C (urea method)[b]	Method D (ammonium hydroxide method)
°C	%	%	%	%
650	19.2	3.9	3.1	4.5
800	9.8	2.3	1.7	2.4
950	3.4	1.0	1.0	1.2
1100	0.6	0.0	0.0	0.2
1200	0.2	0.0	0.0	0.1
1200 (2nd hour)	Ref. value	Ref. value	Ref. value	Ref. value

[a] After charring of the filter paper, the precipitates were ignited at 500° for 8 hours before being ignited for 1 hour at each of the stated temperatures.

[b] Chloride, but not sulphate or succinate, was present.

Each of the four experiments described above was performed in duplicate on two separate occasions so that four values were obtained for each. These results were averaged to obtain the values reported in the table. Agreement between the replicates was quite good, thus indicating the negligible effects of weighing errors and possible variations of muffle temperatures.

In order to reduce exposure of the precipitates to the atmosphere to a minimum, and thus approximate more closely the conditions encountered in a thermogravimetric ignition, the experiments described for Method *B* and Method *C* were repeated (each in duplicate) with slight modification. After the filter papers were burned off, overnight at 525° this time, ignitions were carried out as before. However, after each incremental ignition, one set of precipitates from *B* and *C* was transferred, red-hot and covered, to a desiccator containing phosphorus pentoxide and allowed to cool before weighing. Because the weight was known to within a few milligrams, the time of weighing and hence exposure to the atmosphere was very short. The other set of precipitates from *B* and *C* was allowed to cool for 3 minutes in the atmosphere before being placed in the desiccator. The results of these experiments are shown in Table II.

(b) *Ignition in a thermobalance*

Precipitates were prepared by Methods *A*, *B*, and *C* as previously described. Filter papers and precipitates were charred and ignited overnight at 525°. Then the precipitates were placed in a

quartz-fibre thermobalance and heated from room temperature to about 600° in 45 minutes, while a stream of dry air was passed over the sample. The weight and temperature at this point were taken as base values; the temperature was then raised by nominal 50-degree increments every 50 minutes, the exact temperature being measured with a thermocouple. Because constant temperature was reached in every case in about 10 minutes, the alumina was thus held at each temperature value for 40 minutes
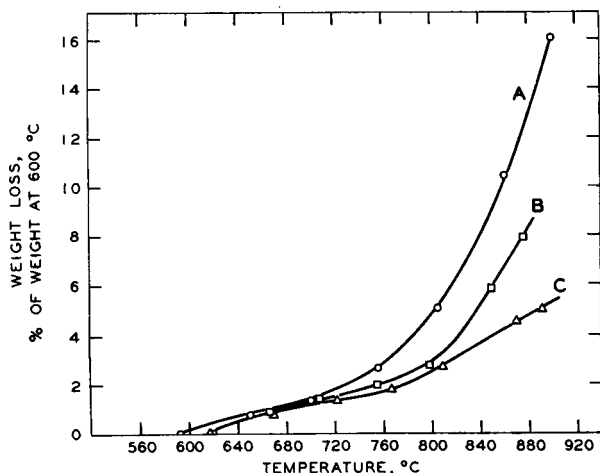
FIG. 1.—Ignition of aluminas after preliminary charring.

before being heated to a higher value. The percentage cumulative weight loss at each temperature level was calculated using as a base value the weight at the initial temperature, nominally 600°. The results for the three precipitates are plotted in Figure 1. All weights are uncorrected for buoyancy in air.

TABLE II.—EFFECT OF ATMOSPHERIC EXPOSURE ON WEIGHT OF IGNITED
ALUMINIUM OXIDE PRECIPITATES

| | Per cent excess weight over final reference value | | | |
| Temperature | Precipitate placed in desiccator immediately upon removal from furnace | | Precipitate placed in desiccator after 3-minute cooling in atmosphere | |
	Method B (urea-basic succinate method)	Method C (urea method)[a]	Method B (urea-basic succinate method)	Method C (urea method)[a]
°C	%	%	%	%
650	2.4	2.5	3.1	2.8
800	1.8	1.9	2.4	2.6
950	1.6	1.6	1.9	2.2
1100	0.3	0.4	0.4	0.5
1200	Ref. value	Ref. value	Ref. value	Ref. value

[a] Chloride, but not sulphate or succinate, was present.

In a final experiment, a precipitate obtained by Method A was thoroughly air-dried, transferred to the thermobalance, heated rapidly to about 600°, and then heated in 50-degree increments as before. Percentage weight losses were calculated using the initial, i.e. the air-dried, value as a base. The results are plotted in Figure 2.
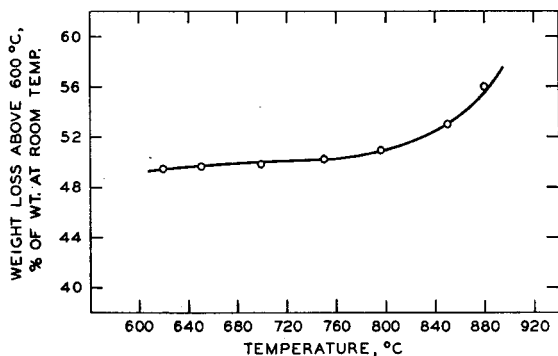
FIG. 2.—Ignition of basic aluminium sulphate.

DISCUSSION

The results in both Table I and Table II show quite clearly that the minimum *conventional* ignition requirement for several of the aluminium oxide precipitates is 1 hour at 1100° (following charring of the paper). Where sulphate is present, as in the basic sulphate method, an even higher temperature is indicated.

Although some of the results in Table II were obtained in a way tending to minimise the effect of atmospheric contamination upon the precipitates, they do not afford unequivocal proof that higher ignition temperatures are mandatory, in contrast to Duval's recommendation of lower values. This proof is given finally by the results obtained with the thermobalance as is shown by the plots of Fig. 1 and 2. The figures show a continuing weight loss up to 900° (the limit of the thermobalance). It is interesting to note in Fig. 2 that the weight of the precipitate is relatively constant between 620° and 760° and upon further heating begins to lose weight again. Although the discontinuously rising temperature did not duplicate exactly the dynamic conditions used by Duval, it is nevertheless concluded that Duval's recommendations for minimum ignition temperatures below 700° must be used with great caution.

This conclusion is supported by the work of Erdey and Paulik[4], who repeated Duval's dynamic thermogravimetry on aluminas precipitated by various reagents. Their thermograms differed from those obtained by Duval. From their experiments they concluded that only precipitates that are formed with the hydrargillite crystal structure can be converted to water-free alumina at relatively low temperature. The internal structure of the precipitate, in turn, is primarily determined by the conditions of precipitation (such as rate, temperature, concentration), and influenced to only a small extent by the nature of the precipitating agent.

They attribute the lower ignition temperatures reported by Duval not to the reagents used but to differences in the physical conditions of precipitation, which produced, for Duval, precipitates with an internal structure similar to that of hydrargillite. They imply that such conditions might be difficult to reproduce, because they had noted in their work that the compositions and structures were not exactly the same even for preparations precipitated in parallel with each other under ostensibly the same conditions. Even small variations have a marked effect upon the structure and hence upon the ignition temperature.

Other workers[5,6] have also shown the importance of precipitation conditions in determining the thermal stability of precipitated aluminas. Imelik and co-workers[5]

showed, for example, that it is possible to obtain constant weight at a low temperature without completely eliminating water. Wiele[7] has found that with aluminas precipitated by ammonia or thiosulphate ignition at 1200° it is necessary to remove water completely, and that even after ignition at this temperature, the precipitate is still hygroscopic and should be weighed rapidly.

In view of the authors' results and evidence presented by other investigators, it is recommended that a minimum ignition temperature of 1200° should be used for aluminium oxide precipitates which are to be ignited and weighed by conventional techniques, and that such precipitates be weighed as rapidly as possible.

Zusammenfassung—Wenngleich andere Autoren auf Grund thermogravimetrischer Untersuchungen gezeigt haben, dass es möglich ist für Aluminiumoxyd-Niederschläge konstantes Gewicht bei Temperaturen unter 700°C zu erreichen, muss auf Grund der vorliegenden Untersuchungen gefolgert werden, dass zumindest bei Anwendung konventioneller Glüh- und Wägeverfahren die sichere Mindesttemperatur zum Konstantglühen von Aluminiumoxyd 1200°C ist.

Résumé—Bien que d'autres auteurs aient montré par analyse thermogravimétrique de précipités d'oxyde d'aluminium, que l'on peut parfois atteindre un poids constant à des températures inférieures à 700°, les résultats de la présente étude indiquent que, tout au moins pour les techniques courantes de calcination et de pesée, une température minimum de 1200° est nécessaire pour la calcination à poids constant de l'oxyde d'aluminium.

REFERENCES

[1] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, *Applied Inorganic Analysis*, 2nd edition, New York, John Wiley and Sons, Inc., 1953, pp. 500–505.
[2] H. H. Willard and N. K. Tang, *Ind. Eng. Chem. Analyt.*, 1937, **9**, 357.
[3] C. Duval, *Inorganic Thermogravimetric Analysis*, Amsterdam, Elsevier Publishing Company, 1953, pp. 105–116.
[4] L. Erdey and F. Paulik, *Acta Chim. Acad. Sci. Hung.*, 1955, **7**, 45.
[5] B. Imelik, M. V. Mathieu, M. Prettre, and S. Teichner, *J. Chim. Phys.*, 1954, **51**, 651.
[6] J. H. Lewis and C. A. Taylor, *J. Appl. Chem.*, 1958, **8**, 223.
[7] H. Wiele, *Analyt. Chim. Acta.* 1956, **15**, 326.

DETERMINATION OF THE ACTUAL CONTENT OF ACID CHLORIDE IN THE CHLORIDES OF CARBOXYLIC ACIDS

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Summary—A new method has been evolved for the determination of the actual contents of acid chloride, and of the amounts of free hydrochloric acid and free carboxylic acid resulting from decomposition, in carboxylic acid chlorides. The sample to be analysed is treated with anhydrous ethanol. The acid chloride reacts with ethanol to form an ester. The volume of standard alkali consumed in saponifying this ester indicates the actual content of acid chloride in the sample.

THE chlorides of carboxylic acids are materials of great fundamental importance in preparative organic chemistry, in analytical chemistry and in industrial organic chemistry.

Most of them are extremely labile, due to their strong acylating activity. They decompose partially by the action of atmospheric moisture, yielding the corresponding carboxylic acid and hydrochloric acid. Therefore samples of carboxylic acid chlorides almost always contain some free carboxylic acid and hydrochloric acid, in addition to their actual content of carboxylic acid chloride. Few authors[6,7] have dealt with the analysis of these compounds. One of the most used methods for the evaluation of carboxylic acid chlorides, that suggested by Siggia and Stahl[4], is rather cumbersome and often difficult to apply.

In certain work we required to evaluate palmityl chloride, a substance used in the pharmaceutical industry. As no suitable method was found in the literature available to us, a new procedure had to be worked out.

In essence, the method may be summarised as follows. Palmityl chloride was treated with anhydrous ethanol, producing ethyl palmitate and hydrochloric acid through the acylating action of palmityl chloride. Free palmitic acid present in the sample as a product of previous decomposition did not react with ethanol. The total content of hydrochloric acid in the ethanolic solution (hydrochloric acid formed during ester formation plus hydrochloric acid formed as a result of earlier decomposition) can be titrated with a standard solution of alkali using methyl red as indicator. (The pH of an ethanolic solution of palmitic acid is the same as for the colour change of methyl red.) Subsequently, titration with alkali is continued in the presence of phenolphthalein as indicator. This latter procedure indicates the free palmitic acid content of the sample. Under the experimental conditions chosen, the ester does not react with alkali. The ethanolic solution contains ester in an amount equivalent to the acid chloride content of the sample, and this ester can be hydrolysed in hot solution by treatment with excess alkali. The acid chloride content of the sample can then be calculated from the quantity of alkali required for saponifying the ester.

Carboxylic acids with fewer carbon atoms than palmitic acid are stronger acids, and their ethanolic solution shows an acid reaction with respect to methyl red. The content of free carboxylic acid and hydrochloric acid formed during decomposition in samples of the chlorides of these acids cannot be determined by this acidimetric method using two indicators. On titrating with alkali in the presence of methyl red, a portion of free organic acid will be neutralised in addition to hydrochloric acid. The complete analysis of acid chlorides of this type is carried out by titrating the hydrochloric acid liberated during formation of ester, together with the hydrochloric acid and organic acid ultimately present due to decomposition, with standard alkali hydroxide solution using phenolphthalein as indicator. Then the titrated solution is treated with excess alkali and the quantity of alkali required for the saponification of ester equivalent to the actual content of acid chloride is determined, by titration with standard sulphuric acid solution. Finally the amount of hydrochloric acid liberated during ester formation and that of hydrochloric acid due to decomposition are determined by a Volhard argentometric titration. From the results (content of total acid, actual content of acid chloride and content of chloride) not only the actual acid chloride content but also the quantity of free carboxylic acid and hydrochloric acid due to decomposition can be calculated.

In some exceptional cases, acid chlorides may contain impurities, resulting from improper storage, which can be acylated (e.g. phenols, alcohols etc.). These contaminants will obviously be present in the acid chloride in the form of esters. In the present method, esters will raise the apparent content of acid chloride. However, as these esters produce no acid on reaction of the acid chloride with ethanol, their presence is evident on taking into account the quantity of free hydrochloric acid developed during ester formation and that of alkali required for the saponification of the ester. In the presence of contaminating esters, more alkali is consumed in the saponification than corresponds to the quantity of hydrochloric acid liberated during the reaction of acid chloride with ethanol. In the case of samples of undecomposed chlorides of carboxylic acids, both these values are obviously identical. However, in practice the chlorides of carboxylic acids always contain some free hydrochloric acid and carboxylic acid, due to decomposition. Thus, in general, more alkali is needed to neutralise the hydrochloric acid content of the reaction mixture of acid chloride and ethanol, than is required for the saponification of the ester.

In the course of evolving this method, the conditions for ester formation in the reaction of palmityl chloride (and other carboxylic chlorides) with ethanol were investigated. It was found that on dissolving palmityl chloride and acetyl chloride in anhydrous ethanol ($0\cdot05$–$0\cdot20$ g chloride in 20 ml of ethanol), conversion to ester was complete in 10 minutes at room temperature. With benzoyl chloride or chloro-acetyl chloride, ethanol was more slowly acylated. To facilitate ester formation, the ethanolic solution was heated with the latter acid chlorides for 5 min in a hot-water bath. Contrary to reports in the literature, no special acid-binding substance (such as e.g. pyridine) is needed in an ethanolic solution to ensure quantitative ester formation. Acid (protons) liberated during ester formation is bound by the solvent molecule and alcoholium ion is formed.

In addition the conditions of hydrolysis of ethyl palmitate, acetate, chloroacetate and benzoate were investigated. It was found that a $0\cdot1N$ solution of alkali does not react with these esters when the free acid developed during ester formation

(plus the original acid content of the sample) are titrated in the presence of phenol-phthalein as indicator at 0° (in melting ice). The colour of a solution overtitrated with one drop of $0.1N$ alkali does not change for some minutes. (The only exception is with ethyl chloroacetate, which decomposes somewhat more readily. On determining this compound, the colour of a solution titrated to pink in the presence of phenolphthalein faded in about a minute.) Further, it was found that the esters mentioned above can be saponified quantitatively in an hour when treated on a hot-water bath with at least 40–50% excess of alkali. In the case of palmityl chloride care must be taken to maintain in the reaction mixture during hydrolysis an ethanol content sufficient to keep the undecomposed ester in solution.

EXPERIMENTAL

Reagents (analytical grade)

Anhydrous ethanol: 100·0%, dehydrated by metallic calcium according to Winkler.[5]
Sodium hydroxide: $0.1N$ solution.
Hydrochloric acid: $0.1N$ (or sulphuric acid) solution.
Silver nitrate: $0.1N$ solution.
Ammonium thiocyanate: $0.1N$ solution.
Methyl red indicator.
Phenolphthalein indicator.
Ferric nitrate indicator: 10% solution of ferric nitrate in 10% nitric acid.

Determination of the content of hydrochloric acid and of free carboxylic acid

About 20 ml of anhydrous ethanol are poured into a 100-ml Erlenmyer flask with a ground-glass stopper, which has been carefully dried or repeatedly rinsed with anhydrous ethanol. After drying the ground joint thoroughly, the flask is weighed on an analytical balance, and a sample of carboxylic acid chloride equivalent to about 6–12 ml of $0.1N$ sodium hydroxide solution is weighed into the flask with analytical accuracy. A glass funnel, with a small piece of cotton wool, to serve as a reflux condenser, is then placed in the mouth of the flask. The reaction mixture is heated for 5 min on a hot-water bath, and is then cooled in melting ice. In the case of acetyl chloride and palmityl chloride, ester formation is completed even at room temperature in 10 min.

In the case of palmityl or stearyl chloride, the quantity of hydrochloric acid liberated during ester formation, together with the final free hydrochloric acid content of the sample, are established by titration with $0.1N$ sodium hydroxide in the presence of two drops of methyl red as indicator. Then 5 drops of phenolphthalein indicator are added and the free carboxylic acid content of the sample is measured by further titration with the standard solution of sodium hydroxide. When analysing acid chlorides of strong acids, the hydrochloric acid liberated during ester formation together with the content of initial free hydrochloric acid and free carboxylic acid after the reaction with anhydrous ethanol, are titrated with $0.1N$ sodium hydroxide in the presence of 5 drops of phenolphthalein indicator. When not only the determination of the actual content of acid chloride but a complete analysis is needed, the excess of alkali is back-titrated with standard sulphuric acid solution. Then chloride is precipitated with an excess of $0.1N$ silver nitrate solution, about 1 g of potassium nitrate is added to the reaction mixture, which is boiled to complete coagulation and excess silver nitrate is titrated with $0.1N$ ammonium or potassium thiocyanate, using 1 ml of ferric nitrate solution as indicator.

Determination of the actual content of acid chloride in the sample

About 1·5–2·0 times as much $0.1N$ sodium hydroxide as was used in the previous titration is added with analytical accuracy to the solution which has already been titrated with sodium hydroxide using phenolphthalein as indicator. If the reaction mixture becomes turbid on adding alkali, 96% ethanol is added until the liquid clears. The flask is then heated on the hot-water bath for about an hour and excess alkali is back-titrated with $0.1N$ hydrochloric or sulphuric acid until the pink colour of phenolphthalein completely disappears. The quantity of $0.1N$ sodium hydroxide required for saponifying the ester is a measure of the actual content of acid chloride.

CALCULATION OF THE RESULTS

The actual composition of the sample is expressed by the formulae

$$\text{Percentage of acid chloride} = \frac{100[\{C - (B + D)\}M]}{A}$$

$$\text{Content of free HCl of sample, } \% = \frac{100[E - \{C - (B + D)\} \, 3 \cdot 646]}{A}$$

$$\text{Content of free carboxylic acid of sample, } \% = \frac{100\{(B - E)Mc\}}{A}$$

where A is the weight of sample, B the volume of $0 \cdot 1 N$ alkali consumed in the presence of phenolphthalein, C the total volume of $0 \cdot 1 N$ alkali consumed, D the volume of $0 \cdot 1 N$ acid consumed when back-titrating the excess alkali, E the volume of $0 \cdot 1 N$ silver nitrate consumed when titrating the chloride content in A mg of sample (in the case of palmityl chloride E refers to $0 \cdot 1 N$ alkali), and M is $1/10$ of the milligram-molecular weight of the acid chloride analysed (i.e. $27 \cdot 487$ for palmityl chloride, $7 \cdot 850$ for acetyl chloride, $11 \cdot 295$ for chloroacetyl chloride, and $14 \cdot 057$ for benzoyl chloride), Mc is $1/10$ of the milligram-molecular weight of the carboxylic acid analysed (i.e. $25 \cdot 64$ for palmitic acid, $6 \cdot 005$ for acetic acid, $9 \cdot 45$ for chloroacetic acid and $12 \cdot 213$ for benzoic acid). Of these values, A is expressed in milligrams whilst B-E are expressed in ml. When $E < C - (B + D)$, the sample contains ester contaminants.

Control tests

In our control tests, the following samples were used.
1. Palmityl chloride, analytical grade, refined by distillation,
2. Palmityl chloride, analytical grade,
3. Palmityl chloride, technical grade,
4. Acetyl chloride, analytical grade,
5. Acetyl chloride, technical grade,
6. Chloroacetyl chloride, analytical grade,
7. Benzoyl chloride, analytical grade.

The content of total carboxylic acid and hydrochloric acid (i.e. of acid chloride plus hydrochloric acid and carboxylic acid produced during decomposition) was measured in the analytical grade samples by the method prescribed in *Ph. Hung. V* for the determination of the saponification number. On hydrolysis by alkali, the content of chloride was measured in the samples, by argentimetry. In the case of palmityl chloride and benzoyl chloride, the content of total carboxylic acid (i.e. that of acid chloride plus that of free carboxylic acid produced during decomposition) was isolated and determined by an appropriate method, after hydrolysis by alkali. The results of measurements were in fair accordance with the results obtained by the newly evolved method.

With this new method, the contents of acid chloride, free hydrochloric acid and free carboxylic acid were determined in the listed samples. The combined values of the results were compared with the weighed amounts (cf. Table I).

The relative error of the method lies within $\pm 1.0\%$. Some results are summarised in Tables I and II.

Table I.—Results of the complete analysis

Nature of sample	Sample weighed, mg	Actual content of acid chloride		Decomposition products				Total	
				HCl		Carboxylic acid			
		mg	%	mg	%	mg	%	mg	%
Acetyl chloride, technical	104·0	83·5	80·31	1·31	1·26	19·20	18·46	104·0	100·0
	118·0	94·4	80·03	0·73	0·62	21·80	18·47	116·9	99·1
Benzoyl chloride, analytical grade	95·8	94·6	98·75	0·80	0·83	0·0	0·0	94·5	99·58
	211·4	210·4	99·53	1·2	0·57	0·0	0·0	211·6	100·1
Palmityl chloride, analytical grade refined by distillation	127·4	121·7	95·5	0·25	0·2	4·59	3·6	126·5	99·3
	207·9	200·2	96·3	0·31	0·15	7·07	3·4	207·6	99·85
Palmityl chloride, analytical grade	139·5	132·9	95·3	0·0	0·0	5·58	4·0	138·5	99·3
	123·2	117·0	95·0	0·0	0·0	5·05	4·1	122·1	99·1
Palmityl chloride, technical grade	143·5	130·6	91·0	0·86	0·6	8·18	5·7	139·6	97·3
	208·7	189·1	90·6	1·25	0·6	12·10	5·8	202·5	97·0

Table II.—Actual content of acid chloride in various carboxylic acid chlorides

Nature of sample	Amount weighed, mg	Actual content of acid chloride	
		mg	%
Acetyl chloride, analytical grade	43·5	43·1	99·1
	66·9	65·7	98·2
	106·6	105·0	98·5
Acetyl chloride technical grade	104·0	83·5	80·3
	118·0	94·4	80·0
Chloroacetyl chloride, analytical grade	79·6	77·7	97·6
	117·4	114·2	97·3
Benzoyl chloride, analytical grade	95·8	94·6	98·8
	211·4	210·4	99·5
Palmityl chloride, analytical grade, refined by distillation	127·4	121·7	95·5
	207·9	200·2	96·3
Palmityl chloride, analytical grade	139·5	132·9	95·3
	123·2	117·0	95·0
Palmityl chloride, technical grade	143·5	130·6	91·0
	208·7	189·1	90·6

Zusammenfassung—Verfasser geben einen Arbeitsgang zur Untersuchung verschiedener Carbonsäurechloride zwecks Bestimmung ihrer effektiven Säurechloridgehalte sowie ihrer eventuellen infolge Hydrolyse entstandenen Salzsäure, sowie Carbonsäuregehalte an. Die Carbonsäurechloride reagieren mit absolutem Äthanol unter Bildung von Estern. Aus der Esterzahl dieser Lösung lässt sich der Carbonsäurechloridgehalt berechnen.

Wird das Reaktionsgemenge im Falle von Palmityl- bzw. Stearylsäurechloride nach der Esterifizierung und vor der Esterzahlbestimmung zuerst gegen Methylrot, dann gegen Phenolphthalein genau neutralisiert, so kann auch die eventuelle freie Salzsäure, bzw. Carbonsäure berechnet werden. Bei der Untersuchung von Acetylchlorid neutralisiert man gegen Phenolphthalein und bedient sich bei der Esterzahlbestimmung einer volumetrischen Schwefelsäure. Nach Durchführung einer Gesamtchlorbestimmung kann der Gehalt an freier Salzsäure bzw. Carbonsäure ebenfalls berechnet werden.

Résumé—On développe une nouvelle méthode pour la détermination de la teneur en chlorure d'acide présent et de la quantité d'acide chlorhydrique et carboxylique libre formés après décomposition, dans des échantillons de différents chlorures d'acides carboxyliques. L'échantillon à analyser est traité par de l'éthanol anhydride. Le chlorure d'acide réagit avec l'éthanol pour former un ester. Le volume de base alcaline titrée consommé dans la saponification de l'ester correspond à la teneur en chlorure d'acide présent.

REFERENCES

[1] D. M. Smith and W. M. Bryant, *J. Amer. Chem. Soc.*, 1935, **57**, 61.

[2] *Idem, ibid.*, 841.

[3] J. Mitchell and C. E. Askby, *ibid.*, 1945, **67**, 161.

[4] S. Siggia, *Quantitative Organic Analysis via Functional Groups*, John Wiley, New York, 1954, p. 55.

[5] L. Winkler, *Ber.*, 1915, **38**, 3612; *Z. angew. Chem.*, 1916, **29**, I, 18.

[6] J. Mitchell and D. M. Smith. *Aquametry*, Interscience Publ., New York, 1948, p. 369.

[7] B. Saville, *Analyst.*, 1957, **82**, 269.

SPECTROPHOTOMETRIC DETERMINATION OF FLUORIDE USING LANTHANUM CHLORANILATE

Kiyoko Hayashi, Taeko Danzuka and Keihei Ueno*

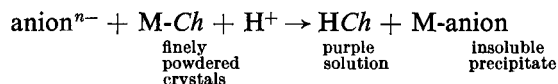Research Laboratory, Dojindo and Co., Ltd., Kumamoto, Japan

Summary—Spectrophotometric determination of fluoride has been investigated using lanthanum chloranilate. It has been found possible to determine 2–200 ppm of fluoride with an accuracy of $\pm 2\%$, if the proper reaction conditions are chosen. Sulphate, chloride and nitrate ions do not interfere up to 200 ppm. Application of this procedure to fluoride determination in organic fluorocompounds is described.

INTRODUCTION

The use of chloranilic acid (2:5-dichloro-3:6-dihydroxy-*p*-benzoquinone) as an analytical reagent for various cations has been known for many years. However, since Bertolacini and Barney[1,3] proposed the photometric determination of sulphate by utilising the metathesis reaction between barium chloranilate and sulphate ion, the application of polyvalent metal chloranilates to the photometric determination of various anions has received considerable attention. Thus, mercuric chloranilate has been used for the determination of chloride ion[2,3] and strontium chloranilate has been proposed for the determination of fluoride ion.[3]

The photometric determination of anions using metal chloranilate depends on the reaction

$$\text{anion}^{n-} + \text{M-}Ch + \text{H}^+ \rightarrow \text{H}Ch + \text{M-anion}$$

finely powdered crystals	purple solution	insoluble precipitate

On addition of a finely powdered metal chloranilate to the sample solution containing a suitable anion, the metal salt of the anion is precipitated, with the liberation of purple acid chloranilate ion (H*Ch*). After the reaction, excess metal chloranilate and insoluble metal salt are filtered off, and acid chloranilate ion is determined photometrically in the filtrate; this corresponds to the amount of fluoride in the sample. The sensitivity of the determination is, therefore, dependent mainly upon the insolubility of the metal salt formed by the metathesis. The sensitivity of the fluoride determination with strontium chloranilate will not be very high, since the solubility product of strontium fluoride is not small enough.

On the other hand, the solubility of lanthanum fluoride is very low, and therefore lanthanum chloranilate has been tried for fluoride determination in an analogous manner.† This reagent has been found to give much more satisfactory results than strontium chloranilate.

The procedure with the lanthanum reagent is rapid and simple, and 2 to 200 ppm of fluoride can be determined with an accuracy of $\pm 2\%$.

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† During the course of this investigation, Fisher Scientific Co. (U.S.A.) announced the availability of lanthanum chloranilate as an analytical reagent for fluoride determination, but no detailed account has been available to the present authors.

EXPERIMENTAL

Reagents

Lanthanum chloranilate was prepared by mixing a hot solution of 20 g of chloranilic acid in 4.6 litres of distilled water with a solution of 17 g of lanthanum oxide (99·9%) in 27 ml of nitric acid (sp. gr. 1·42) and 200 ml of distilled water. After standing overnight, the fine dense precipitate of lanthanum chloranilate was collected by filtration and washed with distilled water until the filtrate was free from nitrate. The dark grey product was dried under a heating lamp, and was kept in an amber bottle. The yield was almost quantitative, and the reagent can be kept for an indefinite period without appreciable deterioration.

Standard fluoride solution (approximately 4000 ppm of F^-) was prepared by dissolving 7·8 g of ammonium fluoride in 1 litre of distilled water, and the fluoride ion concentration was determined by indirect EDTA titration via calcium fluoride.[4]

Buffer solutions employed in this investigation, ranged from pH 2 to 7, and were prepared according to the standard recipes as follows: Acetate buffer, pH 2 (sodium acetate and hydrochloric acid); acetate buffers, pH 4, 5 and 7 (sodium acetate and acetic acid); phthalate buffer, pH 6 (potassium acid phthalate and potassium hydroxide); succinate buffer, pH 7 (sodium succinate).

Methylcellosolve, ethanol (95%) and all other reagents were reagent grade.

Apparatus

Spectrophotometric determinations were carried out by a Beckman Model DU spectrophotometer equipped with a tungsten lamp and 1-cm Corex cells. A glass-electrode pH meter was used for all pH measurements, and a mechanical shaking apparatus with a time switch was employed to ensure constant reaction conditions.

General procedure

The following general procedure was employed to investigate the effects of reaction conditions and of various interfering ions: Pipette the standard fluoride solution containing 0·2–10 mg of fluoride into a 100-ml volumetric flask. To this, add 10 ml of buffer solution, 50 ml of water-miscible organic solvent and 0·2 g of lanthanum chloranilate (crystalline powder), and dilute the mixture to volume with distilled water. After shaking the flask on a shaking machine for a given period, filter the solution through a filter paper. Discard the first portion of filtrate, then collect the middle portion in a Corex cell. Determine the optical density of this solution at 530 mμ against a reagent blank.

RESULTS AND DISCUSSION

Selection of absorption peak

The absorption spectrum of acid chloranilate ion in aqueous solution has two maxima, one in the visible region (520–550 mμ) and the other in the ultraviolet region (280–350 mμ); the intensity of the ultraviolet peak is 20–30 times greater than that of the visible one. Either maximum can be used for the photometric determination of chloranilic acid up to a concentration as high as 100 mg per 100 ml.

With the absorption peak in the ultraviolet region a higher sensitivity is possible than in the case of visible spectrophotometry; but ultraviolet spectrophotometry suffers from more interference, especially in the analysis of actual samples. It was therefore decided to utilise the absorption peak in the visible region so that the procedure would be less influenced by foreign material, although there would be some sacrifice of sensitivity; and so that a visible spectrophotometer or a filter photometer could be used instead of the more expensive ultraviolet spectrophotometer.

Effect of organic solvent

As in the case of sulphate determination using barium chloranilate,[1,3] and of chloride determination using mercuric chloranilate.[2,3] addition of a water-miscible

organic solvent increased the sensitivity of the colour reaction. Presumably the addition of organic solvent reduces the solubility or dissociation of the insoluble salt. Of the organic solvents investigated, only methylcellosolve and ethanol were found to be useful, and this is shown in Fig. 1. At any given pH (*i.e.* with a given buffer solution) methylcellosolve gave better sensitivity than ethanol.
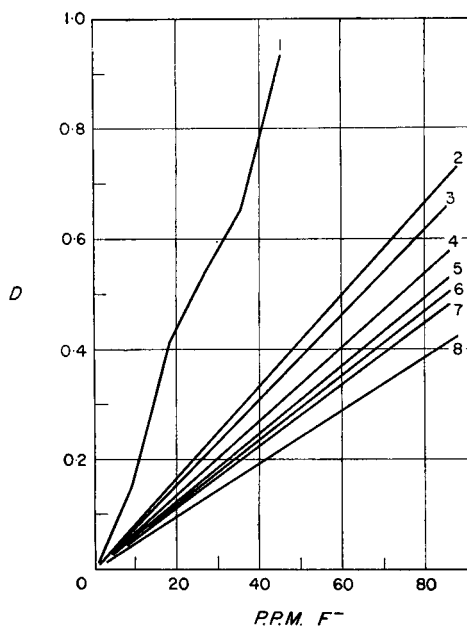
FIG. 1.—Effect of buffer solution and solvent on calibration curves
1. Acetate buffer pH 2, 1:1 ethanol:water
2. Acetate buffer pH 4, 1:1 methylcellosolve:water
3. Acetate buffer pH 4, 1:1 ethanol:water
4. Succinate buffer pH 7, 1:1 methylcellosolve:water
5. Acetate buffer pH 7, 1:1 methylcellosolve:water
6. Succinate buffer pH 7, 1:1:2 ethanol:methylcellosolve:water
7. Succinate buffer pH 7, 1:1 ethanol:water
8. Acetate buffer pH 7, 1:1 ethanol:water
(shaking time, 20 minutes)

Effect of pH and the buffer composition

As the absorption spectrum of acid chloranilate ion is markedly influenced by the pH of solution, the sensitivity and the reproducibility of the colour reaction are also dependent on pH. The intensity of the absorption maximum decreases with increasing pH of the solution, and the influence of pH is more marked in the lower pH range (pH 1–2). Therefore, if the colour reaction is carried out at pH 2, the sensitivity becomes higher, but reproducible results are very difficult to obtain. When the pH of the reaction medium is increased to 7, the reproducibility is improved, but the sensitivity decreases. At intermediate pH values (pH about 4), the sensitivity is sufficiently high without too great a sacrifice of reproducibility. The reaction was therefore carried out at pH 4, if no interfering ion was present in the sample. However, if anions such as sulphate, nitrate or chloride were present, the reaction was carried out at pH 7 where the photometric determination of chloranilate ion was less influenced by those anions.

While the absorbance of the reagent blank is generally low and is almost constant in the range pH 4–6, the composition of the buffer solution and the nature of the organic solvent may affect the absorbance of the reagent blank markedly, as shown in Table I. Of the buffer solutions, phthalate buffer (pH 6) gave an abnormally high blank value and was therefore unsatisfactory. Regarding the reagent blank, a lower value for the reagent blank was found for ethanol than for methylcellosolve.

TABLE I.—INFLUENCE OF BUFFER SOLUTIONS AND ORGANIC SOLVENTS UPON THE REAGENT BLANK ABSORBANCE AT 530 mμ.

Buffer and pH	Absorbance in	
	50% ethanol	50% methylcellosolve
Succinate 7	0·019	0·047
Acetate 7	0·018	0·070
Phthalate 6	0·125	0·360
Acetate 5	0·013	0·044
Acetate 4	0·010	0·038

Reaction time

The method of shaking is fairly important in this reaction, since the metathesis reaction occurs on the surface of the crystalline particle of lanthanum chloranilate. Although the results obtained using manual shaking are fairly reproducible, it is better to employ a mechanical shaker to ensure constant conditions. A suitable rate of shaking is 350 strokes per minute. As the reaction is heterogeneous, colour development depends on time of shaking as shown in Fig. 2. The absorbancy
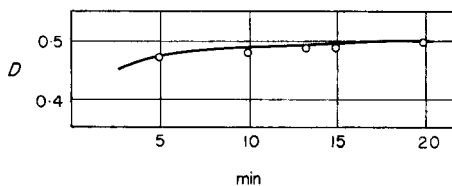
FIG. 2.—Effect of shaking time on colour development
86 ppm of F⁻
Succinate buffer pH 7; 1:1 ethanol:water

increases with increasing duration of shaking, but the value becomes nearly constant after 15 minutes, and reproducible results are obtained when the spectrophotometric determinations are carried out after 20 minutes shaking in these conditions.

Interfering ions

Almost all cations interfere in the determination, since the absorption spectrum of acid chloranilate is more or less influenced by the cations. Even sodium and potassium ions, if present in large amounts, influence the absorbancy. Although it has been reported that the interference of these two cations can be cancelled by adding large amount of sodium or potassium ion to the reagent blank,[5] it was found desirable to remove all cations in the sample solution by ion-exchange before the determination.

TABLE II.—INTERFERENCES OF SULPHATE, CHLORIDE AND NITRATE

Buffer, pH	Solvent	With no interfering ion	Absorbance[a]											
			With sulphate				With chloride				With nitrate			
			400 ppm	% error	200 ppm	% error	400 ppm	% error	200 ppm	% error	400 ppm	% error	200 ppm	% error
Succinate, 7	Methylcellosolve	0·458	0·501	+9·4	0·493	+7·6	0·467	+2·0	0·467	+2·0	0·457	−0·2	0·473	+3·3
	Methylcellosolve and ethanol (1 : 1)	0·411	0·435	+5·8	0·425	+3·4	0·414	+0·7	0·412	+0·2	0·401	−2·4	0·407	−1·0
	Ethanol	0·388	0·397	+2·3	0·392	+1·0	0·384	−1·0	0·384	−1·0	0·386	−0·5	0·390	+0·5
Acetate, 7	Methylcellosolve	0·428	0·465	+8·6	0·450	+5·1	0·410	−4·3	0·409	−4·4	0·425	−0·7	0·426	−0·5
	Ethanol	0·321	0·374	+16·5	0·374	+16·5	0·324	+0·9	0·326	+1·6	0·324	+0·9	0·330	+2·8
Acetate, 4	Methylcellosolve	0·564	0·647	+14·7	0·623	+10·5	0·548	−2·8	0·559	−0·9	0·558	−1·1	0·578	+2·5
	Ethanol	0·562	0·612	+8·9	0·597	+6·2	0·526	−6·4	0·542	−3·6	0·550	−2·1	0·570	+1·4

[a] Absorbance was measured after treating the sample, containing 70 ppm of F⁻, according to the standard procedure. Values shown in the table are the average of five determinations.

Efforts to find a suitable masking agent for certain cations were unsuccessful. The only exception in respect of interference is ammonium ion which does not interfere even in large amounts.

The interferences of anions were investigated using ammonium salts of various anions, and the results are shown in Table II, which shows that chloride, nitrate and sulphate do not interfere appreciably up to the 200 ppm-level if the proper pH and buffer solution are chosen. However, in the presence of larger amounts of anions, the interferences cannot be overlooked, and calibration curves have to be prepared using standard solutions containing the same amount of interfering anions.

Recommended procedure

On the basis of these results, the following procedure is recommended for the determination of fluoride: Place the sample solution, containing 0·2–10 mg of fluoride ion, in a 100-ml volumetric flask. To this, add 10 ml of 0·03M sodium succinate (pH 7), 50 ml of 95% ethanol and 0·2 g of lanthanum chloranilate (crystalline powder*), and make the solution to 100 ml with distilled water. Shake the flask for 20 minutes, and filter the solution through a filter paper. Discard the first portion of the filtrate, and collect the middle portion in a cell for spectrophotometric measurement. Read the light absorbancy at 530 mμ against a reagent blank.

FLUORINE DETERMINATION IN ORGANIC FLUORINE COMPOUNDS

Since the lanthanum chloranilate method is very convenient for determination of fluorine in samples free from cations, determination of fluorine in organic fluoro-compounds, after a suitable decomposition, is one of the promising applications of the method. For example, if the flask combustion method[6] is combined with this chloranilate procedure, it is possible to carry out a single determination in 50 minutes with satisfactory accuracy.

Determination of fluorine in 2-thenoyltrifluoroacetone

A weighed amount of 2-thenoyltrifluoroacetone (about 50 mg) was decomposed in a Schöniger flask containing 30 ml of distilled water. After combustion, the flask was shaken for 10 minutes to ensure complete absorption of the decomposition products. The contents of the flask were quantitatively transferred to a 100-ml volumetric flask and diluted to volume with distilled water. The chloranilate procedure was carried out on 15–30 ml aliquots of this solution. The results of the determinations are shown in Table III.

TABLE III.—DETERMINATION OF FLUORINE IN 2-THENOYLTRIFLUOROACETONE

Amount of sample, *mg*	Absorbancy	Fluorine, *mg*		
		Observed	Theoretical	Error %
48	0·200	12·13	12·32	−1·5
48·5	0·203	12·33	12·45	−1·0

Zusammenfassung—Die spektrophotometrische Bestimmung von Fluorid unter Verwendung eines neuen Reagenses (Lanthanchloranilat) wurde studiert. Es wurde gezeigt, dass es möglich ist 2–200 ppm Fluorid mit einer Genauigkeit von ±2% zu bestimmen, wenn geeignete Reaktionsbedingungen eingehalten werden. Sulfate, Chlorid und Nitrationen stören nicht in Mengen bis zu 200 ppm. Die Anwendung der neuen Methode auf die Fluorbestimmung in organischen Fluorverbindungen wird beschrieben.

* The amount of lanthanum chloranilate need not be accurately measured and can be weighed on an ordinary laboratory balance.

Résumé—Le dosage spectrophotométrique du fluorure a été étudié en utilisant un nouveau réactif, le chloranilate de lanthane. On montre qu'il est possible de doser 2 à 200 p.p.m. de fluorure avec une précision de $\pm 2\%$ si l'on choisit des conditions de réaction appropriées. Les ions sulfate, chlorure et nitrate ne gênent pas jusqu'à une teneur de 200 p.p.m. Les auteurs décrivent une application de ce procédé au dosage du fluor dans les composés organiques fluorés.

REFERENCES

[1] R. J. Bertolacini and J. E. Barney, *Analyt. Chem.*, 1957, **29**, 281.
[2] J. E. Berney and R. J. Bertolacini, *ibid.*, 1187.
[3] R. J. Bertolacini and J. E. Berney, *ibid.*, 1958, **30**, 202.
[4] K. Sato and Y. Osumi, *Osaka Kōgyō Gijutsu Shikenjo Kihō*, 1956, **7**, 232.
[5] R. E. U. Frost-Jones and J. T. Yardley, *Analyst*, 1952, **77**, 468.
[6] W. Schöniger, *Mikrochim. Acta*, 1955, 123; 1956, 869.

COMPLEXOMETRIC DETERMINATION OF MERCURY[II] AND ALUMINIUM IONS

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Summary—Mercury[II] ions can be titrated directly in slightly acid medium by Na_2-EDTA using a diphenylcarbazide + *o*-phenanthroline indicator system. This indicator system is suitable, with a little modification, for detecting the end-point in the back-titration of aluminium ions by mercury[II] nitrate. Xylenol Orange indicator is also suitable for this purpose. Moderate amounts of alkaline earth metals or magnesium, or large amounts of alkali metal salts, do not interfere with the method.

DIRECT complexometric determination of mercury[II] ions, using metal indicators, is only possible if acid is also added; without a suitable complexing agent mercury[II] ions cannot persist in solution in alkaline media. In the literature, Xylenol Orange,[1] Methyl Thymol Blue[2] and the Cu-PAN indicator system[3] are recommended for end-point detection. There is a brief note on the use of PAR.[4] Recently, easily dissociated mercury[II] salts have been used for back-titration with potentiometric end-point detection.[5–8] Because of the small number of indicators suitable for an acid medium (pH 4-6) it seemed advisable to examine the possibility of using for this purpose colorimetric reagents which give a strong colour reaction with mercury[II] ion. Diphenylcarbazide, diphenylcarbazone and *p*-dimethylaminobenzylidinerhodanine have been examined as metal indicators.

Reagents

0·05M *Disodium ethylenediaminetetra-acetate (Na₂-EDTA) solution*: dissolve 18·605 g of Na_2-EDTA in distilled water and make up to 1 litre. Determine the factor of the solution against pure zinc using Eriochrome Black T indicator.

0·01M *Na₂-EDTA solution*: obtained by diluting the 0·05*M* solution.

0·05M *(slightly acid) mercury[II] nitrate solution*: dissolve 11 g of mercury[II] oxide in 20 ml of 1 : 1 nitric acid with constant shaking. Filter the cloudy solution and bring its volume with water to about 950 ml. One ml of this solution contains 10·03 mg mercury ion. Determine the factor against potassium thiocyanate, and also against sodium chloride, using sodium nitroprusside and potassium iodate indicator.[9] Titration with Na_2-EDTA using Xylenol Orange agrees closely with the values thus obtained.

0·01M *and* 0·001M *(slightly acid) mercury[II] nitrate*: made from the 0·05*M* solution suitably diluted with water.

0.05M *(slightly acid) aluminium nitrate solution*: dissolve 1·35 g of metallic aluminium (99·99%) in 40 ml of conc. nitric acid, and make with water to 1 litre.

Other solutions. 20% hexamethylenetetramine buffer, 0·2% ethanolic *o*-phenanthroline, 0·04*M*, 0·02*M*, 0·01*M* and 0·005*M* ethanolic diphenylcarbazide; 0·01*M* ethanolic diphenylcarbazone.

Determination of mercury[II] ions (end-point detection by diphenylcarbazide)

Examination of the indicator system. Diphenylcarbazide was first recommended by Cazeneuve[10] for the detection of mercury ions, giving in moderately acid medium (pH 3·6-7·0) a bright violet-blue

precipitate, or, in more dilute solution, a colour. The structure of the complex is uncertain; it may be the chelate complex of mercury[II] ions with either diphenylcarbazide or with diphenylcarbazone (the oxidation product of diphenylcarbazide).[11-12] Diphenylcarbazone is produced by air-oxidation of diphenylcarbazide.

Job's curve, determined with equimolar solutions (Fig. 1), and the extinction-concentration
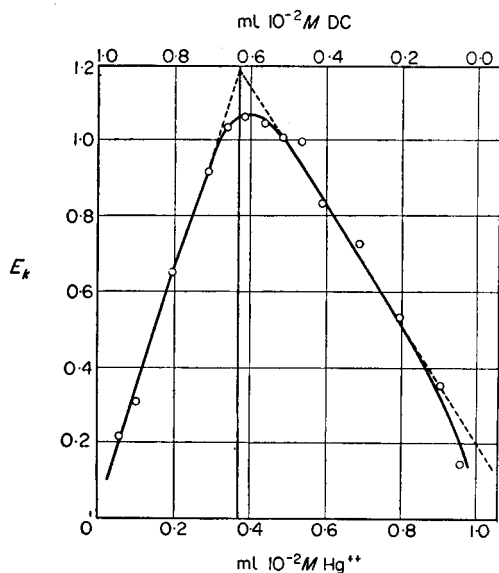
FIG. 1.
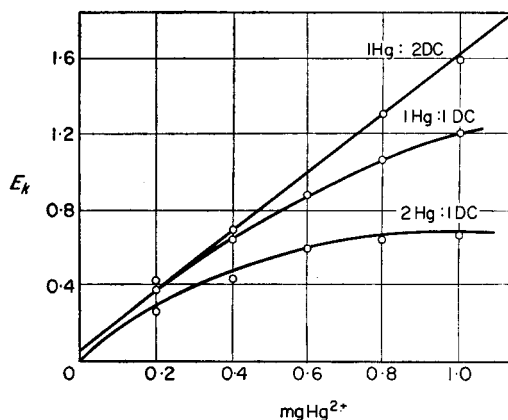
FIG. 2.

relation of mercury[II] and diphenylcarbazide solutions of different ratio (Fig. 2) both indicate that the composition of the complex is 1:2 Hg:organic complex (the latter being referred to as DC.)

The photometric measurements were made by pipetting a convenient amount of mercury solution and 5 ml of 20% buffer solution into a flask, adding the required amounts of water and diphenyl-carbazide solution, making to the mark, shaking, and measuring the violet solution at the maximum of the absorption curve in a long cuvette with an S53 filter after 20 min.

The apparent stability constant was determined by Job's method from the position of the extinction

maximum of the non-equimolar solutions.[13] From the experimental results (summarised in Table I) the apparent stability constant can be calculated from the following equation:*

$$K'_{Hg(DC)_2} = \frac{(p-1)^2 \cdot (2-3x)}{\Gamma^2[p(p+2)x-2]^3} \cdot$$

Mercury[II] ions react with Na_2-EDTA in moderately acid solution forming HgY^{2-} (Y^{4-} = ethylene-diaminetetra-acetate ion).
The stability constant[14] of this reaction,

$$K_{HgY} = 10^{21 \cdot 8},$$

and the apparent stability constant[14] at pH = 5,

$$K'_{HgY} = 10^{15 \cdot 3}.$$

The relation of the K'_{HgY} and $K'_{Hg(DC)_2}$ values indicates that the end-point of the complexometric titration of mercury[II] should readily be detected with diphenylcarbazide indicator. In spite of this,

TABLE I.—DETERMINATION OF THE STABILITY CONSTANT OF THE $Hg(DC)_2$ COMPLEX

$[Hg^2]^+$, mole/litre	$[DC]$, mole/litre	$[DC]/[Hg^{2+}]$	x	$K'_{Hg(DC)_2}$* pH 6·5
10^{-3}	5×10^{-3}	5	0·40	$10^{6 \cdot 7}$
10^{-3}	1×10^{-2}	10	0·26	$10^{6 \cdot 8}$
10^{-3}	2×10^{-2}	20	0·20	$10^{6 \cdot 3}$

we found that the violet colour of the indicator complex does not disappear at the end-point, and only does so after over-titration by 2–3 ml. On reverse titration a pale rose colour appears well before the equivalence-point, and gradually becomes stronger on further titration. Acting on the information that sometimes a good result can be obtained in such cases by using additives that simulate catalysis of the indicator reaction[15] we found, in fact, that with a small amount of o-phenanthroline present, end-points of both forward and reverse titrations can be detected precisely with diphenylcarbazide. The diphenylcarbazide + o-phenanthroline indicator system works reversibly and acts quickly; and, being a uni-coloured indicator system, is very sensitive to change in the mercury concentration.

The behaviour of the diphenylcarbazide indicator can be explained by the assumption that it does not form a genuine solution with the mercury[II] ions, but a colloidal one, which does not react with the necessary velocity. We are as yet unable to propose any explanation of the increase in reaction velocity caused by o-phenanthroline. According to the work of Anderegg[16] it forms with mercury[II] a very stable complex with an $Hg(Ph)_2$ structure. It does not seem likely that its role can be explained as a redox effect, because its presence is also necessary for reversible working of diphenyl-carbazone indicator, and the redox potentials are almost the same, whether o-phenanthroline is present in the solution or not. Investigations are under way to determine if a "phenanthroline-mercury-diphenylcarbazide" complex forms; this could provide an explanation. We have, however, attained no result with "alcoholic dosing", which often helps an indicator system to act reversibly.

Determination of experimental conditions

The stability constant of the o-phenanthroline-mercury[II] complex is 10^{19}, so that Na_2-EDTA cannot decompose this complex. Therefore in titrating mercury[II] ions a negative error occurs (positive in the reverse titration) which depends on the amount of o-phenanthroline. In 0·05M titrations the diphenylcarbazide indicator works properly in the presence of 1·5 ml of 0·2 per cent o-phenanthroline; the corresponding value for an 0·01M titration is half this amount. This amount of o-phenanthroline consumes 0·03 ml of 0·05M titrating solution, which is negligible in practice.

In a uni-coloured indicator system the transition depends on the indicator concentration. In this case, observation of the end-point is best in $10^{-4}M$ indicator solution—0·2 ml of 0·04M diphenyl-carbazide per 100 ml. The mercury[II] concentration at the equivalence-point is so low that at this

* Γ = $[Hg^{2+}]$ Mole/l, r′ = $[DC]$ Mole/l, p = Γ'/Γ. x = volume of complex-forming solution giving maximum extinction, $K'_{Hg(DC)_2}$ = apparent stability constant.

indicator concentration the coloured Hg(DC)$_2$ complex does not pass the visibility limit (about $2 \times 10^{-6}M$ by photometric measurements). Therefore the solution is without colour at the equivalence-point.

The titration is only slightly pH sensitive, but, depending on the acidity of the solution, may be carried out after adding 5–10 ml of 20% hexamethylenetetramine to the solution buffered thus to pH 5-6.

Taking all these factors into account, the following procedure is recommended for the determination of mercury^{II} ions.

TABLE II.—TITRATION OF Hg^{2+} IONS

with 0·05M Na$_2$-EDTA			with 0·01M Na$_2$-EDTA		
Hg^{2+} ion added, mg	Hg^{2+} ion found, mg	Deviation, mg	Hg^{2+} ion added, mg	Hg^{2+} ion found, mg	Deviation, mg
50·15	50·26	+0·11	10·03	10·12	+0·09
100·30	100·70	+0·40	20·06	20·17	+0·11
150·45	151·25	+0·80	30·09	30·07	−0·02
201·60	202·10	+0·50	40·12	39·98	−0·14
250·75	252·65	+1·90	50·15	50·04	−0·11

Procedure

To the solution, containing 50–250 mg of mercury^{II}, add 5–10 ml of 20% hexamethylenetetramine, 1·5 ml of 0·2% ethanolic o-phenanthroline, and 5–6 drops of 1% freshly prepared ethanolic diphenylcarbazide, and make up with water to a volume of about 100 ml. Titrate this solution with 0·05M Na$_2$-EDTA, constantly shaking, and making additions drop by drop near the end of the titration, to the disappearance of the violet colour. If the mercury content of the solution is only 10–15 mg, add only half the amount of o-phenanthroline, and titrate with 0·01M Na$_2$-EDTA.

Table II summarises results obtained by this method. The standard deviation of the system is ±0·05 ml at 20 ml of 0·05M titrating solution. The percentage standard deviation is ±0·24.

Alkali metal sulphates and nitrates (up to 5 g) do not cause trouble, nor does fluoride ion, halides forming a stable complex with mercury^{II} ions, but cyanide, thiocyanate, manganese^{II} and mercury^{I} interfere. With mercury^{I} ions present, disproportioning causes metallic mercury to separate at the pH employed.

By this method the mercury content of a mercury^{II} nitrate preparation was found to be 60·9%; by a Volhard determination it was 61·0%; the corresponding values for a mercury^{II} sulphate preparation were 66·3% and 66·8%.

Diphenylcarbazone is less suitable for the end-point detection in this titration. In the foam on the surface of the solution violet granules can be seen—it is probable that some solid mercury complex is precipitated—and there is 1% over-consumption. With p-dimethylaminobenzylidenerhodanine the end-point of the titration cannot be determined.

Back-titration of aluminium ions with mercury^{II} nitrate solution

The direct complexometric titration of aluminium ions is rather difficult, although the stability constant of the aluminium-EDTA complex[14] is relatively high ($K_{AlY} = 10^{16.1}$). This is because, in the first place, the formation of aluminium ethylenediaminetetra-acetate is not momentary; and, in addition, the determination is pH-sensitive because of hydrolytic phenomena and the formation of hydroxyl complexes. The number of aluminium reagents that can be used for end-point detection is small.

Theis[18] proposed a direct titration in hot solution at pH 4 with Chrome-azurol S as indicator, but preferred a back-titration method. Taylor[19] titrated Na$_2$-EDTA solution with aluminium solution using haematoxylin indicator. The method of Flaschka and Abdine,[20] who titrate the aluminium in hot solution at pH 3 with

PAN indicator, with a small quantity of Cu^{II} complexonate present, is also essentially a back-titration method.

At present, exact results can be obtained only with back-titration methods. Among them the titrations carried out in moderately acid medium (in the range pH 3-6) are more interesting because of the absence of the interference of alkaline earth metals, manganese and magnesium. Aluminium can therefore be determined in glass, silicates, rocks, in the presence of calcium and magnesium, without prior separation.

Wänninen and Ringbom[17,21] dealt in detail with theoretical aspects of the back-titration method, with the titration error and with the effects of the Na_2-EDTA excess and of the pH of the solution on the end-point. Their investigations elucidated the background of the different empirical procedures.

Iron^{III} chloride was first used as back-titrant, with potentiometric,[22] and, later, with a salicyclic acid[23] indication. The most frequently proposed titrating solution is probably a zinc solution. For end-point detection either a reagent sensitive to zinc ions, such as dithizone,[21] Xylenol Orange,[24] or a reagent indicating aluminium ions, such as Eriochrome Cyanine R,[25,26] ferri-ferrocyanide + benzidine, or dimethyl-naphthidine[26,27] may be used. Cadmium^{II} back-titrant has been used with Eriochrome Cyanine R indicator;[25] in more acid medium thorium^{IV} nitrate with Alizarin-S indicator[28,29]; copper^{II} salt with Pyrocatechol Violet,[30] PAN[31] or Calcein W fluorescent indicator;[32] copper-zinc^{II} mixed titrating solution with the Variamine Blue-thiocyanate redox indicator system.[33] Přibil and his co-workers examined the possibility of employing Xylenol Orange indicator, which is very useful in acid medium, for back-titration with lead nitrate, zinc sulphate and thorium nitrate solutions.[24]

Experimental conditions for formation of aluminium^{III} ethylenediaminetetra-acetate

Because of the different procedures given in the literature, we first examined conditions for quantitative formation of aluminium ethylenediaminetetra-acetate, then the effect of pH, of excess of Na_2-EDTA, and of several extraneous salts on the end-point. The results are summarised in Table III. The velocity of formation of the aluminium complex is increased by 2–3 min heating, since it was found that the excess of Na_2-EDTA used did not bind the aluminium quantitatively in the cold. For the back-titration, mercury^{II} nitrate solution and the diphenylcarbazone-*o*-phenanthroline indicator system were used. Diphenylcarbazide cannot be used in this case, since in the presence of aluminium ethylenediaminetetra-acetate the colour development of the indicator complex is so slow that the violet colour produced by excess of mercury^{II} cannot be seen even after considerable over-titration. The reversibility of the diphenylcarbazone indicator is assured by addition of 0.5 ml of 0.2% *o*-phenanthroline, so that once more an indicator correction need not be taken into account, especially since the factor of the Na_2-EDTA solution was determined against mercury^{II} solution.

Determination of aluminium by back-titration with mercury^{II}

Add 20–200 per cent excess of Na_2-EDTA to a nitric acid or sulphuric acid solution containing 1–20 mg of aluminium ion, and adjust the volume to about 100 ml with distilled water. Neutralise the solution with sodium hydroxide to the slight rose colour of phenolphthalein, and re-acidify with 1 ml of $1N$ nitric acid. Heat for 2–3 minutes, cool, and add 10 ml of 20% hexamethylenetetramine.

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TABLE III.—THE EFFECT OF EXPERIMENTAL CONDITIONS ON THE DETERMINATION OF Al^{3+}

Al^{3+} added, mg	$0.05M$ Na_2-EDTA ml	Condition of solution	Al^{3+} found, mg	Deviation, mg
10·12	25	Neutralisation + 1 ml N HNO$_3$	10·12	—
10·12	15	Neutralisation + 2 ml N HNO$_3$	10·11	−0·01
10·12	15	Neutralisation + 5 ml N HNO$_3$	9·91	−0·21
10·12	25	Neutralisation + 10 ml N HNO$_3$	9·81	−0·31
10·12	10		10·16	+0·04
10·12	12		10·18	+0·06
10·12	15	Neutralisation + 1 ml N HNO$_3$	10·12	—
10·12	20		10·21	+0·09
20·24	20		20·31	+0·07
20·24	25		20·26	+0·02
20·24	25	Acid Al^{3+} solution without previous neutralisation	19·95	−0·29
20·24	50		20·20	−0·04
10·12	25	10 g KNO$_3$	10·15	+0·03
10·12	25	10 g K$_2$SO$_4$	10·27	+0·15
10·12	25	1 mg Ca^{2+}	10·11	−0·01
10·12	25	10 mg Ca^{2+}	10·12	—
10·12	25	100 mg Ca^{2+}	10·19	+0·07
6·72	25	1 mg Mg^{2+}	6·74	+0·02
6·72	25	10 mg Mg^{2+}	6·74	+0·02
6·72	25	100 mg Mg^{2+}	6·75	+0·03

TABLE IV.—DETERMINATION OF Al^{3+} ION

Al^{3+} added, mg	Diphenylcarbazone indicator		Xylenol Orange indicator	
	Al^{3+} found, mg	Deviation, mg	Al^{3+} found, mg	Deviation, mg
1·350	1·323	−0·027	1·336	−0·014
2·70	2·70	—	2·71	+0·01
6·75	6·72	−0·03	6·75	—
13·50	13·57	−0·03	13·47	−0·03
20·25	20·21	−0·04	20·27	+0·02

Titrate with mercury^{II} nitrate solution, with 0·2 ml of $0.01M$ diphenylcarbazone and 0·5 ml of 0·2% o-phenanthroline present, constantly shaking, until the appearance of the violet colour. The end-point is very sharp. Or use 10 drops of 0·1% aqueous Xylenol Orange in 100 ml end volume: the transition is then from yellow to violet-red. The results obtained with the two-indicator system are summarised in Table IV.

DISCUSSION

Mercury^{II} nitrate solution can be usefully employed for back-titration of aluminium ions in slightly acid medium. Excess is clearly indicated by the diphenylcarbazone-o-phenanthroline indicator system, or by Xylenol Orange.

The more acid the solution, the greater excess of Na_2-EDTA is needed to bind the aluminium ions quantitatively, *i.e.*, to move the equilibrium

$$Al^{3+} + H_2Y^{2-} \rightleftharpoons AlY^- + 2H^+$$
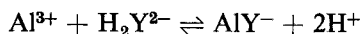
to the right. The pH setting after heating and cooling only influences the formation of the AlY^- complex slightly.

In back-titration, although the complex of mercury[II] with ethylenediaminetetra-acetate is much more stable than that of aluminium, no exchange reaction between aluminium ethylenediaminetetra-acetate and mercury[II] of the titrating solution was found. According to the literature, no exchange reaction is found with iron[III], thorium[IV] or lead[II] solutions; this may be explained to some extent by the assumption that the velocity of the displacement reaction
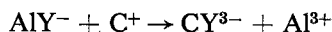
$$AlY^- + C^+ \rightarrow CY^{3-} + Al^{3+}$$
(where C^+ represents the cation of the back-titration solution)

is very small in the cold as compared with the velocity of the development of the coloured indicator complex.

The determination of excess Na_2-EDTA by mercury[II] nitrate is only slightly sensitive to hexamethylenetetramine concentration. It is immediately apparent whether the buffering is sufficient. In too acid a solution a white cloudiness and a slight water-blue colour can be seen at the point where the titrant is being added. In such a case more buffer can be added in the course of the titration.

Large amounts of alkali metal salts, or alkaline earth metal or magnesium salts, as well as fluoride ion, do not interfere with the determination of aluminium. With larger amounts of calcium (value marked * in Table IV) the end-point is somewhat uncertain. Chloride ion causes some trouble, and the determination is therefore only possible in nitric acid or sulphuric acid medium. With manganese[II] salts present, the end-point is so uncertain that an exact titration cannot be carried out.

Zusammenfassung—Zweiwertiges Quecksilber kann mit ÄDTA in leicht saurem Medium unter Verwendung des Diphenylcarbazid-o-phenanthrolin-Systems als Indicator direkt titriert werden. Mit geringen Abänderungen kann die Methode zur Bestimmung von Aluminium durch Rücktitration mit Quecksilbersalzlösung verwendet werden. Auch Xylenolorange ist ein geeigneter Indicator. Grosse Mengen Alkalisalze und und mittelere Konzentrationen von alkalischen Erden und Magnesium stören nicht.

Résumé—On peut titrer immédiatement les ions mercuriques en solution faiblement acide par Na_2-EDTA en utilisant le système diphénylcarbazide-o.phénanthroline comme indicateur. On peut utiliser le système indicateur avec une petite modification pour déceler le point équivalent du titrage en retour des ions aluminium par le nitrate mercurique. Le xylénol orange est aussi un indicateur convenable. Une quantité modérée d'ions alcalino-terreux ou d'ions magnésium ou une grande quantité de sels alcalins ne gêne pas dans cette méthode.

REFERENCES

[1] R. Přibil and E. Körös, *Acta Pharm. Hung.*, 1957, **27**, 1.
[2] J. Körbl and R. Přibil, *Coll. Czech. Chem. Comm.*, 1958, **23**, 873.
[3] H. Flaschka, A. J. Barnard and W. C. Broad, *Chem.-Analyst*, 1958, **47**, 52.
[4] P. Wehber, *Z. analyt. Chem.*, 1959, **166**, 186.
[5] J. Polcin, *Coll. Czech. Chem. Comm.*, 1957, **22**, 1057.
[6] H. Khalifa, *Z. analyt. Chem.*, 1958, **159**, 410.
[7] H. Khalifa, R. Patzak and G. Doppler, *ibid.*, **161**, 264.

[8] H. Khalifa, *Analyt. Chim. Acta*, 1958, **18**, 310.

[9] L. Erdey, *Volumetric Analysis*, 2nd. edition, Budapest 1956, p. 288.

[10] M. P. Cazeneuve, *Bull. Soc. Chim.*, 1900, **23**, 592.

[11] F. J. Welcher, *Organic Analytical Reagents*, Princeton Vol. III, pp. 430, 456.

[12] I. M. Korenmann and A. S. Ojahovszkaja, *Zsurn. Him.*, No. 44655, 1954.

[13] P. Job, *Ann. Chim.*, 1928, 10, **9**, 113.

[14] G. Schwarzenbach, R. Gut and G. Anderegg, *Helv. Chim. Acta*, 1954, **37**, 937.

[15] R. Přibil and co-workers, private communication.

[16] G. Anderegg, *Helv. Chim. Acta*, 1959, **42**, 344.

[17] A. Ringbom and E. Wänninen, *Analyt. Chim. Acta*, 1954, **11**, 153.

[18] M. Theis, *Z. analyt. Chem.*, 1955, **144**, 106.

[19] M. P. Taylor, *Analyst*, 1955, **80**, 153.

[20] H. Flaschka and H. Abdine, *Z. analyt. Chem.*, 1956, **152**, 77.

[21] E. Wänninen and A. Ringbom, *Analyt. Chim. Acta*, 1955, **12**, 308.

[22] R. Přibil, Z. Koudela and B. Matyska, *Coll. Czech. Chem. Comm.*, 1951, **16**, 80.

[23] G. W. C. Milner and J. L. Woodhead, *Analyst*, 1954, **79**, 363.

[24] M. Houda, J. Körbl, V. Bažant and R. Přibil, *Coll. Czech. Chem. Comm.*, 1959, **24**, 700.

[25] I. Sajó, Magy. Kém. Folyóirat, 1953, **59**, 319.

[26] *Idem, ibid.*, 1954, 60, 268.

[27] H. Flaschka and H. Abdine, *Mikrochim. Acta*, 1955, 37.

[28] H. Flaschka, K. Ter Haar and J. Bazen, *ibid.*, 1953, 345.

[29] K. Ter Haar and J. Bazen, *Analyt. Chim. Acta*, 1954, **10**, 23.

[30] V. Patrovský and M. Huka, *Coll. Czech. Chem. Comm.*, 1957, **22**, 37.

[31] D. H. Wilkins and L. E. Hibbs, *Analyt. Chim. Acta*, 1958, **18**, 372.

[32] L. E. Hibbs and D. H. Wilkins, *Talanta*, 1959, **2**, 16.

[33] P. Wehber, *Metall.*, 1956, **10**, 211.

THE INDIRECT COMPLEXOMETRIC TITRATION OF ALUMINIUM

A STUDY OF THE WÄNNINEN-RINGBOM METHOD

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Summary—In the indirect complexometric titration of aluminium according to the procedure of Wänninen and Ringbom, the AlY^- complex behaves as an indifferent substance, thus considerably reducing the calculated titration error. Actual titrations of 2–0·02 millimoles of aluminium, with varying excesses of EDTA, and with zinc as standard substance, gave mean yields of 99·93% (0·1M titrant) and 100·04% (0·01M titrant) with standard deviations of 0·072 and 0·063, respectively. Some features of the method are discussed.

IN 1955 Wänninen and Ringbom[1] published a method for the indirect complexometric titration of aluminium. In this method an excess of EDTA is added to the aluminium solution, the pH is adjusted to 4·5 with an acetate buffer, ethanol is added to a concentration of 40–50% by volume and the excess of EDTA is titrated with zinc sulphate solution using dithizone as indicator for zinc ions. The addition of ethanol serves to keep the dithizone in solution. The colour change from greenish-violet to red is marked and very sharp.

The method proposed by the above authors was based on calculations of the titration error; these showed that the error would be rather dependent on variations of such factors as the excess of EDTA and the concentration of the aluminium complex. The EDTA complexes of aluminium and zinc have about the same value for their stability constants (pK = 16·1 and 16·5, respectively). The titration error should be at a minimum if the final concentrations of the two metal complexes are about the same and the pZn chosen for the end-point is equal to the pAl at the equivalence point. When one or both of these conditions are not fulfilled, the titration error may rise to considerable values (Table II). Wänninen and Ringbom propose, therefore, the use of 0·2–0·5 millimoles of aluminium and 0·3–0·7 millimoles of EDTA in a volume which probably may have been about 100 ml. The seven titrations carried out in the above experimental conditions show deviations from −0·66% to +0·8%, but mostly smaller than 0·1%. No experiments were published, however, verifying the calculated errors outside the standard conditions.

Naturally, a pre-requisite for the validity of the calculated titration errors is that the solution equilibrium should adjust itself. Observations on another complexometric titration method for aluminium made this assumption seem rather dubious. The year before Wänninen and Ringbom's publication, Milner and Woodhead[2] published a similar method in which the excess of EDTA was titrated with ferric chloride and the end-point detected with salicylic acid. The results obtained were fairly good; this has been confirmed in the present laboratory. The large stability constant of the iron-EDTA-complex seems to make this method theoretically

dubious. This contradiction of the results actually obtained may be explained by inertness of reaction of the aluminium-EDTA-complex which, then, is assumed to behave more or less as an indifferent substance. This might also occur in Wänninen and Ringbom's method, thus giving it a far wider range than its originators anticipated. As the method is outstanding in regard to colour contrast and sharpness of the end-point, it is to be preferred to other methods whenever possible; it is, therefore, further investigated in this paper.

EXPERIMENTAL

Reagents

Only reagent grade chemicals were used. Water and hydrochloric acid were quartz-distilled, acetic acid and ethanol Pyrex-distilled. Ammonia was prepared from tank-ammonia.

Standard solutions were prepared on a weight basis because the use of weight burettes was intended.

Aluminium standard solution: $0.1M$ by weight, prepared by dissolving 2.7 g of aluminium ribbon (Merck, 99.99%) in 100 ml of $6.4M$ hydrochloric acid in a Pyrex flask, fitted with a splash trap, and diluting to 1000 g. To facilitate the dissolution, 1 micromole of copper sulphate was added.

Zinc standard solution: $0.1M$ by weight, prepared in the same apparatus from 6.5 g of zinc rod (Johnson, Matthey & Co, "Specpure") and 200 ml of $1.5M$ hydrochloric acid; the zinc rod was wrapped in platinum gauze to facilitate dissolution.

EDTA standard solutions: It was found that certain preparations of the disodium salt of EDTA differed in sharpness of end-point in the titration. Re-precipitation of EDTA or recrystallisation of its disodium salt from ethanol-water mixtures improved the end-point sharpness. The latter procedure was used for preparing $0.1M$ by weight EDTA solution which was standardised against the zinc solution according to the method given below. $0.01M$ standard solutions were prepared from those above through dilution by weight.

Dithizone solution: $0.0004M$, prepared by dissolving 25.6 mg of dithizone in 250 ml of 95% ethanol.

Buffer solution: 1 mole ammonium acetate, 1 mole acetic acid per litre.

Thymol blue solution: 0.1%.

Procedure

Appropriate amounts of aluminium and EDTA standard solutions were weighed out from weight burettes into a 250-ml Vycor beaker. Water was added to about 40 ml, followed by 2 drops of thymol blue and, if necessary, dilute ammonia to about pH 2. The solution was heated and maintained near boiling during the dropwise addition of 10 ml of buffer, then left to stand for a couple of minutes before cooling to room temperature. After addition of an equal volume of 95% ethanol and 2.5 ml dithizone solution, the solution was titrated with zinc standard solution from a weight burette to a distinctly red colour. A drop in the pH, which occurred when the consumption of zinc was large, was compensated for by adding dilute ammonia during the titration, the dithizone also serving as a pH indicator. An indicator correction of -0.00012 millimoles was applied to the zinc consumed.

The EDTA solution was standardised against the zinc solution in the same way, omitting the heating.

RESULTS

Titration of EDTA with zinc in the absence of the aluminium complex

Starting from the data and equations given by Wänninen and Ringbom, the error in the titration of EDTA with zinc is calculated from the equation

$$\Delta_{\text{EDTA}}, \% = \frac{[\text{Zn}^{2+}] - \sum_{i=0}^{4} [\text{H}_i\text{Y}]}{[\text{ZnY}^{2-}]} \cdot 100$$

where EDTA $= H_4Y$. Table I shows the error calculated in this way for pH $= 4.5$ and pZn $= 6$ at the colour transition point as assumed by Wänninen and Ringbom for the aluminium titration. The titration error does not exceed $\pm 0.06\%$ in the concentration range 0·05–0·001 M.

Titration of excess EDTA in the presence of the aluminium complex

If an excess of EDTA is added to an aluminium solution and the pH is adjusted to the appropriate value, the complex AlY^- is formed quantitatively. Titrating the

TABLE I.—ERROR CALCULATED ON TITRATION OF
EDTA WITH ZINC SOLUTION

$pZnY^{2-}$ at equiv. point	Δ_{EDTA}, %
1·3	−0·03
1·6	−0·03
2·0	−0·02
2·3	−0·01
2·7	+0·03
3·0	+0·06
3·3	+0·2
3·7	+0·5
4·0	+1·0
5·0	+10

excess of EDTA with zinc in order to determine the amount of EDTA consumed by the aluminium will, according to Wänninen and Ringbom, give an error of

$$\Delta_{Al}, \% = \frac{\sum\limits_{i=0}^{4} [H_iY] - [Al^{3+}] - [Zn^{2+}]}{[AlY^-]} \cdot 100$$

which can be calculated from the equations and data given by these authors. Results for some extreme cases of such a calculation are given in Table II; the conditions at the colour transition point are assumed to be pH $= 4.5$ and pZn $= 6$. The calculated titration error is considerable with a small excess of EDTA $i.e.$ low concentration of ZnY^{2-}, at the equivalence point.

The above calculation involves the pre-requisite that the solution equilibrium really adjusts itself. However, as there is reason to assume that AlY^- reacts very slowly it may, as a second hypotheses, be proposed that AlY^- is completely indifferent. In the equation for the titration error $[Al^{3+}]$ will, then, not represent the concentration at the end-point, but the concentration in equilibrium with the added excess of EDTA on formation of AlY^-. This concentration, however, is, under the experimental conditions of Table II, sufficiently small to be neglected and the equation for the titration error will be

$$\Delta_{Al}, \% \,(AlY^- \text{ indiff.}) = \frac{\sum\limits_{i=0}^{4} [H_iY] - [Zn^{2+}]}{[AlY^-]} \cdot 100$$

i.e. the titration error with changed sign will be the same as for titration of EDTA with zinc, calculated on the amount of aluminium. Some calculated results, for extreme cases, are given in Table II.

To decide which of these two hypotheses comes nearest to the truth, the titrations presented in Table II were carried out. The results show that the aluminium complex behaves as an indifferent substance within the limits of experimental error.

TABLE II.—TITRATION OF ALUMINIUM AT VARIOUS EXCESSES OF EDTA

excess EDTA added		Zn con- sumed, mmoles	Al		Error, %		
%	mmoles		found, mmoles	added, mmoles	found	calcd. accd. to W. and R.	calcd. with Al-complex indifferent
Titrations performed with 0·1M solutions							
1	1·0127	0·0121	1·0008	1·0015	−0·07	−2·5	−0·01
1	1·0104	0·0093	1·0011	1·0021	−0·10	−2·5	−0·01
20	1·2037	0·1986	1·0051	1·0055	−0·04	−0·007	+0·006
20	1·1975	0·1944	1·0031	1·0042	−0·11	−0·007	+0·006
20	1·2027	0·1997	1·0030	1·0035	−0·05	−0·007	+0·006
28	1·1320	0·2458	0·8862	0·8866	−0·05		
40	2·5121	0·7255	1·7866	1·7867	−0·01		
49	2·0015	0·6609	1·3406	1·3409	−0·02		
68	1·4990	0·6033	0·8957	0·8956	+0·01		
73	0·3074	0·1297	0·1777	0·1779	−0·11		
100	1·9970	0·9941	1·0029	1·0048	−0·19	+0·04	+0·007
100	2·0053	1·0058	0·9995	1·0011	−0·16	+0·04	+0·007
100	2·0116	1·0067	1·0049	1·0062	−0·13	+0·04	+0·007
134	1·0509	0·6018	0·4491	0·4494	−0·07		
159	0·5041	0·3093	0·1948	0·1946	+0·10		
Titrations performed with 0·01M solutions							
1	0·10086	0·00084	0·10002	0·09995	+0·07	−25	−0·1
1	0·10073	0·00086	0·09987	0·09979	+0·08	−25	−0·1
11	0·11126	0·01072	0·10054	0·10049	+0·06		
20	0·12003	0·01973	0·10030	0·10027	+0·03	−1·1	−0·08
20	0·11979	0·01923	0·10056	0·10050	+0·06	−1·1	−0·08
21	0·06068	0·01052	0·05016	0·05013	+0·06		
44	0·03041	0·00921	0·02120	0·02117	+0·15		
51	0·15031	0·05040	0·09991	0·09985	+0·06		
100	0·19993	0·09992	0·10001	0·10009	−0·08	−0·3	−0·02
101	0·10056	0·05054	0·05002	0·05001	+0·02		
145	0·05062	0·02999	0·02063	0·02064	−0·05		

The accuracy and precision obtained were as follows: For the titration of 2–0·2 millimoles of aluminium by 0·1M solutions, the mean yield is 99·93% with a standard deviation of 0·072; for the titration of 0·1–0·02 millimoles of aluminium, the mean yield is 100·04% with a standard deviation of 0·063.

The deviation of the mean yield from 100% may be due to an error in the standardisation of EDTA against zinc; also, a difference in purity of the zinc and aluminium preparations used may add to the errors. In practice it is better to standardise

the EDTA solution against high purity aluminium and use a zinc sulphate solution, standardised against the EDTA solution, for back titration. The bias of the yield will then disappear.

DISCUSSION

EDTA reacts very slowly with the hydroxo complexes of aluminium. Hence, it is essential, as Wänninen and Ringbom found, to add the EDTA before the buffer; the opposite causes low results. Milner and Woodhead boil the solution to speed up the formation of AlY^-. Observations in this laboratory have shown, moreover, that care must be exercised when any excess of acid is neutralised with ammonia; local excesses of ammonia obviously form slowly reacting hydroxo complexes. A reliable

TABLE III.—10 ML $0.1M$ Al-EDTA COMPLEX WITH
ABOUT 10% EXCESS OF EDTA TITRATED WITH $0.1M$
ZINC AT VARIOUS pH-VALUES.

pH before addn. of ethanol	Zinc soln. consumed, ml	Colour of indicator before colour change
4·4	1·044	Greyish-violet
4·7	1·046	
5·0	1·057	Brownish-yellow
5·5	1·078	
6·0	1·100	Intensely yellow
6·7	1·105	

method is to add ammonia to about pH 2 (thymol blue), then boil, add the buffer dropwise and keep the solution hot for 2 minutes before cooling it. The faint yellow colour of thymol blue does not interfere with the titration.

Variations of pH within the range 4·4–5·0 in the titration, do not cause any serious error, as will be seen from Table III. The colour change is not quite as sharp at higher pH values as in the range mentioned. The small additional consumption of zinc at higher pH may be due to the formation of aluminium hydroxo complexes combined with liberation of EDTA. Wänninen and Ringbom, on account of this assumption, are of the opinion that the titration will give poor results at higher pH values. However, in this case also, the inertness of the AlY^- is advantageous.

A saturated solution of dithizone in 95% ethanol was found to be about $0.0005M$; hence, a concentration of $0.0004M$ for the indicator solution was considered appropriate. Of this solution 2·5 ml (0·001 millimole of dithizone) were used per 100 ml, a larger amount giving too strongly coloured a solution. Titration of this amount of dithizone with $0.001M$ zinc solution indicated that the colour change most obvious to the eye occurs at a zinc consumption of about 0·12 ml, *i.e.* $\frac{1}{4}$ of the indicator has been consumed for the formation of $ZnDz_2$. Thus, this amount, 0·00012 millimole, has been subtracted from zinc consumed in the titrations as indicator correction.

The above circumstances lead to a pZn at the end-point deviating somewhat from that calculated according to Wänninen and Ringbom. It seems, however, to be of little value to recalculate the errors, as the equilibrium constants in the water-ethanol mixture are not known with sufficient accuracy.

Zusammenfassung—Bei der indirekten komplexometrischen Titration von Aluminium nach der Methode von Wänninen und Ringbom verhält sich der AlY⁻-Komplex als indifferente Substanz, wodurch der berechnete Titrationsfehler wesentlich herabgesetzt wird. Titrationen von 0.02-2 Millimolen Aluminium unter Verwendung wechselnden Mengen überschüssiger ÄDTA und mit Zink als Urtitersubstanz ergaben Genauigkeiten von 99.93 % (Titrator 0.1 m) und 100.04 % (Titrator 0.01 m). Die entsprechenden Standardabweichungen waren 0.072 bzw. 0.063. Einige die Methode betreffende Gesichtpunkte werden diskutiert.

Résumé—Dans le titrage en retour de l'aluminium par le complexon selon le procédé de Wänningen et Ringbom, le complexe AlY⁻ se comporte comme une substance indifférente, réduisant considérablement l'erreur de titrage calculée. Actuellement, les titrages de 2 à 0,02 millimoles d'aluminium, avec des excès variables d'EDTA et avec le zinc comme substance étalon fournissent un rendement moyen de 99,93 pour cent (réactif titrant 0,1 M) et 100,04 pour cent (réactif titrant 0,01 M) avec un écart-type de 0,072 et 0,063 respectivement. On discute quelques caractéristiques de la méthode.

REFERENCES

[1] E. Wänninen and A. Ringbom, *Analyt. Chim. Acta*, 1955, **12**, 308.
[2] G. W. C. Milner and J. L. Woodhead, *Analyst*, 1954, **79**, 363.

LETTER TO THE EDITOR

SIR,

IN his letter headed "An Appeal" which appeared in the February edition of *Talanta* A. A. Moss makes a specific if incomplete reference to a paper which appeared in *The Analyst*. Despite the incompleteness of the reference I, and I presume others, must conclude that the paper is mine.[1]

I question his good taste in illustrating a general point by a specific reference, since the incompleteness does little to mask the identity of the author. Of more importance however, this isolated and selected reference leaves the reader with the impression, intended or otherwise, that my method is one of the inferior and suspect ones to which he refers.

A. A. Moss has presumably found that sodium peroxide gains in weight due to the absorption of water and carbon dioxide. This rate of increase is small, approximately 0.0002 g in 20 secs, but the purpose in quoting the weight of peroxide to four places of decimals was to emphasise the importance of weighing the amount as accurately as the material and balance would allow since the acidity of the final solution is important. The whole of my instructions were aimed at maintaining as tight a control over the operations as possible and a note to this effect was added. Surely nothing slipshod here!

I am willing to demonstrate in my own laboratory, where this method is in routine use, that even in inexpert hands it will give the results claimed for it providing the instructions are closely followed.

I am in sympathy with some of the aims of the appeal but I would suggest humility as the correct approach to the testing of other people's work; it does not follow that a method should be rejected or criticised if one person cannot obtain reliable results, as anyone who has served on an Analysis Committee will know.

Finally, I think it will be unfortunate if papers are to be delayed or rejected on grounds of style or presentation as original ideas however badly expressed are still useful.

Yours faithfully,

S. GREENFIELD.

Analytical Methods Section
Research Laboratory.
Albright and Wilson (Mfg) Ltd.
Oldbury, Birmingham, England

REFERENCES

[1] S. Greenfield, *Analyst*, 1959, **84**, 380.

BOOK REVIEWS

The Analysis of Titanium and Its Alloys. Third edition. Imperial Chemical Industries Limited, London, S.W.1. 1959. Pp. 119. 21s.

THE appearance of a third edition of this useful work is evidence of the popularity of the first two editions and of the steadily increasing interest in the metallurgy of titanium.

This latest edition retains the same clear format as previously, but there are significant changes in the contents which reflect the considerable amount of research work which has obviously preceded publication. This is also shown in the wealth of detail and ancillary data included.

The inclusion of a figure for the standard deviation of each method is a praiseworthy feature, which is regrettably absent in many works of this type.

Prominent amongst the many additional and alternative methods are the replacement of the turbidimetric method for chloride determination by a much more elegant amperometric method, and the inclusion of a method for determination of boron. Another welcome addition is the colorimetric determination of small amounts of nitrogen, which is of particular importance in view of the influence exerted by small traces of this element on the metallurgical properties of titanium.

Refinements of methods previously described include a gas pressure method for routine carbon determination; a differential absorptiometric procedure for large amounts of molybdenum in presence of tungsten; an additional colorimetric method for copper, using the well tried diethyl dithiocarbamate; and a technique for phosphorus determination at low levels.

As in previous editions, there is a section covering sampling of the various forms of titanium metal, while an additional most useful chapter is devoted to the identification of titanium alloys by means of simple and rapid spot tests, employing a virtually non-destructive technique on the metal surface.

This third edition forms an essential part of the literature on the analysis of titanium and its alloys. It is strongly recommended to all workers in this field.

J. BURGESS

Chemical Analysis, Volume 9: Analytical Chemistry of Titanium Metals and Compounds. MAURICE CODELL. Pp. 378. Interscience Publishers, New York, 1959. $12.00.

THE rapid growth of the titanium industry has made it necessary to analyse a great many titanium-containing materials. Performance of such analyses has been hampered by the scattered sources for such information throughout the scientific literature. This book is designed to overcome this difficulty by providing a compact source for this wide spread information.

Unpublished laboratory reports as well as scientific journals have been used to compile this authoritative summary. Doubtful procedures have been tested to insure reliability. By intelligent modification of the principles presented in this book, analytical chemists should be able to analyse any titanium-containing sample.

The first 101 pages deal with the fundamental chemistry of titanium, the sampling and separation problems encountered with titanium-containing materials, emission spectrographic and vacuum-line methods for analysing various substances in titanium-rich materials, and procedures for determining titanium.

The remainder of the book is devoted to the analysis of metals and non-metals in titanium and titanium alloys, and to the analysis of titanium-base materials. Detailed information concerning

the various procedures for determining a specific element are presented and thoroughly discussed. An evaluation of alternative methods is given, along with statements about the suitable range and interferences of each method. This will simplify the selection of suitable methods for a particular sample.

There is a bibliography of 233 references. However, the more recent literature, including 1958, is not satisfactorily covered.

The writing throughout the book is simple and direct, making many of the highly technical sections relatively easy to understand. This book is essential reading for the chemist with analytical problems involving titanium, and adequately fills a void that had existed in this field.

F. H. FIRSCHING

Optics and Spectroscopy, Vol. VI, No. 1. The Optical Society of America, National Bureau of Standards, Washington, 25, D.C., U.S.A. Jan. 1959. Pp. 84. Single copy price $3.00.

THIS is the first issue of the translated version of the Russian journal *Optika i Spektroskopiia* which is published monthly in two volumes a year. This journal is being translated on the initiative of the Optical Society of America and the translation, together with the Journal of the Optical Society of America, will be received by all members and subscribers of the Society.

Articles in this issue, the translation of the first number of the sixth volume of the Russian journal, cover a variety of subjects including theoretical and experimental studies of the optical properties of crystals, experimental studies of the temperature of sparks, studies of fluorescence—*e.g.* of poly-styrene excited by electron bombardment, and several studies of the electronic and vibrational spectra of fairly complicated compounds of mainly chemical interest.

In this issue there were no articles on spectroscopic or other optical instruments and most of the articles would normally be classified as physical chemistry or chemical physics. This may, however, be an accidental characteristic of this particular issue.

The translation seems well done and few errors were noticed. The type size used in the theoretical papers is at times uncomfortably small.

DAVID PULLIN

Reactor Technology, Report No. 10. Chemistry. A.E.C. Research and Development Report KAPL-2000-7. Office of Technical Services, Department of Commerce, Washington 25, D.C., U.S.A. *September* 1959. Pp. x + 62. $2.00.

THIS document is one of a series of progress reports, the stated aim of which is to keep industry informed of unclassified developments in the various fields of reactor technology. The subject matter is discussed under five headings, analytical chemistry, spectroscopy, radiochemistry, physical chemistry and corrosion and coolant chemistry. The material presented will be of general interest to analysts associated with atomic energy work, but to analysts in other fields the usefulness is mainly restricted to the sections on analytical chemistry (analysis of zirconium and niobium-based materials) and spectroscopy (isotopic analysis of uranium and boron by mass spectrometry and emission spectrographic analysis of zirconium and stainless steel).

J. K. FOREMAN

NOTICES

The following meetings have been arranged:

Thursday 12 *May* 1960: **Society for Analytical Chemistry,** Midlands Section. Mr. D. HOLNESS: *Applications of Gas-Liquid Chromatography in the Analysis of Essential Oils.* Gas Showrooms, Nottingham, England, 7.0 p.m.

Friday 13 *May* 1960: **Society for Analytical Chemistry,** North of England Section and Microchemistry Group. *Corrosion.* Hull, England.

Friday 20 *May* 1960: **Society for Analytical Chemistry,** Western Section and Physical Methods Group. *Atomic Absorption Spectroscopy.* Conference Room, Municipal Building, Poole, England, 6.30 p.m.

Friday 27 *May* 1960: **Society for Analytical Chemistry,** Western Section. **Royal Institute of Chemistry,** South Western Section. Dr. W. H. N. COOPER: *Trace Elements in Sea Water.* Plymouth.

Wednesday–Friday 8–10 *June* 1960: **Society for Analytical Chemistry, Institute of Petroleum:** Discussion Group of the Hydrocarbon Research Group. Symposium on *Gas Chromatography.* Assembly Rooms, Edinburgh, Scotland.

Wednesday 22 *June* 1960: **Society for Analytical Chemistry,** Microchemistry Group. London Discussion Meeting, "The Feathers", Tudor Street, London, E.C.4. 6.30 p.m.

The eighty-sixth Annual General Meeting of the Society for Analytical Chemistry was held at the Queen's Hotel, Birmingham, on Wednesday 2 March 1960, with the President, Mr. R. C. CHIRNSIDE in the Chair. The following Officers and Members of Council were elected for the forthcoming year:

President:	R. C. CHIRNSIDE
Past Presidents serving on the Council:	J. W. HAMENCE, D. W. KENT-JONES, J. R. NICHOLLS, K. A. WILLIAMS
Vice-Presidents:	D. C. GARRETT, MAGNUS A. PYKE, J. G. SHERRATT
Hon. Treasurer:	A. J. AMOS
Hon. Secretary:	R. E. STUCKEY
Hon. Assistant Secretaries:	L. BREALEY (Programmes), S. A. PRICE
Other Members of Council:	N. L. ALLPORT, D. M. W. ANDERSON, B. BAGSHAWE, E. BISHOP, H. E. BROOKES, C. H. R. GENTRY, E. Q. LAWS, W. M. LEWIS, R. F. MILTON, F. C. J. POULTON, C. WHALLEY, J. T. YARDLEY.
Ex-Officio Members:	J. R. EDISBURY (Chairman, North of England Section), A. N. HARROW (Chairman, Scottish Section), G. V. JAMES (Chairman, Western Section), S. H. JENKINS (Chairman, Midlands Section), F. HOLMES (Chairman, Microchemistry Group), G. W. C. MILNER (Chairman, Physical Methods Group), J. I. M. JONES (Chairman, Biological Methods Group).

The Meeting was followed immediately by the sixth Bernard Dyer Memorial Lecture, given by Professor A. C. FRAZER, M.B., B.S., Ph.D., D.Sc., F.R.C.P., M.D., Professor of Medical Biochemistry and Pharmacology in the University of Birmingham. Professor FRAZER's subject was *Chemical Analysis and Medical Progress.*

The sixteenth Annual General Meeting of the Microchemistry Group of the Society for Analytical Chemistry was held on Friday 19 February 1960 in the Postgraduate Medical School, Ducane Road, London, W.12. The chair was taken by the Chairman of the Group, Mr. F. HOLMES.

The following were elected Officers of the Group for the forthcoming year:

Chairman:	Mr. F. HOLMES
Vice-Chairman:	Mr. C. WHALLEY
Hon. Secretary:	Mr. D. W. WILSON, Sir John Cass College, Jewry Street, Aldgate, London, E.C.3.
Hon. Treasurer:	Mr. G. INGRAM.

The fifth Annual General Meeting of the Midlands Section of the Society for Analytical Chemistry was held on Wednesday 23 March 1960 in the Technical College, Nottingham. The Chairman of the Section, Dr. S. H. JENKINS, F.R.I.C., F.Inst.S.P., presided.

The following were elected Officers of the Section for the forthcoming year:

Chairman:	Dr. S. H. JENKINS
Vice-Chairman:	Dr. H. C. SMITH
Hon. Secretary:	Mr. G. W. CHERRY, 48, George Frederick Road, Sutton Coldfield, Warwickshire, England.
Hon. Treasurer:	Mr. F. C. J. POULTON
Hon. Asst. Secretary:	Mr. R. ADKINS.

The Chemical Society of London is co-operating with the British Department of Scientific and Industrial Research in providing complete translations of the *Russian Journal of Inorganic Chemistry* (from Jan. 1959), the *Russian Journal of Physical Chemistry* (from July 1959), and *Russian Chemical Reviews* (from Jan. 1960). Subscription rates per annum for the first two of these are (beginning with the Russian January issue) £30 or $90, with a reduction of 25 per cent for College or University Libraries. The price for the first six issues of the *Russian Journal of Physical Chemistry* is *pro rata.* The subscription rate for *Russian Chemical Reviews* per annum is £12 or $36 (£9 or $27 for College or University Libraries.)

The world distributors of these Journals are Cleaver-Hume Press Ltd., 31, Wright's Lane, London, W.8, who can supply full information and specimen sections.

PAPERS RECEIVED

Radio-frequency methods in analytical chemistry: M. F. C. LADD and W. H. LEE. (2 *March* 1960).

A new procedure in the low-temperature wet oxidation of organic compositions: Perchloric and periodic acids as oxidants: The "Periodic acid liquid fire reaction". G. FREDERICK SMITH and HARVEY DIEHL. (9 *March* 1960).

The estimation of the stabilities of bivalent transition metal complexes and deviations from the Irving-Williams order: D. L. LEUSSING. (11 *March* 1960).

Liquid-liquid extraction of iron^{III} with tributylphosphate: Separation from mixtures: SANTOSH K. MAJUMDAR and ANIL K. DE. (14 *March* 1960).

UV Spectrophotometric determination of trace amounts of selenium with *o*-phenylenediamine: HISAE ARIYOSHO, MICHIO KINIWA and KYOJI TOEI. (14 *March* 1960).

Organic analysis, XXVI: Determination of reducing sugars with 3:6-dinitrophthalic acid: TSUTOMU MOMOSE, YOSHIKO MUKAI and MITSUKO WATANABE. (15 *March* 1960).

Thiazolyl analogues of 1-(2-pyridylazo)-naphthol: V. SVOBODA. (18 *March* 1960).

Amperometric determination of glucose, fructose and saccharose without additional external voltage: E. MICHALSKI, K. CZARNACKI and M. IGNACZEK. (18 *March* 1960).

Analytical applications of 3-acetyl-4-hydroxycoumarin—II: Spectrophotometric determination of iron^{II}: A. N. BHAT and B. D. JAIN. (18 *March* 1960).

Applications of metallochromic indicators in colorimetry—I: Spectrophotometric determination of minute amounts of copper with analogues of glycine thymol blue. M. KOCH, V. SVOBODA and J. KÖRBL. (23 *March* 1960).

Lithium chloride in non-aqueous potentiometric titrations: E. L. GROVE. (26 *March* 1960).

PUBLICATIONS RECEIVED

Modern Methods of Analysis of Copper and its Alloys: CHARLES M. DOZINEL. Translated by GEORGE R. ANDRASO. Ets. Georges Thone, Liege, 1960. Pp. 239. $32.00.

Instrumental Methods of Chemical Analysis, 2nd Edition. GALEN W. EWING. McGraw-Hill Publishing Co., London: McGraw-Hill Book Co., Inc., New York, 1960. Pp. viii + 454. 69s.

Quantitative Inorganic Analysis, 2nd Edition. R. BELCHER and A. J. NUTTEN. Butterworths Scientific Publications, London, 1960. Pp. x + 390. 35s.

Separation and Identification of Food Colours permitted by the Colouring Matters in Food Regulations, 1957. Association of Public Analysts, Bank Chambers, 16, Southwark Street, London, S.E.1, 1960. Pp. vi + 31. 21s.

Heterometry. M. BOBTELSKY. D. Van Nostrand Company, Ltd., London: Elsevier Publishing Company, Amsterdam, 1960. Pp. viii + 229. 42s.

Automatic Titrators. J. P. PHILLIPS. Academic Press Inc., New York, 1959. Pp. viii + 225. $6.00.

NOTES FOR CONTRIBUTORS

1. General

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

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

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

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

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

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

2. Script Requirements

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

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

3. Summaries will not be required for short or preliminary communications. For other contributions the essential contents of each paper should be briefly recapitulated in a summary at the beginning of the paper. This should be in the language of the paper, but for German or French papers an English version should also be provided wherever possible. Summaries of papers will be printed in all three languages, and authors who are able to provide translations of their summaries are asked to do so.

4. Illustrations should be separated from the typescript of the paper and legends should also be typed on a separate sheet. Line drawings which require redrawing should include all relevant details and clear instructions for the draughtsman. If figures are already well drawn, it may be possible to reproduce them direct from the originals, or from good photoprints, if these can be provided; it is not possible to reproduce from prints with weak lines. Illustrations for reproduction should normally be about twice the final size required. The lettering should be sufficiently large and bold to permit this reduction. The following standard symbols should be used on line drawings, since they are easily available to the printers:

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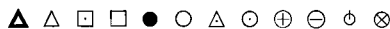
5. Tables should if possible be so constructed as to be intelligible without reference to the text, every table and column being provided with a heading. Units of measure must always be clearly indicated. Unless it is essential to the argument, tables should not list the results of individual experiments, but should summarise results by an accepted method of expression, e.g., standard deviation. The same information should not be reproduced in both tables and figures.

6. References should be indicated in the text by consecutive superior numbers; and the full reference, including title of paper where desired, should be given in a list at the end of the paper in the following form:

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

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

7. Except in the case of preliminary communications, proofs will be sent to authors for correction when their contribution is first set, but there is rarely time for page proofs also to be sent for checking. This will be done, however, when the amount of alteration makes it advisable.

8. Because of the international character of the Journal, no rigid rules concerning spelling, notation or abbreviation need be observed by authors, but each paper or series of papers should be self-consistent as to symbols and units.

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