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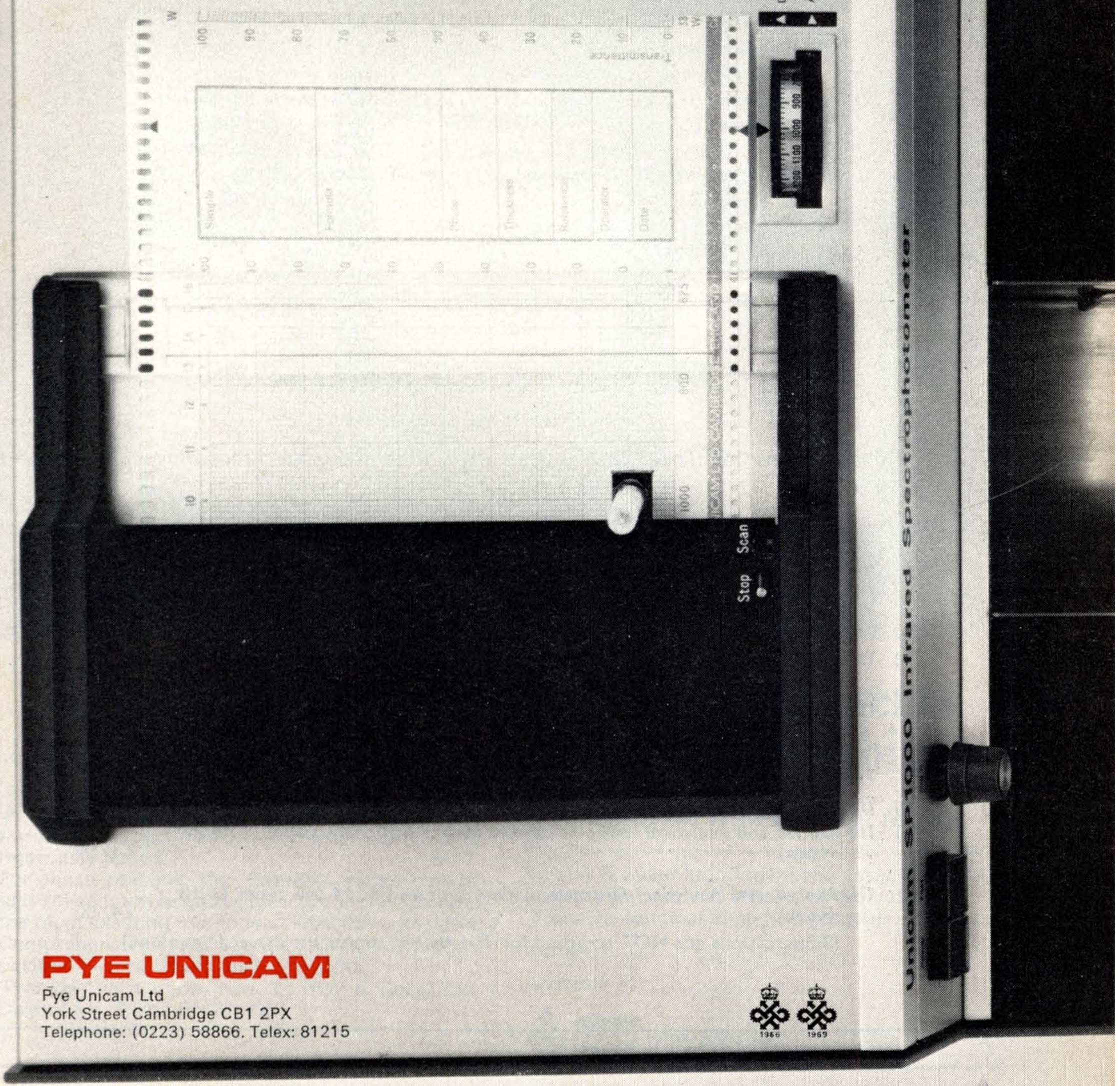
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Mass and Charge Transfer Kinetics and Coulometric Current Efficiencies

Part III. Pattern Theory and its Application to Oxidation - Reduction Electrode Processes

Electrode processes are divided into three classes on the basis of the speed of the charge-transfer process: fast, which are fully described by mass-transfer theory; moderate, which require the complete rigorous mass *plus* charge-transfer theory; and slow, which can be treated rigorously by a simplified theory. This simplified theory is developed into pattern theory, from which pattern equations are derived that are explicitly descriptive of the behaviour pattern of slow reactions and demonstrate the involvement of mass-transfer processes therein. From pattern theory, methods based upon voltammetric scans are developed for the rapid experimental determination of k and α when the conditional potential and limiting current are measurable and also when either or both are unknown. These methods are applicable *in situ* during a coulometric determination, and current efficiencies can be evaluated from the values obtained. Calculated and experimental scans and efficiencies show excellent agreement.

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Analyst, 1972, **97**, 761–771.

Mass and Charge Transfer Kinetics and Coulometric Current Efficiencies

Part IV. The Application of Pattern Theory to Solvent-molecule and Solvent-ion Reactions and the Evaluation of Current Efficiencies

The previously developed pattern theory has been applied to background reactions of the solvent and its ions, with water used as the example. Pattern and behaviour equations are developed and discussed, and methods are described for the rapid *in situ* determination of charge-transfer coefficients and conditional rate constants when a limiting current is known and when it is not, for the reduction of hydrogen ions and water molecules and for the oxidation of hydroxyl ions and water molecules. The voltammetric behaviour of these reactions is rationalised and the determination of coulometric current efficiencies and regulation of conditions to attain the best current efficiency are discussed.

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Analyst, 1972, **97**, 772–782.

Thermometric Determination of Acid Anhydrides in the Presence of the Parent Acids

A thermometric method is described for the determination of some carboxylic acid anhydrides. The anhydride is added to a methanolic solution of morpholine and the unreacted morpholine is titrated with a methanolic solution of hydrochloric acid. In most instances, the presence of large amounts of the parent acid has no effect on the determination and for 0·5 mmol of anhydride the accuracy is about ±1 per cent.

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Analyst, 1972, **97**, 783–786.

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THE ANALYST

Mass and Charge Transfer Kinetics and Coulometric Current Efficiencies

Part III.* Pattern Theory and its Application to Oxidation - Reduction Electrode Processes

By E. BISHOP

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Electrode processes are divided into three classes on the basis of the speed of the charge-transfer process: fast, which are fully described by mass-transfer theory; moderate, which require the complete rigorous mass *plus* charge-transfer theory; and slow, which can be treated rigorously by a simplified theory. This simplified theory is developed into pattern theory, from which pattern equations are derived that are explicitly descriptive of the behaviour pattern of slow reactions and demonstrate the involvement of mass-transfer processes therein. From pattern theory, methods based upon voltammetric scans are developed for the rapid experimental determination of k and α when the conditional potential and limiting current are measurable and also when either or both are unknown. These methods are applicable *in situ* during a coulometric determination, and current efficiencies can be evaluated from the values obtained. Calculated and experimental scans and efficiencies show excellent agreement.

FOR coulometric determinations of high efficiency, whether potentiostatic or amperostatic, such as are viable in standards work and absolute coulometry, it is extremely difficult experimentally to determine the precise separation or current efficiency loss when this is in the parts per million region. It is both simpler and more accurate to calculate efficiencies or efficiency losses from the mass and charge-transfer rate parameters determined *in situ* under the exact experimental conditions of the coulometric process. To this end, a mathematical theory of electrode processes for any number of oxidation - reduction reactions or ion-combination reactions together with the simultaneous solvent-molecule and solvent-ion reactions has been developed within the practical context.[1] The theory is completely rigorous and has been programmed for a digital computer. Prolonged computer exploration has permitted the identification of the influential parameters and the study of the effects of their variation.[2] From this study two distinct patterns of behaviour emerged, mass transfer alone and charge transfer alone; and three regions of conditions could be distinguished, according to the speed of the electrode processes.

(*a*) *Fast reactions*—When the charge-transfer overpotential, η_a, is experimentally insignificant, say less than 1 mV throughout the current - potential graph, then the voltammetric behaviour and the reaction rate (the conditional mass-transfer rate constant) required in the calculation of current efficiency are fully described by mass-transfer theory and the concentration term, η_c, is alone significant. For the simpler reactions the behaviour is revealed by mere inspection of the equations.[1]

(*b*) *Moderate reactions*—A boundary or transition region exists between fast and slow reactions, in traversing which, from fast to slow, the mass-transfer pattern collapses into the charge-transfer pattern and the reverse direction of the electrode reaction loses its influence. Thus, the concentration and diffusion coefficient of the reaction product lose their influence, are "mopped up,"[2] and factors such as the number of electrons transferred, n, the apparent diffusion layer thickness, δx, and the diffusion coefficient of the reactant (that is, the conditional mass-transfer rate constant of the reactant) change their influence. In this region the complete rigorous mass *plus* charge-transfer theory[1] must be used, and charge-transfer rate parameters can be extracted by computer curve fitting,[3] or, less accurately, by Tafel plots, or, better, Lewartowicz[4] or Allen and Hickling[5] plots.

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* For details of Parts I and II of this series, see reference list on p. 771. For Part IV, see p. 772.

(*c*) *Slow reactions*—When the charge-transfer process becomes sufficiently slow, say when $|n\eta_a|$ exceeds about 60 mV and certainly when it exceeds 120 mV, a very regular charge-transfer pattern emerges. In this pattern, the charge-transfer coefficient, α, n and the temperature, T, have a linear effect on potential, and change in value of other parameters, X_1 to X_2, produces a cathodic potential shift of $[2{\cdot}303\ RT/(\alpha nF)]\log_{10}(X_1/X_2)$ or an anodic potential shift of $[2{\cdot}303\ RT/((1-\alpha)nF)]\log_{10}(X_1/X_2)$. Product parameters, such as concentration and diffusion coefficient, are wholly without influence. This region is the charge-transfer "pattern region." If at least part of the voltammetric scan is clear of the terminal region (see below), then the simplified "pattern theory" to be developed gives an adequate, indeed rigorous, treatment that fully describes the charge-transfer behaviour pattern and offers a simple method of determination of the charge-transfer rate parameters required for current efficiency calculations, under the exact conditions of the coulometric determination.

Terminal region—Region (*c*) is bounded by modulation of the shape of the voltammetric graph by the onset of the next reaction in the sequence: for amperostatic intermediates by the solvent reactions; for solvent-ion reactions by solvent-molecule reactions; and for potentiostatic separations by the reaction of the species from which separation is required.

THE REGION BOUNDARIES

The general form of all the charge-transfer equations is[1]

$$\frac{I}{IOS} = \exp\left[\frac{-\alpha nF}{RT}\eta_a\right] - \exp\left[\frac{(1-\alpha)nF}{RT}\eta_a\right] \quad \ldots \quad (1)$$

in which I is the current associated with the particular reaction, and IOS is the analogue of the exchange current when a current is passing through the electrode and an external circuit. For cathodic reactions I is positive and η_a is negative, and

$$\exp\left[\frac{-\alpha nF}{RT}\eta_a\right] \geqslant 1 \text{ and } \exp\left[\frac{(1-\alpha)nF}{RT}\eta_a\right] \leqslant 1 \quad \ldots \quad (2)$$

while for anodic reactions I is negative, η_a is positive and

$$\exp\left[\frac{-\alpha nF}{RT}\eta_a\right] \leqslant 1 \text{ and } \exp\left[\frac{(1-\alpha)nF}{RT}\eta_a\right] \geqslant 1 \quad \ldots \quad (3)$$

When η_a is small, IOS will be very large compared with I, and the difference between the exponential terms in equation (1) will be small. When η_a is large, IOS will be very small compared with I, and one of the exponential terms in equation (1) will be negligible compared with the other. The term less than unity in equation (2) or (3) will, in effect, vanish.

(*a*) *Fast*—The experimental context and the accuracy of measurement of potential will define the value of η_a that can be considered to be insignificant. Let this be ϕ mV: substitution into equation (1) then defines the fast boundary as

$$\frac{I}{IOS} \leqslant \exp\left[\frac{-10^{-3}\,\alpha nF}{RT}\phi\right] - \exp\left[\frac{10^{-3}\,(1-\alpha)nF}{RT}\phi\right] \quad \ldots \quad (4)$$

By substituting the known values of the constants, converting to the base 10, and unding the figures to the correct accuracy at 25 °C—

$$\frac{I}{IOS} \leqslant \text{antilog}_{10}\,(-0{\cdot}017\,\alpha n\phi) - \text{antilog}_{10}\,(0{\cdot}017\,(1-\alpha)n\phi) \quad \ldots \quad (5)$$

For instance, for n = 2, $\alpha = 0{\cdot}5$ and $\phi = 1$ mV, if I is less than 0·66 IOS, the reaction can be presumed to be fast and can be treated by mass-transfer theory.

(*b*) *Moderate*—The upper (fast) boundary is as above, when $\eta_a \leqslant \phi$, and the lower (slow) boundary is when $\eta_a \geqslant \theta$, which will be defined below. Equation (5) defines the upper boundary. The slow boundary is given by

$$\frac{I}{IOS} \leqslant \exp\left[\frac{10^{-3}\,\alpha nF}{RT}\theta\right] - \exp\left[\frac{10^{-3}\,(1-\alpha)nF}{RT}\theta\right] \quad \ldots \quad (6)$$

or, at 25 °C,

$$\frac{I}{IOS} \leqslant \text{antilog}_{10}\,(-0{\cdot}017\,\alpha n\theta) - \text{antilog}_{10}\,(0{\cdot}017\,(1-\alpha)n\theta) \quad \ldots \quad (7)$$

Thus, when $n = 1$, $\alpha = 0{\cdot}5$ and $\theta = 118$ mV, if I is less than 100 IOS, then the reaction is not sufficiently slow to be treated by pattern theory and requires the complete mass *plus* charge-transfer theory.

(*c*) *Slow: pattern region*—If the charge-transfer process is sufficiently slow, one of the terms in equation (1) can be neglected, and the condition can be defined in terms of the experimental error in the measurements of the current in voltammetric scans. Let this be expressed as a percentage error, π.

Cathodic reactions—By applying the condition of an error of π per cent. in the current to equation (1)—

$$\exp\left[\frac{(1-\alpha)\mathrm{n}F}{RT}\eta_{\mathrm{a}}\right] \leqslant \frac{\pi}{100}\exp\left[\frac{-\alpha\mathrm{n}F}{RT}\eta_{\mathrm{a}}\right] \quad \ldots \quad \ldots \quad (8)$$

Therefore

$$\frac{\exp\left[\frac{(1-\alpha)\mathrm{n}F}{RT}\eta_{\mathrm{a}}\right]}{\exp\left[\frac{-\alpha\mathrm{n}F}{RT}\eta_{\mathrm{a}}\right]} \leqslant \frac{\pi}{100}$$

Therefore

$$\exp\left[\frac{\mathrm{n}F}{RT}\eta_{\mathrm{a}}\right] \leqslant \frac{\pi}{100}$$

and

$$\mathrm{n}\eta_{\mathrm{a}} \leqslant \frac{2{\cdot}303\,RT}{F}\log_{10}\frac{\pi}{100} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (9)$$

At 25 °C,

$$\mathrm{n}\eta_{\mathrm{a}} \leqslant 0{\cdot}05916\log_{10}\frac{\pi}{100} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (10)$$

Anodic reactions—By applying the same condition—

$$\exp\left[\frac{-\alpha\mathrm{n}F}{RT}\eta_{\mathrm{a}}\right] \leqslant \frac{\pi}{100}\exp\left[\frac{(1-\alpha)\mathrm{n}F}{RT}\eta_{\mathrm{a}}\right] \quad \ldots \quad \ldots \quad (11)$$

whence, by a simplification similar to that which gave equation (9),

$$\mathrm{n}\eta_{\mathrm{a}} \geqslant \frac{2{\cdot}303\,RT}{F}\log_{10}\frac{100}{\pi} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (12)$$

At 25 °C,

$$\mathrm{n}\eta_{\mathrm{a}} \geqslant 0{\cdot}05916\log_{10}\frac{100}{\pi} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (13)$$

With the sign of η_{a} taken into account, the percentage error, π, in current arising from the simplification will be as follows for the values of $|\mathrm{n}\eta_{\mathrm{a}}|$ and $|I/IOS|$ given below—

$\lvert\mathrm{n}\eta_{\mathrm{a}}\rvert$	$\lvert I/IOS\rvert$	π
0·059 V	10	10 per cent.
0·118 V	10^2	1 per cent.
0·177 V	10^3	0·1 per cent.

Thus, the slow boundary of region (*b*) and the fast boundary of region (*c*), the pattern region, can be set in accordance with the accuracy of the experimental measurements.

USES AND APPLICATION OF PATTERN THEORY

Within the pattern region, explicit algebraic expressions can be written for η_{a}, which serve several purposes. Firstly, they can be transformed into "behaviour" equations that reveal parameter effects by simple inspection. Secondly, they can be used for the extraction of the values of the electrode kinetic parameters from experimental voltammetric scans. Thirdly, the values so obtained under the same conditions and with the same electrodes as those which are to be used in a coulometric determination can be used to calculate current efficiencies under the experimental conditions. Indeed, this process can be carried out at any time during an actual determination, and any change in current efficiency can be detected. If the limiting current, IL, and therefore the mass-transfer rate constant, $D/\delta x$ or one of its variants,[1] and the conditional potential, E_0', of the active system can be obtained or measured, then solutions for the over-all conditional charge-transfer rate constant, k, and α are simple as the method involving the fraction of the limiting current can be applied. If, because of overlapping of waves, the limiting current cannot be measured with adequate accuracy, and/or if, because the exchange current is too small, E_0' cannot be measured, then the arbitrary-current method must be used with due appraisal of its accuracy. Hence, seven derivations are required—

(*a*) the behaviour equation: (*i*) rigorous and (*ii*) simplifications;

(*b*) the solution for α with (*i*) IL known and (*ii*) IL unknown; and

(*c*) the solution for k with (*i*) k_{mass} known, (*ii*) k_{mass} unknown and (*iii*) E_0' unknown.

These are required for two directions of reaction, anodic and cathodic, and for eight reactions: oxidation - reduction with all components soluble, one species insoluble; ion-combination reactions with all components soluble, one species insoluble; solvent-ion reactions, reduction of hydrogen ion, oxidation of hydroxyl ion; and solvent-molecule reactions, oxidation and reduction of water. A full treatment would therefore call for derivation of at least 112 equations, and so it is necessary to be selective. In this paper, the method will be illustrated with reference to oxidation - reduction reactions with all species soluble. This treatment will indicate the process to be applied for the treatment of the simpler ion-combination reactions. The special and, in respect of evaluation of current efficiencies, crucial solvent-ion and solvent-molecule reactions are dealt with in the following paper.

PATTERN THEORY FOR SOLUBLE OXIDATION - REDUCTION SYSTEMS

CATHODIC PROCESSES—

Within the required limits, the second exponential in equation (1) becomes insignificant, and substitution of the expanded value for IOS^1 into the resulting equation gives

$$I = \mathrm{n}FAk\,[\mathrm{Ox}]_{\mathrm{s}}^{(1-\alpha)}\,[\mathrm{Red}]_{\mathrm{s}}^{\alpha}\exp\left[\frac{-\alpha \mathrm{n}F}{RT}\eta_{\mathrm{a}}\right] \quad \ldots \quad \ldots \quad \ldots \quad (14)$$

where A is the area of the electrode and the subscript S denotes the concentration at the electrode surface arising from mass transfer. By taking logarithms—

$$-\frac{\alpha \mathrm{n}F}{RT}\eta_{\mathrm{a}} = \ln\frac{I}{\mathrm{n}FAk\,[\mathrm{Ox}]_{\mathrm{s}}^{(1-\alpha)}\,[\mathrm{Red}]_{\mathrm{s}}^{\alpha}} \quad \ldots \quad \ldots \quad \ldots \quad (15)$$

By solving for η_{a}, converting to the base 10 and separating the terms—

$$\eta_{\mathrm{a}} = -\frac{2{\cdot}303\,RT}{\alpha \mathrm{n}F}\cdot\left\{\log_{10}\frac{I}{\mathrm{n}FA\,[\mathrm{Ox}]_{\mathrm{s}}} + \alpha\log_{10}\frac{[\mathrm{Ox}]_{\mathrm{s}}}{[\mathrm{Red}]_{\mathrm{s}}} - \log_{10}k\right\} \quad \ldots \quad (16)$$

It should be noted that, when multiplied out, the middle term on the right-hand side is η_{c}.[1]

The pattern equation: (i) *rigorous*—It must be emphasised that the limiting current of a reaction is a fictitious quantity that can be attained only when the working electrode potential, E_{we}, is infinitely negative for cathodic reactions or infinitely positive for anodic reactions, and treatments that give it real significance are self-contradictory. However, a close approach to the limiting current is experimentally possible: when $E_{\mathrm{we}} = E_0' + \eta_{\mathrm{a}} \pm 0{\cdot}36$ V, the current is within 1 p.p.m. of the theoretical limiting current. If the limiting current region of a voltammetric scan is reasonably well defined, a reasonably accurate value of IL and therefore of the mass-transfer rate constant can be derived. In this treatment the mass-transfer rate constant will be chosen to be $D/\delta x$, where D is the thermal diffusion coefficient, and this can be obtained from[1]

$$\frac{D_{\mathrm{ox}}}{\delta x} = \frac{IL}{\mathrm{n}FA\,[\mathrm{Ox}]_{\mathrm{B}}} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (17)$$

where the subscript B refers to concentrations in the bulk of the solution, for the cathodic direction of the reaction

$$\mathrm{Ox} + \mathrm{n}\epsilon \underset{i_a}{\overset{i_c}{\rightleftharpoons}} \mathrm{Red} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (18)$$

If the current in equation (16) is expressed as a fraction, f, of the limiting current, then

$$I = \mathrm{f}\, IL \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (19)$$

and by solving for the contact layer concentrations by mass-transfer theory[1] in terms of the fractions of the limiting current—

$$[\mathrm{Ox}]_\mathrm{S} = [\mathrm{Ox}]_\mathrm{B} - \frac{\delta x\, \mathrm{f}\, IL}{\mathrm{n}FAD_\mathrm{ox}} = [\mathrm{Ox}]_\mathrm{B} - \frac{\delta x\, \mathrm{fn}FAD_\mathrm{ox}\,[\mathrm{Ox}]_\mathrm{B}}{\mathrm{n}FAD_\mathrm{ox}\,\delta x} = (1-\mathrm{f})\,[\mathrm{Ox}]_\mathrm{B} \quad \ldots \quad (20)$$

$$[\mathrm{Red}]_\mathrm{S} = [\mathrm{Red}]_\mathrm{B} + \frac{\delta x\, \mathrm{f}\, IL}{\mathrm{n}FAD_\mathrm{red}} = [\mathrm{Red}]_\mathrm{B} + \frac{\delta x\, \mathrm{fn}FAD_\mathrm{ox}\,[\mathrm{Ox}]_\mathrm{B}}{\mathrm{n}FAD_\mathrm{red}\,\delta x}$$

$$= [\mathrm{Red}]_\mathrm{B} + \mathrm{f}\,\frac{D_\mathrm{ox}}{D_\mathrm{red}}[\mathrm{Ox}]_\mathrm{B} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (21)$$

Substitution for I, $[\mathrm{Ox}]_\mathrm{S}$ and $[\mathrm{Red}]_\mathrm{S}$ in equation (16) gives

$$\eta_{\mathrm{a}_\mathrm{f}} = -\frac{2{\cdot}303\,RT}{\alpha \mathrm{n}F}\left\{\log_{10}\frac{\mathrm{fn}FAD_\mathrm{ox}\,[\mathrm{Ox}]_\mathrm{B}}{\mathrm{n}FA\,(1-\mathrm{f})\,[\mathrm{Ox}]_\mathrm{B}\,\delta x} + \alpha\log_{10}\frac{(1-\mathrm{f})\,[\mathrm{Ox}]_\mathrm{B}}{[\mathrm{Red}]_\mathrm{B} + \mathrm{f}\frac{D_\mathrm{ox}}{D_\mathrm{red}}[\mathrm{Ox}]_\mathrm{B}} - \log_{10}k\right\} \quad \ldots \quad (22)$$

$$\eta_{\mathrm{a}_\mathrm{f}} = -\frac{2{\cdot}303\,RT}{\alpha \mathrm{n}F}\left\{\log_{10}\frac{D_\mathrm{ox}}{\delta x} - \log_{10}k + \log_{10}\frac{\mathrm{f}}{(1-\mathrm{f})} + \alpha\log_{10}\frac{(1-\mathrm{f})\,[\mathrm{Ox}]_\mathrm{B}}{[\mathrm{Red}]_\mathrm{B} + \mathrm{f}\frac{D_\mathrm{ox}}{D_\mathrm{red}}[\mathrm{Ox}]_\mathrm{B}}\right\} \quad \ldots \quad (23)$$

Equation (23) is the pattern equation for the particular reaction, and shows that the mass-transfer rate constant, $D_\mathrm{ox}/\delta x$, is directly implicated in the charge-transfer overpotential, which is logarithmically proportional to the ratio of the mass-transfer and charge-transfer rate constants—

$$\eta_\mathrm{a} \propto \log_{10}\left(\frac{\text{mass-transfer rate constant}}{\text{charge-transfer rate constant}}\right) \quad \ldots \quad \ldots \quad \ldots \quad (24)$$

The terms in f define the sigmoid shape of the voltammetric graph, and f represents the portion of the graph that has been traversed. The equation reveals plainly the potential shift of $2{\cdot}303\,RT/(\alpha \mathrm{n}F)$ V for a ten-fold change in D_ox, δx and k and the inverse proportionality to n and α.[2] When the final term of equation (23) is multiplied out it is found to be $-\eta_\mathrm{c}$: this result means that although $[\mathrm{Red}]_\mathrm{B}$ and D_red appear in the expression for η_a, they do so in opposition to their function in the concentration term, η_c, and therefore have no influence on the working electrode potential in the pattern region. If the resistance overpotential is neglected, the working electrode potential, E_we,[1] is given by

$$E_\mathrm{we} = E_\mathrm{o}' + \eta_\mathrm{a} + \eta_\mathrm{c}$$

$$E_\mathrm{we} = E_\mathrm{o}' - \frac{2{\cdot}303\,RT}{\alpha \mathrm{n}F}\left\{\log_{10}\frac{D_\mathrm{ox}}{\delta x} - \log_{10}k + \log_{10}\frac{\mathrm{f}}{(1-\mathrm{f})}\right\} - \eta_\mathrm{c} + \eta_\mathrm{c}$$

$$= E_\mathrm{o}' - \frac{2{\cdot}303\,RT}{\alpha \mathrm{n}F}\left\{\log_{10}\frac{D_\mathrm{ox}/\delta x}{k} + \log_{10}\frac{\mathrm{f}}{(1-\mathrm{f})}\right\} \quad \ldots \quad \ldots \quad \ldots \quad (25)$$

Hence, $[\mathrm{Red}]_\mathrm{B}$ and D_red retain significance in η_a but disappear from E_we and no paradox is presented.

The pattern equation: (ii) *simplifications*—The simplification of equation (25) is not a simplification of $\eta_{\mathrm{a}_\mathrm{f}}$, but is a consequence of the properties of the charge-transfer process and the involvement therein of mass-transfer processes. It is helpful to note some simplifications of equation (23) under particular conditions. When $[\mathrm{Red}]_B = 0$, that is, when a solution of "pure" Ox, free from product, is scanned, then

$$\eta_{a_f} = -\frac{2{\cdot}303\,RT}{\alpha nF}\left\{\log_{10}\frac{D_{ox}/\delta x}{k} + \alpha\log_{10}\frac{D_{red}}{D_{ox}} + (1-\alpha)\log_{10}\frac{\mathrm{f}}{(1-\mathrm{f})}\right\} \quad .. \quad (26)$$

or, if limiting currents could be separately measured for equimolar solutions of Ox and Red under identical stirring conditions, then

$$\eta_{a_f} = -\frac{2{\cdot}303\,RT}{\alpha nF}\left\{\log_{10}\frac{D_{ox}/\delta x}{k} + \alpha\log_{10} - \frac{IL_{red}}{IL_{ox}} + (1-\alpha)\log_{10}\frac{\mathrm{f}}{(1-\mathrm{f})}\right\} \quad .. \quad (27)$$

which shows the influence of the diffusion current ratio and that it opposes the mass-transfer potential shift generated by this term. When $D_{ox} = D_{red}$, which, if tabulated values could be relied upon in an experimental context, is frequently a close approximation, then

$$\eta_{a_f} = -\frac{2{\cdot}303\,RT}{\alpha nF}\left\{\log_{10}\frac{D_{ox}/\delta x}{k} + \log_{10}\frac{\mathrm{f}}{(1-\mathrm{f})} + \alpha\log_{10}\frac{(1-\mathrm{f})\,[\mathrm{Ox}]_B}{[\mathrm{Red}]_B + \mathrm{f}\,[\mathrm{Ox}]_B}\right\} \quad .. \quad (28)$$

Equation (28) again demonstrated that $[\mathrm{Red}]_B$ decreases η_a but increases η_c.

When $[\mathrm{Red}]_B = 0$ and $D_{ox} = D_{red}$, concentration terms vanish and

$$\eta_{a_f} = -\frac{2{\cdot}303\,RT}{\alpha nF}\left\{\log_{10}\frac{D_{ox}/\delta x}{k} + (1-\alpha)\log_{10}\frac{\mathrm{f}}{(1-\mathrm{f})}\right\} \quad .. \quad .. \quad (29)$$

which emphasises the independence of η_{a_f} with respect to $[\mathrm{Ox}]_B$ and electrode area, and reveals the shape and slope of the voltammetric scan—

$$\eta_{a_f} = -\frac{(1-\alpha)}{\alpha}\cdot\frac{2{\cdot}303\,RT}{\mathrm{n}F}\log_{10}\frac{\mathrm{f}}{(1-\mathrm{f})} + \text{constant} \quad .. \quad .. \quad (30)$$

The solution for α*:* (i) *limiting current known*—The potential E at a current $I = \mathrm{f}\,IL$, as in graph 1 in Fig. 1, is given by equation (25) as

$$E_f = E_0' - \frac{2{\cdot}303\,RT}{\alpha nF}\left\{\log_{10}\frac{D_{ox}}{\delta x} + \log_{10}\frac{\mathrm{f}}{(1-\mathrm{f})} - \log_{10}k\right\} \quad .. \quad .. \quad (31)$$

$D_{ox}/\delta x$ can be obtained from the reasonably well defined limiting current plateau of graph 1 in Fig. 1. By taking two points on the scan at currents $\mathrm{f}_1\,IL$ and $\mathrm{f}_2\,IL$ with potentials E_{f_1} and E_{f_2}, substituting into equation (31) and subtracting one from the other, then

$$E_{f_1} - E_{f_2} = \Delta E = \frac{2{\cdot}303\,RT}{\alpha nF}\log_{10}\frac{\mathrm{f}_2}{(1-\mathrm{f}_2)}\cdot\frac{(1-\mathrm{f}_1)}{\mathrm{f}_1} \quad .. \quad .. \quad (32)$$

and, solving for α—

$$\alpha = \frac{2{\cdot}303\,RT}{\Delta E\mathrm{n}F}\log_{10}\frac{\mathrm{f}_2\,(1-\mathrm{f}_1)}{\mathrm{f}_1\,(1-\mathrm{f}_2)} \quad .. \quad .. \quad .. \quad .. \quad (33)$$

If one of the points is chosen as the half-wave potential, $E_{\frac{1}{2}}$, $\mathrm{f} = 0{\cdot}5$, and the other at any value of f, then equation (33) simplifies to

$$\alpha = \frac{2{\cdot}303\,RT}{(E_{\frac{1}{2}} - E_f)\,\mathrm{n}F}\log_{10}\frac{\mathrm{f}}{(1-\mathrm{f})} \quad .. \quad .. \quad .. \quad (34)$$

By taking a random series of pairs of points, a statistically evaluated value for α can be found, and by taking a sequence of pairs of points along the wave any change in α with current density can be detected.[3]

The solution for α*:* (ii) *limiting current unknown*—When α is small, or when the succeeding wave overlaps the sample wave, as in graph 2 in Fig. 1, it may be difficult or impossible to measure the limiting current, and f is unknown so that the method involving the fraction of the limiting current must be replaced by the arbitrary-current method. Conversion of equation (33) back into terms of current gives

$$\alpha = \frac{2{\cdot}303\,RT}{\Delta E\mathrm{n}F}\log_{10}\frac{I_2}{I_1}\cdot\frac{(IL_{ox} - I_1)}{(IL_{ox} - I_2)} \quad .. \quad ... \quad (35)$$

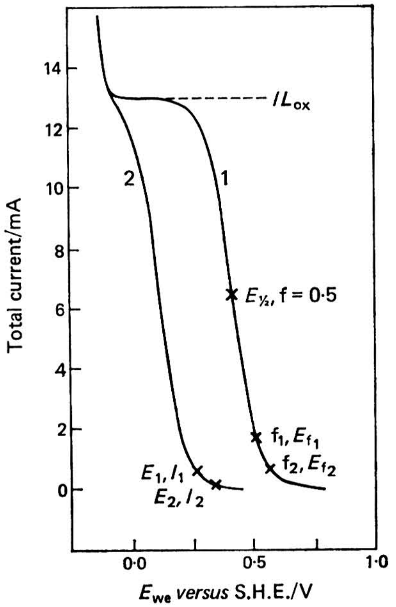

Fig. 1. Cathodic voltammetric scans of systems: (1) showing a well defined limiting current region; and (2) merging with the hydrogen-ion wave and lacking a limiting current region

In equation (35), I_2 and I_1 can readily differ by a factor of 2 to 10, but if they are small compared with the limiting current, as with the points marked on graph 2 in Fig. 1, then $IL_{ox} - I_1$ will not differ significantly from $IL_{ox} - I_2$, and the logarithm of their ratio will be close to zero. If an approximate value for the limiting current can be deduced from the scan, as with graph 2 in Fig. 1, or a guess can be made from the mass-transfer equations[1] of $IL \approx n\,[Ox]_B/3$ A cm^{-2} under conditions of very efficient stirring, then, provided that the condition of equation (10) is satisfied, sufficiently small values of I_1 and I_2 can be chosen to give an approximate value of α from

$$\alpha \approx \frac{2{\cdot}3\,RT}{\Delta E n F}\log_{10}\frac{I_2}{I_1} \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (36)$$

By using a fairly high concentration of Ox and taking the points in the region of 1 to 5 per cent. of the estimated IL, good values for α will be obtained.

The solution for k*:* (i) *Limiting current and* E_o' *known*—Substitution into equation (25) of one of the points $I = f_1\,IL$ and $f_2\,IL$ at E_{f_1} and E_{f_2}, *e.g.*, that at E_{f_1} and the value of α from equation (33), gives

$$E_{f_1} = E_o' - \frac{2{\cdot}303\,RT}{nF}\cdot\frac{\Delta E n F}{2{\cdot}303\,RT\log_{10}\dfrac{f_2\,(1-f_1)}{f_1\,(1-f_2)}}\left\{\log_{10}\frac{D_{ox}/\delta x}{k} + \log_{10}\frac{f_1}{(1-f_1)}\right\}$$

Therefore

$$\frac{E_{f_1} - E_o'}{\Delta E}\log_{10}\frac{f_2\,(1-f_1)}{f_1\,(1-f_2)} = -\log_{10}\frac{D_{ox}}{\delta x} - \log_{10}\frac{f_1}{(1-f_1)} + \log_{10} k$$

and

$$\log_{10} k = \frac{E_{f_1} - E_o'}{\Delta E}\log_{10}\frac{f_2\,(1-f_1)}{f_1\,(1-f_2)} + \log_{10}\frac{f_1}{(1-f_1)} + \log_{10}\frac{D_{ox}}{\delta x} \qquad \ldots \quad \ldots \quad (37)$$

Equation (37) can be evaluated in conjunction with the value of $D_{\mathrm{ox}}/\delta x$ from equation (17). If one of the points is taken at $E_{\frac{1}{2}}$, $\mathrm{f} = 0{\cdot}5$, and the other at E_{f} and f, then equation (37) simplifies to

$$\log_{10} k = \frac{E_{\frac{1}{2}} - E_0'}{E_{\frac{1}{2}} - E_{\mathrm{f}}}\log_{10}\frac{\mathrm{f}}{(1-\mathrm{f})} + \log_{10}\frac{D_{\mathrm{ox}}}{\delta x} \qquad .. \qquad .. \qquad (38)$$

Again, a random series of points will give a statistical appraisal of k, and a sequence of points will reveal any change in k with current density, which again is not an uncommon phenomenon.

The solution for k: (ii) *limiting current unknown*—The same approximations and conditions as those applied in deriving equation (36) can be used, together with the substitution of $IL/(\mathrm{n}FA[\mathrm{Ox}]_{\mathrm{B}})$ for $D_{\mathrm{ox}}/\delta x$, for the point E_1, I_1 on graph 2 in Fig. 1—

$$\frac{E_1 - E_0'}{E_1 - E_2}\log_{10}\frac{I_2}{I_1} = -\log_{10}\frac{IL}{\mathrm{n}FA\,[\mathrm{Ox}]_{\mathrm{B}}} - \log_{10}\frac{I_1}{IL} + \log_{10} k$$

whence

$$\log_{10} k \approx \frac{E_1 - E_0'}{E_1 - E_2}\log_{10}\frac{I_2}{I_1} + \log_{10}\frac{I_1}{\mathrm{n}FA\,[\mathrm{Ox}]_{\mathrm{B}}} \qquad .. \qquad .. \qquad .. \qquad (39)$$

The currents I_1 and I_2 must be small compared with IL.

The solution for k: (iii) E_0' *unknown*—When the exchange current is very small, or when other factors prevent the reproducible measurement of E_0', some other reference potential must be used in equation (38) or (39) for evaluating k. In the first place, the tabulated value, $E^{\ominus}$, the thermodynamic standard potential, could be used to find an effective value of $k_{E^{\ominus}}$, which can be used in current efficiency calculations, just as $E^{\ominus}$ would have to be used when calculating potentials. If no value of $E^{\ominus}$ can be found then the zero of the potential scale, the potential of the S.H.E., could be used and k_0 calculated. If any reference potential other than E_0' is used, this fact should be clearly stated in the results.

ANODIC PROCESSES—

If the limits imposed by equation (13) are observed, equation (6) simplifies to

$$I = -\,\mathrm{n}FAk\,[\mathrm{Ox}]_{\mathrm{S}}^{(1-\alpha)}\,[\mathrm{Red}]_{\mathrm{S}}^{\alpha}\exp\left[\frac{(1-\alpha)\,\mathrm{n}F}{RT}\eta_{\mathrm{a}}\right] \qquad .. \qquad .. \qquad (40)$$

By taking logarithms, converting to the base 10 and solving for η_{a}—

$$\eta_{\mathrm{a}} = +\frac{2{\cdot}303\,RT}{(1-\alpha)\,\mathrm{n}F}\left\{\log_{10}\frac{-I}{\mathrm{n}FA\,[\mathrm{Ox}]_{\mathrm{S}}} + \alpha\log_{10}\frac{[\mathrm{Ox}]_{\mathrm{S}}}{[\mathrm{Red}]_{\mathrm{S}}} - \log_{10} k\right\} \qquad .. \qquad (41)$$

The pattern equation: (i) *rigorous*—With due recollection of the fictitious nature of limiting currents, the anodic direction of reaction (18) gives

$$\begin{aligned} IL_{\mathrm{red}} &= -\,\mathrm{n}FA\,[\mathrm{Red}]_{\mathrm{B}}\frac{D_{\mathrm{red}}}{\delta x} \\ E &\rightarrow +\infty \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \qquad (42) \\ [\mathrm{Red}]_{\mathrm{S}} &\rightarrow 0 \end{aligned}$$

from which the mass-transfer rate constant, $D_{\mathrm{red}}/\delta x$, can be extracted. By using the method involving the fraction of the limiting current, $I = \mathrm{f}\,IL$, and solving for the contact layer concentrations[1]—

$$[\mathrm{Ox}]_{\mathrm{S}} = [\mathrm{Ox}]_{\mathrm{B}} - \frac{-\,\delta x\,\mathrm{fn}FAD_{\mathrm{red}}\,[\mathrm{Red}]_{\mathrm{B}}}{\mathrm{n}FAD_{\mathrm{ox}}\,\delta x} = [\mathrm{Ox}]_{\mathrm{B}} + \mathrm{f}\frac{D_{\mathrm{red}}}{D_{\mathrm{ox}}}\,[\mathrm{Red}]_{\mathrm{B}} \qquad .. \qquad (43)$$

$$[\mathrm{Red}]_{\mathrm{S}} = [\mathrm{Red}]_{\mathrm{B}} + \frac{-\,\delta x\,\mathrm{fn}FAD_{\mathrm{red}}\,[\mathrm{Red}]_{\mathrm{B}}}{\mathrm{n}FAD_{\mathrm{red}}\,\delta x} = (1-\mathrm{f})\,[\mathrm{Red}]_{\mathrm{B}} \qquad .. \qquad .. \qquad (44)$$

Substitution for I, $[\mathrm{Ox}]_s$ and $[\mathrm{Red}]_s$ in equation (41) gives

$$\eta_a = \frac{2{\cdot}303\,RT}{(1-\alpha)\,\mathrm{n}F}\left\{\log_{10}\frac{\mathrm{fn}FAD_{\mathrm{red}}[\mathrm{Red}]_B}{\delta x\,\mathrm{n}FA\left([\mathrm{Ox}]_B + \mathrm{f}\frac{D_{\mathrm{red}}}{D_{\mathrm{ox}}}[\mathrm{Red}]_B\right)} + \alpha\log_{10}\frac{[\mathrm{Ox}]_B + \mathrm{f}\frac{D_{\mathrm{red}}}{D_{\mathrm{ox}}}[\mathrm{Red}]_B}{(1-\mathrm{f})[\mathrm{Red}]_B} - \log_{10}k\right\} \quad .. \quad (45)$$

If, within the braces, the term $+\log_{10}(1-\mathrm{f})$ is added, and then subtracted, the value of equation (45) is unchanged, but the terms can then be arranged into a pattern similar to that in equation (23). The pattern equation is, therefore,

$$\eta_{a_f} = \frac{2{\cdot}303\,RT}{(1-\alpha)\,\mathrm{n}F}\left\{\log_{10}\frac{D_{\mathrm{red}}}{\delta x} - \log_{10}k + \log_{10}\frac{\mathrm{f}}{(1-\mathrm{f})} + (1-\alpha)\log_{10}\frac{(1-\mathrm{f})[\mathrm{Red}]_B}{\left([\mathrm{Ox}]_B + \mathrm{f}\frac{D_{\mathrm{red}}}{D_{\mathrm{ox}}}[\mathrm{Red}]_B\right)}\right\} \quad .. \quad (46)$$

With the exchange of sign, of $(1-\alpha)$ for α, of $[\mathrm{Red}]_B$ for $[\mathrm{Ox}]_B$, and of D_{red} for D_{ox}, equation (46) is the exact complement of equation (23) and reveals the same behaviour, in fact, a mirror image of the cathodic behaviour. The charge-transfer overpotential depends on the ratio of the mass-transfer and charge-transfer rate constants, a ten-fold change in k, D_{red}, or δx produces a potential shift of $2{\cdot}303\,RT/[(1-\alpha)\,\mathrm{n}F]$ V, and η_a is inversely proportional to $(1-\alpha)$ and n. The term in f defines the sigmoid shape of the voltammetric scan. The final term, when multiplied out, is $-\eta_c$, so that although $[\mathrm{Ox}]_B$ and D_{ox} appear in equation (46) they do so in opposition to their function in the concentration term, η_c, and so have no influence on the working electrode potential in the pattern region.

$$E_{\mathrm{we}} = E_0{}' + \frac{2{\cdot}303\,RT}{(1-\alpha)\,\mathrm{n}F}\left\{\log_{10}\frac{D_{\mathrm{red}}/\delta x}{k} + \log_{10}\frac{\mathrm{f}}{(1-\mathrm{f})}\right\} \quad .. \quad .. \quad (47)$$

Equation (47) is not a simplification of the expression for η_a: it is rigorous and underlines the involvement of the mass-transfer process in the charge-transfer overpotential.

The pattern equation: (ii) *simplifications*—When $[\mathrm{Ox}]_B = 0$, that is a "pure" solution of Red initially free from product is used, then

$$\eta_{a_f} = \frac{2{\cdot}303\,RT}{(1-\alpha)\,\mathrm{n}F}\left\{\log_{10}\frac{D_{\mathrm{red}}/\delta x}{k} + \alpha\log_{10}\frac{\mathrm{f}}{(1-\mathrm{f})} - (1-\alpha)\log_{10}\frac{D_{\mathrm{red}}}{D_{\mathrm{ox}}}\right\} \quad .. \quad (48)$$

When $D_{\mathrm{ox}} = D_{\mathrm{red}}$, then

$$\eta_{a_f} = \frac{2{\cdot}303\,RT}{(1-\alpha)\,\mathrm{n}F}\left\{\log_{10}\frac{D_{\mathrm{red}}/\delta x}{k} + \log_{10}\frac{\mathrm{f}}{(1-\mathrm{f})} + (1-\alpha)\log_{10}\frac{(1-\mathrm{f})[\mathrm{Red}]_B}{[\mathrm{Ox}]_B + \mathrm{f}[\mathrm{Red}]_B}\right\} \quad (49)$$

When $D_{\mathrm{ox}} = D_{\mathrm{red}}$ and $[\mathrm{Ox}]_B = 0$, then

$$\eta_{a_f} = \frac{2{\cdot}303\,RT}{(1-\alpha)\,\mathrm{n}F}\left\{\log_{10}\frac{D_{\mathrm{red}}/\delta x}{k} + \alpha\log_{10}\frac{\mathrm{f}}{(1-\mathrm{f})}\right\} \quad .. \quad .. \quad (50)$$

The solution for $(1-\alpha)$*:* (i) *limiting current known*—From equation (47), by taking two points, $I_1 = \mathrm{f}_1\,IL$ at E_{f_1} and $I_2 = \mathrm{f}_2\,IL$ at E_{f_2}, as in the anodic version of graph 1 in Fig. 1, and subtracting—

$$E_{\mathrm{f}_1} - E_{\mathrm{f}_2} = \Delta E = \frac{2{\cdot}303\,RT}{(1-\alpha)\,\mathrm{n}F}\log_{10}\frac{\mathrm{f}_1}{(1-\mathrm{f}_1)}\cdot\frac{(1-\mathrm{f}_2)}{\mathrm{f}_2} \quad .. \quad .. \quad (51)$$

By solving for $(1-\alpha)$—

$$(1-\alpha) = \frac{2{\cdot}303\,RT}{\Delta E\,\mathrm{n}F}\log_{10}\frac{\mathrm{f}_1(1-\mathrm{f}_2)}{\mathrm{f}_2(1-\mathrm{f}_1)} \quad .. \quad .. \quad .. \quad (52)$$

If one of the points is chosen at f = 0·5, then $E_f = E_{\frac{1}{2}}$ and equation (52) simplifies to

$$(1 - \alpha) = \frac{2{\cdot}303\,RT}{(E_{\frac{1}{2}} - E_f)\,\mathrm{n}F} \log_{10}\frac{(1 - \mathrm{f})}{\mathrm{f}} \quad \cdots \quad (53)$$

Random pairs of points will give a statistical evaluation of $(1 - \alpha)$, while a sequence of pairs of points will reveal any change of $(1 - \alpha)$ with current density.

The solution for $(1 - \alpha)$*:* (ii) *limiting current unknown*—The arbitrary-current device, as in graph 2 in Fig. 1, can be used and points E_1, I_1 and E_2, I_2, taken from an anodic scan, give in place of equation (52)

$$(1 - \alpha) = \frac{2{\cdot}303\,RT}{(E_1 - E_2)\,\mathrm{n}F} \log_{10}\frac{I_1\,(IL - I_2)}{I_2\,(IL - I_1)} \quad \cdots \quad (54)$$

and if the currents are chosen to be less than about 5 per cent. of the estimated limiting current, a reasonable approximation is given by

$$(1 - \alpha) \approx \frac{2{\cdot}3\,RT}{(E_1 - E_2)\,\mathrm{n}F} \log_{10}\frac{I_1}{I_2} \quad \cdots \quad (55)$$

The solution for k*:* (i) *limiting current and* $\mathrm{E_0}'$ *known*—From the measured value of IL_{red} and equation (42), the mass-transfer rate constant, $D_{\mathrm{red}}/\delta x$, or a variant of it,[1] can be calculated, and by taking $(1 - \alpha)$ from equation (52) and substituting it into equation (47) for the point E_{f_1} and $I = \mathrm{f}_1\,IL$, the following equation is obtained after the appropriate algebra—

$$\log_{10} k = \log_{10}\frac{D_{\mathrm{red}}}{\delta x} + \log_{10}\frac{\mathrm{f}_1}{(1 - \mathrm{f}_1)} - \frac{E_{f_1} - E_0'}{E_{f_1} - E_{f_2}} \log_{10}\frac{\mathrm{f}_1\,(1 - \mathrm{f}_2)}{\mathrm{f}_2\,(1 - \mathrm{f}_1)} \quad \cdots \quad (56)$$

Again, if one point is the half-wave potential $E_{\frac{1}{2}}$ and f = 0·5, and the other is E_f at $I = \mathrm{f}\,IL$, then

$$\log_{10} k = \log_{10}\frac{D_{\mathrm{red}}}{\delta x} - \frac{E_{\frac{1}{2}} - E_0'}{E_{\frac{1}{2}} - E_f} \log_{10}\frac{\mathrm{f}}{(1 - \mathrm{f})} \quad \cdots \quad (57)$$

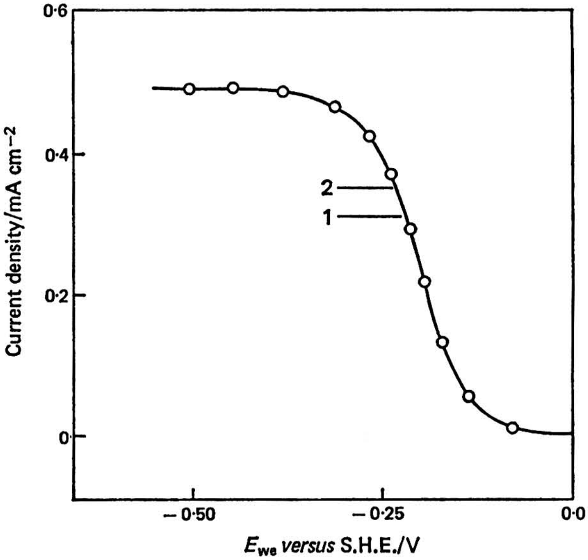

Fig. 2. Voltammetric scan of the generation of tin(II) from tin (IV) in acidic bromide medium. The value of α changes from 0·435 to 0·348 at point 1 and *k* changes from $5{\cdot}1 \times 10^{-9}$ to $3{\cdot}7 \times 10^{-8}$ l cm^{-2} s^{-1} at point 2. The solid line was computed by rigorous theory[1] and the points are experimental values[8]

A random series of points in pairs will afford a statistical evaluation of k, and a sequence will reveal any change in k with current density.

The solution for k: (ii) *limiting current unknown*—The same approximations and conditions as those used in deriving equation (55) can be applied, and if the currents I_1 and I_2 at E_1 and E_2 are small compared with IL_{red}, then for the point E_1, I_1—

$$\log_{10} k \approx \log_{10} \frac{-I_1}{\mathrm{n}FA\,[\mathrm{Red}]_{\mathrm{B}}} - \frac{E_1 - E_0'}{E_1 - E_2} \log_{10} \frac{I_1}{I_2} \quad \ldots \quad \ldots \quad (58)$$

The solution for k: (iii) $\mathrm{E_0}'$ *unknown*—When the conditional potential cannot be measured, k must be referred to some other fixed potential in equation (56) or (58), such as $E^{\ominus}$ or zero, and this fact must be clearly stated in the results.

CONCLUSIONS

The behaviour of oxidation - reduction electrode processes in the pattern region examined by the complete rigorous theory[1] agrees exactly with that predicted by the behaviour equations of pattern theory.[2] Kinetic parameters derived from Tafel (corrected for mass transfer), Lewartowicz[4] and Allen and Hickling[5] methods have been compared experimentally with those calculated by pattern theory and have been found to be in excellent agreement for several quite diverse systems,[3] including some in which α or k, or both, change with current density. Voltammetric graphs computed by the complete rigorous theory[1] from the measured kinetic parameters are completely superimposable on the experimental scans, and computed current efficiencies have agreed closely with experimentally determined current efficiencies. An example is shown in Fig. 2.

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NOTE—References 1 and 2 are to Parts I and II, respectively, of this series.

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Mass and Charge Transfer Kinetics and Coulometric Current Efficiencies

Part IV.* The Application of Pattern Theory to Solvent-molecule and Solvent-ion Reactions and the Evaluation of Current Efficiencies

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The previously developed pattern theory has been applied to background reactions of the solvent and its ions, with water used as the example. Pattern and behaviour equations are developed and discussed, and methods are described for the rapid *in situ* determination of charge-transfer coefficients and conditional rate constants when a limiting current is known and when it is not, for the reduction of hydrogen ions and water molecules and for the oxidation of hydroxyl ions and water molecules. The voltammetric behaviour of these reactions is rationalised and the determination of coulometric current efficiencies and regulation of conditions to attain the best current efficiency are discussed.

THE principles of pattern theory were expounded in the preceding paper,[1] and the boundaries within which it is applicable were derived. The fast limit is when $|n\eta_a| \geqslant |0{\cdot}05916 \log_{10} (\pi/100)|$, where n is the number of electrons transferred, η_a is the charge-transfer overpotential and π is the percentage error of the current measurement. The theory was illustrated by its application to oxidation - reduction reactions with all soluble components, and behaviour equations and solutions for the over-all conditional charge-transfer rate constant, k, and the charge-transfer coefficient, α, from points on a voltammetric scan under the conditions of a coulometric determination were derived for instances when the conditional potential, E_0', and the limiting current were known or unknown. All this is applicable, with some simplification, to oxidation - reduction reactions with one insoluble component, and to ion-combination reactions with all components soluble, or with one or more insoluble components. The purpose is the calculation of current efficiencies, particularly high efficiencies such as those required in standards work and absolute coulometry. To this end, the solvent-molecule and solvent-ion background reactions interpose the most important and most difficult factor, and ultimately impose the upper level of current efficiency that can be attained. Their complexity and difficulties of interpretation[2] make them a unique case that necessitates separate treatment. Equations are numbered sequentially from the preceding paper,[1] in which equations (1) to (58) appear.

BACKGROUND SOLVENT-ION AND SOLVENT-MOLECULE REACTIONS

Because of the greater number of electrons involved in the over-all reactions, background reactions reach the pattern region at quite small charge-transfer overpotentials. For a 1 per cent. error, cathodic reactions can be treated by pattern theory when $-\eta_a$ is greater than 60 mV and anodic reactions when η_a is greater than 30 mV. The difficulties in rationalising these reactions have been strongly emphasised,[2] and many, but not all, of these difficulties apply in the development of pattern equations. Although limiting currents remain hypothetical,[1] but experimentally approachable, for solvent-ion reactions, they are entirely fictitious and unmeasurable for solvent-molecule reactions. The method involving the fraction of the limiting current is applicable to the solvent-ion reactions but cannot be used at all for solvent-molecule reactions; fortunately, the arbitrary-current method gives a much closer approximation to the kinetic parameters than it does with oxidation - reduction reactions.

For the evaluation of current efficiency, only the beginning of the solvent-ion or solvent-molecule wave is needed: once the background current reaches the point where the contact layer is saturated with the gaseous product (IH_2SAT about 2 mA cm^{-2} for cathodic reactions

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* For Parts I, II and III of this series, see reference list on p. 782.

or IO_2SAT about 4 mA cm^{-2} for anodic reactions), the current efficiency will have dropped to an unacceptably low value. In the development of the voltammetric equations,[2] it was possible to combine solvent-molecule and solvent-ion reactions into single equations that automatically changed order when necessary, but experimentally one reaction will normally be dominant as far as current efficiency requirements are concerned when the supporting electrolyte is sufficiently acidic or basic. Ion and molecule waves are separated by about 800 mV, and the nature of the electrode surface and therefore the charge-transfer rate parameters will change drastically on conversion from ion to molecule reactions, and it is legitimate, as well as necessary if a solution is to be reached, to treat the reactions separately. Again, because of the multiplicity of cases to be solved (anodic, cathodic; ion, molecule; pattern equation, solutions for α and k when limiting currents are known and unknown), only the first example of each type of derivation will be given, and later the intermediate steps will be omitted. It will be assumed that in the experimental context the following three conditions are met: $|n\eta_a| > 0{\cdot}118$ V, the current is below gas saturation level, and a single reaction is dominant.

CATHODIC SOLVENT-ION AND SOLVENT-MOLECULE REACTIONS

ACIDIC MEDIA, REDUCTION OF HYDROGEN ION—

The reaction is

$$2H_3O^+ + 2e \underset{i_a}{\overset{i_c}{\rightleftharpoons}} 2H_2O + H_2 \quad .. \quad .. \quad .. \quad .. \quad (59)$$

for which, under the specified conditions the rate equation (1) for this reaction[2] simplifies to

$$I_H = 2FAk_H\,[H^+]_S^{2(1-\alpha_H)}\,[H_2]_S^{\alpha_H}\,[H_2O]_S^{2\alpha_H}\exp\left[\frac{-2\alpha_H F}{RT}\eta_a\right] \quad .. \quad .. \quad (60)$$

where the subscript H identifies the reaction, subscript S denotes contact layer concentrations, and the remaining symbols have the same meaning as before.[1] By taking logarithms, converting to the base 10 and re-arranging the terms, the explicit solution for η_a is obtained[1]—

$$\eta_a = -\frac{2{\cdot}303\,RT}{2\alpha_H F}\left\{\log_{10}\frac{I_H}{2FA\,[H^+]_S^2} + \alpha_H\log_{10}\frac{[H^+]_S^2}{[H_2]_S\,[H_2O]_S^2} - \log_{10}k_H\right\} \quad .. \quad (61)$$

The middle term, when multiplied out, is $-\eta_c$.

The pattern equation—The mass-transfer rate constant, $D_H/\delta x$ or its variants,[2] can be obtained from the limiting current equation (62), and by using the method involving the fraction of the limiting current and the mass-transfer equations,[2] for $I_H = \mathrm{f}\,IL_H$, the contact layer concentrations can be derived as

$$IL_H = \frac{FAD_H\,[H^+]_B}{\delta x}$$

$$E_{we} \rightarrow -\infty$$

$$[H^+]_S \rightarrow 0 \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (62)$$

$$[H^+]_S = (1 - \mathrm{f})\,[H^+]_B \quad .. \quad .. \quad .. \quad .. \quad .. \quad (63)$$

$$[H_2]_S = \mathrm{f}\,\frac{D_H}{2D_{H_2}}\,[H^+]_B \quad .. \quad .. \quad .. \quad .. \quad .. \quad (64)$$

$$[H_2O]_S = \mathrm{f}\,\frac{D_H}{D_{H_2O}}\,[H^+]_B + [H_2O]_B \quad .. \quad .. \quad .. \quad .. \quad (65)$$

where the subscript B denotes concentrations in the bulk of the solution, which is assumed to be free from dissolved hydrogen and oxygen. By substituting into equation (61), simplifying and re-arranging the terms, the rigorous pattern equation is finally obtained—

$$\eta_{a_f} = -\frac{2{\cdot}303\,RT}{2\alpha_H F}\left\{\log_{10}\frac{D_H}{\delta x} - \log_{10}k_H - (1-\alpha_H)\log_{10}[H^+]_B\right.$$

$$\left. + (1-\alpha_H)\log_{10}\frac{\mathrm{f}}{2\,(1-\mathrm{f})^2} - \alpha_H\log_{10}\frac{D_H}{D_{H_2}}\left(\mathrm{f}\,\frac{D_H}{D_{H_2O}}\,[H^+]_B + [H_2O]_B^2\right)\right\} \quad .. \quad (66)$$

When $[H^+]_B$ is low compared with $[H_2O]_B$, *e.g.*, less than 2·5 M, then the final term in equation (66) simplifies to

$$-\alpha_H \log_{10} \frac{D_H}{D_{H_2}} [H_2O]_B^2 \quad \ldots \quad (67)$$

Equation (66) reveals the behaviour pattern, η_a is logarithmically proportional to the ratio of the mass-transfer to charge-transfer rate constants, to the pH of the solution and logarithmically to the water concentration. The concentration dependences disclose the difference in behaviour from oxidation - reduction reactions.[1] The decadic potential shift is $2{\cdot}3\ RT/(2\alpha_H F)$, *i.e.*, $30/\alpha_H$ mV for a ten-fold change in D_H, δx and k_H.

The pH dependence is $-\dfrac{2{\cdot}3\ RT}{F}\dfrac{(1-\alpha_H)}{2\alpha_H}\,pH_B$.

The water dependence approximates to $+\dfrac{2{\cdot}3\ RT}{F}\log_{10}[H_2O]_B$.

The dependence on α_H is complex, as the computed graphs demonstrate.[2,3]

As the middle term of equation (61) is $-\eta_c$, then substitution into $E_{we} = E_o' + \eta_c + \eta_a$ gives

$$E_f = E_o{}'_H - \frac{2{\cdot}303\ RT}{2\alpha_H F}\left\{\log_{10}\frac{D_H/\delta x}{k_H} + \log_{10}\frac{f}{(1-f)^2} - \log_{10}[H^+]_B\right\} \quad \ldots \quad (68)$$

which is similar to equations (25) and (47) for oxidation - reduction reactions, but with the vital addition of the concentration term.

Solution for α: (i) limiting current known—If the limiting current is measurable, as in graph 1 in Fig. 1, and the three primary conditions are met, then by taking two points from the scan, E_{f_1} at $I = f_1\, IL_H$ and E_{f_2} at $I = f_2\, IL_H$, substituting into equation (68), and subtracting E_{f_2} from E_{f_1}—

$$E_{f_1} - E_{f_2} = \frac{2{\cdot}303\ RT}{2\alpha_H F}\log_{10}\frac{f_2(1-f_1)^2}{f_1(1-f_2)^2} \quad \ldots \quad \ldots \quad \ldots \quad (69)$$

from which α_H can be obtained—

$$\alpha_H = \frac{2{\cdot}303\ RT}{2(E_{f_1} - E_{f_2})F}\log_{10}\frac{f_2}{f_1}\left(\frac{1-f_1}{1-f_2}\right)^2 \quad \ldots \quad \ldots \quad \ldots \quad (70)$$

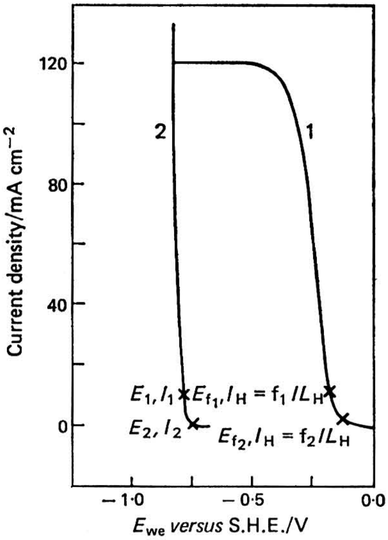

Fig. 1. Cathodic scan of (1) 0·04M perchloric acid and (2) 0·1M sodium hydroxide solution

If the limiting current is less than twice IH_2SAT, then measurements at $E_{\frac{1}{2}}$ and E_{f} give the simplification

$$\alpha_{\mathrm{H}} = \frac{2{\cdot}303\,RT}{2\,(E_{\frac{1}{2}} - E_{\mathrm{f}})\,F} \log_{10} \frac{\mathrm{f}}{2\,(1 - \mathrm{f})^2} \quad \cdot\cdot \quad \cdot\cdot \quad \cdot\cdot \quad (71)$$

Solution for α*:* (ii) *limiting current unknown*—The arbitrary-current method can be applied, provided that the currents are less than IH_2SAT and $-\eta_{\mathrm{a}}$ is greater than $30/\alpha_{\mathrm{H}}$ mV.

For the points E_1, I_1 and E_2, I_2,—

$$E_1 = E_{\mathrm{o}}{'}_{\mathrm{H}} - \frac{2{\cdot}3\,RT}{2\alpha_{\mathrm{H}}\,F}\left\{\log_{10}\frac{I_1}{2\,FA\,[\mathrm{H}^+]^2_{\mathrm{S1}}} - \log_{10} k_{\mathrm{H}}\right\} \quad \cdot\cdot \quad \cdot\cdot \quad (72)$$

$$E_2 = E_{\mathrm{o}}{'}_{\mathrm{H}} - \frac{2{\cdot}3\,RT}{2\alpha_{\mathrm{H}}\,F}\left\{\log_{10}\frac{I_2}{2\,FA\,[\mathrm{H}^+]^2_{\mathrm{S2}}} - \log_{10} k_{\mathrm{H}}\right\} \quad \cdot\cdot \quad \cdot\cdot \quad (73)$$

Subtraction of equation (73) from equation (72) gives

$$E_1 - E_2 = \frac{2{\cdot}3\,RT}{2\alpha_{\mathrm{H}}\,F}\log_{10}\frac{I_2\,[\mathrm{H}^+]^2_{\mathrm{S1}}}{I_1\,[\mathrm{H}^+]^2_{\mathrm{S2}}} \quad \cdot\cdot \quad \cdot\cdot \quad \cdot\cdot \quad (74)$$

From the mass-transfer equation[2]—

$$[\mathrm{H}^+]_{\mathrm{S}} = [\mathrm{H}^+]_{\mathrm{B}} - \frac{I_{\mathrm{H}}\,\delta x}{FAD_{\mathrm{H}}} \quad \cdot\cdot \quad \cdot\cdot \quad \cdot\cdot \quad \cdot\cdot \quad (75)$$

and from equation (62)—

$$\alpha_{\mathrm{H}} = \frac{2{\cdot}3\,RT}{2\,F\,(E_1 - E_2)}\log_{10}\frac{I_2\,(IL_{\mathrm{H}} - I_1)^2}{I_1\,(IL_{\mathrm{H}} - I_2)^2} \quad \cdot\cdot \quad \cdot\cdot \quad \cdot\cdot \quad (76)$$

As IH_2SAT is about 2 mA cm^{-2} in a well stirred solution, for a 1 per cent. error, if $[\mathrm{H}^+]_{\mathrm{B}}$ is greater than 0·066 M,

$$\alpha_{\mathrm{H}} = \frac{2{\cdot}3\,RT}{2\,F\,(E_1 - E_2)}\log_{10}\frac{I_2}{I_1} \quad \cdot\cdot \quad \cdot\cdot \quad \cdot\cdot \quad \cdot\cdot \quad (77)$$

Under the specified conditions, $[\mathrm{H}^+]_{\mathrm{S}} = [\mathrm{H}^+]_{\mathrm{B}}$ and $[\mathrm{H}_2\mathrm{O}]_{\mathrm{S}} = [\mathrm{H}_2\mathrm{O}]_{\mathrm{B}}$ within the same tolerance of 1 per cent.

Solution for k_{H}*:* (i) *limiting current known*—Substitution of α_{H} from equation (71) into equation (68) at the correct current and potential, and simplification, gives

$$\log_{10} k_{\mathrm{H}} = \frac{E_{\mathrm{f}_1} - E_{\mathrm{o}}{'}_{\mathrm{H}}}{E_{\mathrm{f}_1} - E_{\mathrm{f}_2}}\log_{10}\frac{\mathrm{f}_2}{2\,[\mathrm{H}^+]_{\mathrm{B}}\,(1 - \mathrm{f}_2)^2} + \log_{10}\frac{D_{\mathrm{H}}}{\delta x} \quad \cdot\cdot \quad \cdot\cdot \quad (78)$$

where $E_{\mathrm{o}}{'}_{\mathrm{H}}$ in terms of concentrations and the formation constant of water is[2]

$$E_{\mathrm{o}}{'}_{\mathrm{H}} = \frac{2{\cdot}303\,RT}{2F}\log_{10}[\mathrm{H}_2\mathrm{SAT}]_{\mathrm{T,1}}\,[\mathrm{H}_2\mathrm{O}]^2_{\mathrm{1M}} \quad \cdot\cdot \quad \cdot\cdot \quad \cdot\cdot \quad (79)$$

Solution for k_{H}*:* (ii) *limiting current unknown*—Substitution of α_{H} from equation (77) into equation (68), and by taking $D_{\mathrm{H}}/\delta x$ from equation (62), if the correct conditions as applied to equation (77) for I_1, I_2 and $[\mathrm{H}^+]_{\mathrm{B}}$ are met, gives

$$\log_{10} k_{\mathrm{H}} = \frac{E_1 - E_{\mathrm{o}}{'}_{\mathrm{H}}}{E_1 - E_2}\log_{10}\frac{I_2}{I_1} + \log_{10}\frac{I_1}{2\,FA\,[\mathrm{H}^+]^2_{\mathrm{B}}} \quad \cdot\cdot \quad \cdot\cdot \quad \cdot\cdot \quad (80)$$

ALKALINE MEDIA, REDUCTION OF SOLVENT MOLECULES—

The reaction is now

$$2\mathrm{H}_2\mathrm{O} + 2\mathrm{e} \underset{i_{\mathrm{a}}}{\overset{i_{\mathrm{c}}}{\rightleftharpoons}} \mathrm{H}_2 + 2\mathrm{OH}^- \quad \cdot\cdot \quad \cdot\cdot \quad \cdot\cdot \quad \cdot\cdot \quad (81)$$

The rate equation (1) for this reaction[2] simplifies under the specified conditions to

$$I_{\mathrm{Solv}} = 2\,FA\,k_{\mathrm{Solv}}\,[\mathrm{H}^+]_{\mathrm{S}}^{-2\alpha_{\mathrm{Solv}}}\,[\mathrm{H}_2]_{\mathrm{S}}^{\alpha_{\mathrm{Solv}}}\,[\mathrm{H}_2\mathrm{O}]_{\mathrm{S}}^{(2-1\alpha_{\mathrm{Solv}})}\,K_{\mathrm{H_2O}}^{-2\alpha_{\mathrm{Solv}}}\,\exp\left[\frac{-2\alpha_{\mathrm{Solv}}F}{RT}\,\eta_{\mathrm{a}}\right] \cdot\cdot \quad (82)$$

By taking logarithms, converting to the base 10 and re-arranging the terms, the following equation is obtained—

$$\eta_{\mathrm{a}} = -\frac{2{\cdot}303\,RT}{2\alpha_{\mathrm{Solv}}F}\left\{\log_{10}\frac{I_{\mathrm{Solv}}}{2\,FA\,[\mathrm{H_2O}]_{\mathrm{S}}^{2}} + \alpha_{\mathrm{Solv}}\log_{10}\frac{[\mathrm{H^+}]_{\mathrm{S}}^{2}\;K_{\mathrm{H_2O}}^{2}}{[\mathrm{H_2}]_{\mathrm{S}}\,[\mathrm{H_2O}]_{\mathrm{S}}^{2}} - \log_{10}k_{\mathrm{Solv}}\right\} \quad .. \quad (83)$$

As usual, when multiplied out, the middle term is $-\eta_{\mathrm{C}}$. Under these conditions, as illustrated in graph 2 in Fig. 1, the method involving the fraction of the limiting current cannot be applied because the limiting current of solvent reduction in reaction (81) cannot even be approached experimentally: it is of the order of 150 A cm^{-2} in well stirred solutions.

The pattern equation—The limiting current cannot be attained, so the mass-transfer rate constant, $D_{\mathrm{H_2O}}/\delta x$, cannot be measured experimentally; it is therefore not possible to derive an experimentally meaningful pattern equation that shows the influences of the individual parameters. If, however, the fiction that a limiting current exists is permitted temporarily, the method involving the fraction of the limiting current can be formally applied to demonstrate behaviour, but is not admissible in the determination of kinetic parameters. If the individual steps of the derivation are omitted, for reaction (81) on its own and a current $I_{\mathrm{Solv}} = \mathrm{f}\,IL_{\mathrm{Solv}}$, the contact layer concentrations are given by the following three equations—

$$[\mathrm{H_2O}]_{\mathrm{S}} = (1-\mathrm{f})\,[\mathrm{H_2O}]_{\mathrm{B}} \quad .. \quad .. \quad .. \quad .. \quad (84)$$

$$[\mathrm{H_2}]_{\mathrm{S}} = \mathrm{f}\,\frac{D_{\mathrm{H_2O}}}{D_{\mathrm{H_2}}}\,[\mathrm{H_2O}]_{\mathrm{B}} \quad .. \quad .. \quad .. \quad .. \quad (85)$$

(which, from $[\mathrm{H_2SAT}]_{\mathrm{T,P}}$, sets a maximum on f of about 3×10^{-5}), and

$$[\mathrm{OH^-}]_{\mathrm{S}} = [\mathrm{OH^-}]_{\mathrm{B}} + \mathrm{f}\,\frac{D_{\mathrm{H_2O}}}{D_{\mathrm{OH}}}\,[\mathrm{H_2O}]_{\mathrm{B}} \quad .. \quad .. \quad .. \quad (86)$$

Substitution into equation (83) and partial simplification gives

$$\begin{aligned}\eta_{\mathrm{a_f}} = -\frac{2{\cdot}3\,RT}{2\alpha_{\mathrm{Solv}}F}\Bigg\{&\log_{10}\frac{D_{\mathrm{H_2O}}}{\delta x} - \log_{10}k_{\mathrm{Solv}} - \log_{10}[\mathrm{H_2O}]_{\mathrm{B}}\\ &+ \alpha_{\mathrm{Solv}}\log_{10}\frac{(1-\mathrm{f})^{2}}{\mathrm{f}} + \alpha_{\mathrm{Solv}}\log_{10}\frac{\mathrm{f}}{2\,(1-\mathrm{f})^{2}}\\ &+ \alpha_{\mathrm{Solv}}\log_{10}\frac{[\mathrm{H_2O}]_{\mathrm{B}}}{\dfrac{D_{\mathrm{H_2O}}}{D_{\mathrm{H_2}}}\left([\mathrm{OH^-}]_{\mathrm{B}} + \mathrm{f}\,\dfrac{D_{\mathrm{H_2O}}}{D_{\mathrm{OH}}}\,[\mathrm{H_2O}]_{\mathrm{B}}\right)^{2}}\Bigg\} \quad .. \quad .. \quad (87)\end{aligned}$$

which makes certain facts clear: $\eta_{\mathrm{a_f}}$ depends, as usual, on the logarithm of the ratio of the mass-transfer and charge-transfer rate constants, and shows a potential shift of $30/\alpha_{\mathrm{Solv}}$ mV per ten-fold change in δx and k_{Solv}, but the α_{Solv} and concentration dependences are obscure. In the final term, because of the small permitted value of f, $[\mathrm{OH^-}]_{\mathrm{B}}$ cannot be neglected with respect to the term in $[\mathrm{H_2O}]_{\mathrm{B}}$, unless $[\mathrm{OH^-}]_{\mathrm{B}}$ is less than 6×10^{-6} M. However, for the same reason, when the solution is strongly alkaline ($[\mathrm{OH^-}]_{\mathrm{B}}$ greater than 0·06 M), the term in $[\mathrm{H_2O}]_{\mathrm{B}}$ in the denominator becomes less than 1 per cent. of $[\mathrm{OH^-}]_{\mathrm{B}}$ and can then be neglected. At high hydroxyl-ion concentration, when the terms in $[\mathrm{H_2O}]_{\mathrm{B}}$ and in f are combined,

$$\begin{aligned}\eta_{\mathrm{a_f}} = -\frac{2{\cdot}3\,RT}{2\alpha_{\mathrm{Solv}}F}\Bigg\{&\log_{10}\frac{D_{\mathrm{H_2O}}/\delta x}{k_{\mathrm{Solv}}} + (1-\alpha_{\mathrm{Solv}})\log_{10}\frac{\mathrm{f}}{(1-\mathrm{f})^{2}}\\ &- \log_{10}2 - (1-\alpha_{\mathrm{Solv}})\log_{10}[\mathrm{H_2O}]_{\mathrm{B}} - 2\alpha_{\mathrm{Solv}}\log_{10}[\mathrm{OH^-}]_{\mathrm{B}}\\ &+ \alpha_{\mathrm{Solv}}\log_{10}\frac{D_{\mathrm{H_2}}}{D_{\mathrm{H_2O}}}\Bigg\} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (88)\end{aligned}$$

which reveals an over-all $[\mathrm{H_2O}]_{\mathrm{B}}$ dependence of

$$+\frac{(1-\alpha_{\mathrm{Solv}})}{2\alpha_{\mathrm{Solv}}}\cdot\frac{2{\cdot}3\,RT}{F}\log_{10}[\mathrm{H_2O}]_{\mathrm{B}} \quad .. \quad .. \quad .. \quad (89)$$

and an over-all $[\mathrm{OH^-}]_B$ dependence of

$$+\frac{2{\cdot}3\,RT}{F}\log_{10}[\mathrm{OH^-}]_B \approx \frac{2{\cdot}3\,RT}{F}\,\mathrm{pH} \quad .. \quad .. \quad .. \quad (90)$$

Solution for α_{Solv}—The arbitrary-current method must be used. The points E_1, I_1 and E_2, I_2 should be chosen to maintain the current below IH_2SAT, although experimentally supersaturation commonly occurs, as on graph 2 in Fig. 1. Substitution into

$$E_{\mathrm{we}} = E_{\mathrm{o}}{'}_{\mathrm{Solv}} + \eta_{\mathrm{c}} + \eta_{\mathrm{a}}$$

and cancellation of the emergent $-\eta_{\mathrm{c}}$ term, followed by subtraction of E_2 from E_1, gives

$$E_1 - E_2 = \frac{2{\cdot}3\,RT}{2\alpha_{\mathrm{Solv}}F}\log_{10}\frac{I_2\,[\mathrm{H_2O}]^2_{\mathrm{S1}}}{I_1\,[\mathrm{H_2O}]^2_{\mathrm{S2}}} \quad .. \quad .. \quad .. \quad (91)$$

Under the stated conditions, the maximum difference between $[\mathrm{H_2O}]_B$ and $[\mathrm{H_2O}]_S$ is 2×10^{-3} M, so that a very close approximation to α_{Solv} is given by

$$\alpha_{\mathrm{Solv}} = \frac{2{\cdot}3\,RT}{2\,(E_1 - E_2)\,F}\log_{10}\frac{I_2}{I_1} \quad .. \quad .. \quad .. \quad (92)$$

Solution for k_{Solv}—Again, there is no option but to use the arbitrary-current device. From equation (92) and the potential equation[2]—

$$\log_{10}k_{\mathrm{Solv}} = \frac{E_1 - E_{\mathrm{o}}{'}_{\mathrm{Solv}}}{E_1 - E_2}\log_{10}\frac{I_2}{I_1} + \log_{10}\frac{I_1}{2\,FA\,[\mathrm{H_2O}]^2_B} \quad .. \quad .. \quad (93)$$

where $E_{\mathrm{o}}{'}_{\mathrm{Solv}}$ is given by[2]

$$E_{\mathrm{o}}{'}_{\mathrm{Solv}} = \frac{2{\cdot}303\,RT}{2\,F}\log_{10}\frac{[\mathrm{H_2O}]^2_{\mathrm{IM}}\,[\mathrm{H_2SAT}]_{\mathrm{T,1}}}{K^2_{\mathrm{H_2O}}} \quad .. \quad .. \quad .. \quad (94)$$

ANODIC SOLVENT-ION AND SOLVENT-MOLECULE REACTIONS

ALKALINE MEDIA, OXIDATION OF HYDROXYL ION—

The reaction is

$$\mathrm{O_2 + 2H_2O + 4e \underset{i_a}{\overset{i_c}{\rightleftharpoons}} 4OH^-} \quad .. \quad .. \quad .. \quad .. \quad (95)$$

and the rate equation (1) for this reaction[2] simplifies to

$$I_{\mathrm{OH}} = -\,4\,FA\,k_{\mathrm{OH}}\,[\mathrm{H^+}]_S^{-4\alpha_{\mathrm{OH}}}\,[\mathrm{O_2}]_S^{(1-\alpha_{\mathrm{OH}})}\,[\mathrm{H_2O}]_S^{(2+6\alpha_{\mathrm{OH}})}\,K_{\mathrm{H_2O}}^{-4\alpha_{\mathrm{OH}}}\exp\left[\frac{4\,(1-\alpha_{\mathrm{OH}})\,F}{RT}\eta_{\mathrm{a}}\right] \quad (96)$$

in the pattern region and with currents below the gas-saturation level. By taking logarithms, converting to base 10 and re-arranging the terms, the following equation is obtained in terms of hydrogen-ion concentration—

$$\begin{aligned}\eta_{\mathrm{a}} = \frac{2{\cdot}303\,RT}{4\,(1-\alpha_{\mathrm{OH}})\,F}\Bigg\{&\log_{10}\frac{-I_{\mathrm{OH}}\,[\mathrm{H^+}]^4_S\,K^4_{\mathrm{H_2O}}}{4\,FA\,[\mathrm{H_2O}]^8_S}\\ &-(1-\alpha_{\mathrm{OH}})\log_{10}\frac{K^4_{\mathrm{H_2O}}\,[\mathrm{O_2}]_S\,[\mathrm{H^+}]^4_S}{[\mathrm{H_2O}]^6_S} - \log_{10}k_{\mathrm{OH}}\Bigg\} \quad .. \quad .. \quad .. \quad (97)\end{aligned}$$

The middle term, when multiplied out, is $-\eta_{\mathrm{c}}$, and substitution in $E_{\mathrm{we}} = E_{\mathrm{o}}{'}_{\mathrm{OH}} + \eta_{\mathrm{c}} + \eta_{\mathrm{a}}$ gives, still in terms of hydrogen-ion concentration,

$$E_{\mathrm{we}} = E_{\mathrm{o}}{'}_{\mathrm{OH}} + \frac{2{\cdot}303\,RT}{4\,(1-\alpha_{\mathrm{OH}})\,F}\left\{\log_{10}\frac{-I_{\mathrm{OH}}\,[\mathrm{H^+}]^4_S\,K^4_{\mathrm{H_2O}}}{4\,FA\,[\mathrm{H_2O}]^8_S} - \log_{10}k_{\mathrm{OH}}\right\} \quad .. \quad (98)$$

It is often more convenient to work in terms of hydroxyl-ion concentration in alkaline medium, and then equation (97) becomes

$$\eta_{\mathrm{a}} = \frac{2{\cdot}303\,RT}{4\,(1-\alpha_{\mathrm{OH}})\,F}\left\{\log_{10}\frac{-I_{\mathrm{OH}}}{4\,FA\,[\mathrm{OH^-}]^4_S} - (1-\alpha_{\mathrm{OH}})\log_{10}\frac{[\mathrm{O_2}]_S\,[\mathrm{H_2O}]^2_S}{[\mathrm{OH^-}]^4_S} - \log_{10}k_{\mathrm{OH}}\right\} .. \quad (99)$$

and equation (98) becomes

$$E_{\mathrm{we}} = E_{\mathrm{o}}{'}_{\mathrm{OH}} + \frac{2{\cdot}303\,RT}{4\,(1-\alpha_{\mathrm{OH}})\,F}\left\{\log_{10}\frac{-I_{\mathrm{OH}}}{4\,FA\,[\mathrm{OH^-}]^4_S} - \log_{10}k_{\mathrm{OH}}\right\} \quad .. \quad (100)$$

The pattern equation—Reaction (95) alone is involved. The limiting current and diffusion equations can be set up, and then the method involving the fraction of the limiting current can be used to calculate the contact layer concentrations $[\mathrm{H}^+]_\mathrm{S}$, $[\mathrm{OH}^-]_\mathrm{S}$, $[\mathrm{O}_2]_\mathrm{S}$ and $[\mathrm{H}_2\mathrm{O}]_\mathrm{S}$ in terms of the fraction, f, the bulk concentrations and diffusion coefficients. The algebra involved is lengthy and cumbersome, but follows finally the stages in equations (62) to (65) in principle, and can be permitted to be taken as read. Substitution in equation (97) in terms of hydrogen-ion concentration, and keeping the η_c term separate, gives the rigorous pattern equation in one of its many configurations—

$$\eta_{\mathrm{a}_f} = \frac{2{\cdot}303\,RT}{4\,(1-\alpha_\mathrm{OH})\,F}\left\{\log_{10}\frac{D_\mathrm{OH}}{\delta x} - \log_{10} k_\mathrm{OH} + \log_{10}\frac{\mathrm{f}}{4\,(1-\mathrm{f})^4}\cdot\frac{K^3_{\mathrm{H_2O}}\,[\mathrm{H}^+]^3_\mathrm{B}}{[\mathrm{H}_2\mathrm{O}]^6_\mathrm{B}}\right.$$
$$\left. -\,(1-\alpha_\mathrm{OH})\log_{10}\frac{K^4_{\mathrm{H_2O}}\,[\mathrm{H}^+]^4_\mathrm{B}\left([\mathrm{O}_2]_\mathrm{B} + \mathrm{f}\,\dfrac{D_\mathrm{OH}}{4D_{\mathrm{O}_2}}\cdot\dfrac{[\mathrm{H}_2\mathrm{O}]^2_\mathrm{B}}{K_{\mathrm{H_2O}}\,[\mathrm{H}^+]_\mathrm{B}}\right)}{(1-\mathrm{f})^4\,[\mathrm{H}_2\mathrm{O}]^8_\mathrm{B}}\right\} \quad .. \quad .. \quad (101)$$

Substitution in equation (99) in terms of hydroxyl-ion concentration, still keeping the η_c term separate, gives, of the many possible configurations, perhaps the most informative rigorous pattern equation—

$$\eta_{\mathrm{a}_f} = \frac{2{\cdot}303\,RT}{4\,(1-\alpha_\mathrm{OH})\,F}\left\{\log_{10}\frac{D_\mathrm{OH}/\delta x}{k_\mathrm{OH}} + \log_{10}\frac{\mathrm{f}}{4\,(1-\mathrm{f})^4}[\mathrm{OH}^-]^3_\mathrm{B}\right.$$
$$\left. +\,(1-\alpha_\mathrm{OH})\left[\log_{10}[\mathrm{OH}^-]^4_\mathrm{B} - \log_{10}\frac{1}{(1-\mathrm{f})^4} - \log_{10}\left([\mathrm{O}_2]_\mathrm{B} + \mathrm{f}\,\frac{D_\mathrm{OH}}{4D_{\mathrm{O}_2}}\,[\mathrm{OH}^-]_\mathrm{B}\right)\right]\right\} \quad (102)$$

From either equation (101) or equation (102), η_a is again dependent on the logarithm of the ratio of the mass-transfer and charge-transfer rate constants, and the potential shift is $2{\cdot}3\,RT/[4\,(1-\alpha_\mathrm{OH})\,F]$ for a ten-fold change in k_OH and δx, and also in E_we for D_OH. The dependence on pH is

$$-\frac{3}{4}\cdot\frac{2{\cdot}3\,RT}{(1-\alpha_\mathrm{OH})\,F}\,\mathrm{pH}\ \text{for}\ \eta_\mathrm{a}\quad\text{and}\quad \frac{1-4\alpha_\mathrm{OH}}{4-4\alpha_\mathrm{OH}}\cdot\frac{2{\cdot}3\,RT}{F}\,\mathrm{pH}\ \text{for}\ \eta_\mathrm{a}+\eta_\mathrm{c}.$$

The dependence on water concentration is

$$-\frac{2{\cdot}3\,RT}{4\,(1-\alpha_\mathrm{OH})F}\log_{10}[\mathrm{H}_2\mathrm{O}]^6_\mathrm{B} = -\frac{3}{2}\cdot\frac{2{\cdot}3\,RT}{(1-\alpha_\mathrm{OH})F}\log_{10}[\mathrm{H}_2\mathrm{O}]_\mathrm{B}$$

The precise dependence on α_OH is very complex.

Solution for α_OH*:* (i) *limiting current known*—The method involving the fraction of the limiting current can be used, and substitution into equation (98) for $I_\mathrm{OH} = \mathrm{f}\,IL_\mathrm{OH}$ gives

$$E_f = E_{\mathrm{o}}{}'_{\mathrm{OH}} + \frac{2{\cdot}3\,RT}{4\,(1-\alpha_\mathrm{OH})\,F}\left\{\log_{10}\frac{D_\mathrm{OH}/\delta x}{k_\mathrm{OH}} + \log_{10}\frac{\mathrm{f}}{4(1-\mathrm{f})^4} - \log_{10}[\mathrm{OH}^-]^3_\mathrm{B}\right\} \quad .. \quad (103)$$

By taking two points from the anodic scan, E_{f_1} and E_{f_2} at the corresponding currents, which must be less than IO_2SAT, substituting into equation (103) and subtracting, and finally solving for $(1-\alpha_\mathrm{OH})$, the following equation is obtained—

$$(1-\alpha_\mathrm{OH}) = \frac{2{\cdot}3\,RT}{4\,(E_{f_1}-E_{f_2})\,F}\log_{10}\frac{\mathrm{f}_1\,(1-\mathrm{f}_2)^4}{\mathrm{f}_2\,(1-\mathrm{f}_1)^4} \quad .. \quad .. \quad .. \quad (104)$$

Solution for α_OH*:* (ii) *limiting current unknown*—Even at fairly high hydroxyl-ion concentrations, the hydroxyl-ion wave is distorted by the solvent oxidation wave and it is not easy to extract limiting currents accurately. The arbitrary-current method can be applied, with the same current restrictions, to points E_1, I_1 and E_2, I_2 taken from the anodic scan, and substituted into equation (98)—

$$(1-\alpha_\mathrm{OH}) = \frac{2{\cdot}3\,RT}{4\,(E_1-E_2)\,F}\log_{10}\frac{I_1}{I_2}\left(\frac{IL_\mathrm{OH}-I_2}{IL_\mathrm{OH}-I_1}\right)^4 \quad .. \quad .. \quad (105)$$

Unless the currents I_1 and I_2 are indeed extremely small ($-I/A$ less than $1{\cdot}7 \times 10^{-2}\,[\mathrm{OH}^-]_\mathrm{B}$), the assumption that they are negligible with respect to IL_OH is not admissible. If currents are allowed to be as high as IO_2SAT, which reaches 4 mA cm^{-2} in a well stirred oxygen-free solution, then $[\mathrm{OH}^-]_\mathrm{B}$ must be greater than 0·24 M. However, if either of these conditions is met, a reasonable approximation to $(1 - \alpha_\mathrm{OH})$ is given by

$$(1 - \alpha_\mathrm{OH}) = \frac{2{\cdot}3\,RT}{4\,(E_1 - E_2)\,F}\log_{10}\frac{I_1}{I_2} \quad \ldots \quad \ldots \quad \ldots \quad (106)$$

Solution for k$_\mathrm{OH}$*:* (i) *limiting current known*—The use of the method involving the fraction of the limiting current and substitution of $(1 - \alpha_\mathrm{OH})$ from equation (104) into equation (98) gives

$$E_\mathrm{f} = E_{\mathrm{O}'\mathrm{OH}} + \frac{E_{\mathrm{f}_1} - E_{\mathrm{f}_2}}{\log_{10}\frac{\mathrm{f}_1}{\mathrm{f}_2}\left(\frac{1-\mathrm{f}_2}{1-\mathrm{f}_1}\right)^4}\left\{\log_{10}\frac{D_\mathrm{OH}/\delta x}{k_\mathrm{OH}} + \log_{10}\frac{\mathrm{f}}{4\,(1-\mathrm{f})^4} - 3\log_{10}[\mathrm{OH}^-]_\mathrm{B}\right\} \quad (107)$$

Substitution of the appropriate values of potential and current, say E_{f_1} and $I = \mathrm{f}_1\, IL_\mathrm{OH}$, into equation (107) gives the required solution—

$$\log_{10} k_\mathrm{OH} = \log_{10}\frac{D_\mathrm{OH}}{\delta x} + \log_{10}\frac{\mathrm{f}_1}{4\,(1-\mathrm{f}_1)^4} - \frac{E_{\mathrm{f}_1} - E_{\mathrm{O}'\mathrm{OH}}}{E_{\mathrm{f}_1} - E_{\mathrm{f}_2}}\log_{10}\frac{\mathrm{f}_1}{\mathrm{f}_2}\left(\frac{1-\mathrm{f}_2}{1-\mathrm{f}_1}\right)^4$$
$$- 3\log_{10}[\mathrm{OH}^-]_\mathrm{B} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (108)$$

in which

$$\frac{D_\mathrm{OH}}{\delta x} = \frac{IL_\mathrm{OH}}{FA\,[\mathrm{OH}^-]_\mathrm{B}}$$

and[2]

$$E_{\mathrm{O}'\mathrm{OH}} = 0{\cdot}401 + \frac{2{\cdot}3\,RT}{4\,F}\log_{10}\frac{1}{[\mathrm{H_2O}]^2_\mathrm{IM}\,[\mathrm{O_2SAT}]_{\mathrm{T},1}} \quad \ldots \quad \ldots \quad (109)$$

Solution for k$_\mathrm{OH}$*:* (ii) *limiting current unknown*—The arbitrary-current method must be used, and if the result is to be valid the severe restrictions on conditions that were outlined in the development of equation (106) must be obeyed. Then, substitution of $(1 - \alpha_\mathrm{OH})$ from equation (106) into equation (98), and the corollary assumption that $[\mathrm{OH}^-]_\mathrm{S}$ does not differ from $[\mathrm{OH}^-]_\mathrm{B}$ by more than 1 per cent., yields the following approximate value for k_OH—

$$\log_{10} k_\mathrm{OH} = \log_{10}\frac{-I_1}{4\,FA\,[\mathrm{OH}^-]^4_\mathrm{B}} - \frac{E_1 - E_{\mathrm{O}'\mathrm{OH}}}{E_1 - E_2}\log_{10}\frac{I_1}{I_2} \quad \ldots \quad \ldots \quad (110)$$

where $E_{\mathrm{O}'\mathrm{OH}}$ is given by equation (109).

ACIDIC MEDIA, OXIDATION OF SOLVENT MOLECULES—

The reaction is

$$\mathrm{O_2} + 4\mathrm{H_3O^+} + 4\mathrm{e} \underset{i_\mathrm{a}}{\overset{i_\mathrm{c}}{\rightleftharpoons}} 6\mathrm{H_2O} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (111)$$

and the rate equation (1) for this reaction[2] simplifies to

$$I_\mathrm{Solv} = -\,4\,FA\,k_\mathrm{Solv}\,[\mathrm{H}^+]_\mathrm{S}^{4(1-\alpha_\mathrm{Solv})}\,[\mathrm{O_2}]_\mathrm{S}^{(1-\alpha_\mathrm{Solv})}\,[\mathrm{H_2O}]_\mathrm{S}^{6\alpha_\mathrm{Solv}}\exp\left[\frac{4\,(1-\alpha_\mathrm{Solv})\,F}{RT}\,\eta_\mathrm{a}\right] \quad \ldots \quad (112)$$

By taking logarithms, converting to the base 10 and re-arranging the terms in the usual way, the following equation is obtained—

$$\eta_\mathrm{a} = \frac{2{\cdot}3\,RT}{4\,(1-\alpha_\mathrm{Solv})\,F}\left\{\log_{10}\frac{-I_\mathrm{Solv}}{4\,FA\,[\mathrm{H_2O}]^6_\mathrm{S}} - (1-\alpha'_\mathrm{Solv})\log_{10}\frac{[\mathrm{H}^+]^4_\mathrm{S}\,[\mathrm{O_2}]_\mathrm{S}}{[\mathrm{H_2O}]^6_\mathrm{S}} - \log_{10} k_\mathrm{Solv}\right\} \quad (113)$$

As usual, the middle term, when multiplied out, is $-\eta_\mathrm{c}$, and substitution into

$$E_\mathrm{we} = E_{\mathrm{O}'\mathrm{Solv}} + \eta_\mathrm{a} + \eta_\mathrm{c}$$

gives

$$E_\mathrm{we} = E_{\mathrm{O}'\mathrm{Solv}} + \frac{2{\cdot}303\,RT}{4\,(1-\alpha_\mathrm{Solv})\,F}\left\{\log_{10}\frac{-I_\mathrm{Solv}}{4\,FA\,[\mathrm{H_2O}]^6_\mathrm{S}} - \log_{10} k_\mathrm{Solv}\right\} \quad \ldots \quad \ldots \quad (114)$$

The pattern equation—As for the reduction of solvent molecules in alkaline media, the limiting current cannot be measured, so the method involving the fraction of the limiting current is of only hypothetical use in developing a behaviour equation that shows the parameter effects, and is useless for the measurement of kinetic parameters. By temporarily accepting the fiction that a limiting current exists, setting up mass-transfer equations for reaction (111) on its own and solving for the contact layer concentrations at $I_{\mathrm{Solv}} = \mathrm{f}\, IL_{\mathrm{Solv}}$, the following three equations are obtained—

$$[\mathrm{H_2O}]_{\mathrm{S}} = (1 - \mathrm{f})\,[\mathrm{H_2O}]_{\mathrm{B}} \quad \cdots \quad (115)$$

$$[\mathrm{O_2}]_{\mathrm{S}} = [\mathrm{O_2}]_{\mathrm{B}} + \frac{\mathrm{f}}{6}\,\frac{D_{\mathrm{H_2O}}}{D_{\mathrm{O_2}}}\,[\mathrm{H_2O}]_{\mathrm{B}} \quad \cdots \quad (116)$$

(which, if the usual conditions are to be met, sets a maximum on f of about 2 × 10^{-4} in a well stirred oxygen-free solution), and

$$[\mathrm{H^+}]_{\mathrm{S}} = [\mathrm{H^+}]_{\mathrm{B}} + \frac{6}{4}\,\mathrm{f}\,\frac{D_{\mathrm{H_2O}}}{D_{\mathrm{H}}}\,[\mathrm{H_2O}]_{\mathrm{B}} \quad \cdots \quad (117)$$

Although equations (115) to (117) appear to be simple, substitution into equation (113) yields a cumbersome expression. Simplifications are possible for equation (116) when the solution is initially free from oxygen, and for equation (117) when the small value of f is considered; when $[\mathrm{H^+}]_{\mathrm{B}}$ is less than 3×10^{-5} M this term can be neglected with respect to the term in $[\mathrm{H_2O}]_{\mathrm{B}}$, and when $[\mathrm{H^+}]_{\mathrm{B}}$ exceeds 0·3 M the term in $[\mathrm{H_2O}]_{\mathrm{B}}$ becomes negligible with respect to $[\mathrm{H^+}]_{\mathrm{B}}$. These conditions, when added to the maximum placed on f, are very restrictive, but by taking out the middle term of equation (113) as $-\eta_{\mathrm{c}}$ and substituting the following equation is obtained—

$$\eta_{\mathrm{a_f}} = \frac{2{\cdot}3\,RT}{4\,(1 - \alpha_{\mathrm{Solv}})\,F}\left\{\log_{10}\frac{D_{\mathrm{H_2O}}}{\delta x} - \log_{10} k_{\mathrm{Solv}} - \log_{10}\,[\mathrm{H_2O}]^5_{\mathrm{B}} + \log_{10}\frac{\mathrm{f}}{6\,(1 - \mathrm{f})^6}\right\} - \eta_{\mathrm{c}} \quad (118)$$

Equation (118) shows an activation shift that is dependent, as usual, on the logarithm of the ratio of the mass-transfer rate constant to the charge-transfer rate constant, a potential shift of $2{\cdot}3\,RT/\,[4\,(1 - \alpha_{\mathrm{Solv}})\,F]$ per ten-fold change in k_{Solv}, δx and D_{Solv}, and an apparent inverse linearity with $(1 - \alpha_{\mathrm{Solv}})$. The dependence on water concentration is

$$-\frac{5}{4}\cdot\frac{2{\cdot}3\,RT}{(1 - \alpha_{\mathrm{Solv}})\,F}\log_{10}\,[\mathrm{H_2O}]_{\mathrm{B}}$$

Substitution into equation (113) without removing the middle term, but making the simplifications that $[\mathrm{O_2}]_{\mathrm{B}}$ is initially zero and that $[\mathrm{H^+}]_{\mathrm{B}}$ is greater than 0·3 M, gives

$$\eta_{\mathrm{a_f}} = \frac{2{\cdot}3\,RT}{4\,(1 - \alpha_{\mathrm{Solv}})\,F}\left\{\log_{10}\frac{D_{\mathrm{H_2O}}/\delta x}{k_{\mathrm{Solv}}} - \alpha_{\mathrm{Solv}}\log_{10}\,[\mathrm{H_2O}]^5_{\mathrm{B}}\right.$$
$$\left. - (1 - \alpha_{\mathrm{Solv}})\log_{10}\,[\mathrm{H^+}]^4_{\mathrm{B}} - \alpha_{\mathrm{Solv}}\log_{10}\frac{\mathrm{f}}{6\,(1 - \mathrm{f})^6} - (1 - \alpha_{\mathrm{Solv}})\,\frac{D_{\mathrm{H_2O}}}{D_{\mathrm{O_2}}}\right\} \quad \cdots \quad (119)$$

which yields the over-all dependences

$$-\frac{5}{4}\cdot\frac{\alpha_{\mathrm{Solv}}}{(1 - \alpha_{\mathrm{Solv}})}\cdot\frac{2{\cdot}3\,RT}{F}\log_{10}\,[\mathrm{H_2O}]_{\mathrm{B}}$$

and

$$-\frac{2{\cdot}3\,RT}{F}\log_{10}\,[\mathrm{H^+}]_{\mathrm{B}} = \frac{2{\cdot}3\,RT}{F}\,\mathrm{pH}$$

Solution for α_{Solv}—The arbitrary-current device is the only option, and η_{a} must be sufficiently large to bring the voltammetric curve into the pattern region at the currents chosen to be less than IO_2SAT. Then, by taking a pair of points E_1, I_1 and E_2, I_2, substituting into equation (114) and subtracting, the following equation is obtained—

$$E_1 - E_2 = \frac{2{\cdot}3\,RT}{4\,(1 - \alpha_{\mathrm{Solv}})\,F}\log_{10}\frac{I_1\,[\mathrm{H_2O}]^6_{\mathrm{S1}}}{I_2\,[\mathrm{H_2O}]^6_{\mathrm{S2}}} \quad \cdots \quad (120)$$

If the currents meet the stated conditions, then $[H_2O]_{S1} = [H_2O]_{S2} = [H_2O]_B$ to within 0·01 per cent., and so a good value for $(1 - \alpha_{Solv})$ is given by

$$(1 - \alpha_{Solv}) = \frac{2{\cdot}3\,RT}{4\,(E_1 - E_2)\,F} \log_{10} \frac{I_1}{I_2} \quad \ldots \quad \ldots \quad \ldots \quad (121)$$

Solution for k_{Solv}—Again, there is no option but to substitute $(1 - \alpha_{Solv})$ from equation (121) into equation (114) at the appropriate potential and current, when a very close approximation to k_{Solv} is given by

$$\log_{10} k_{Solv} = \log_{10} \frac{-I_1}{4\,FA\,[H_2O]_B^6} - \frac{E_1 - E_{O'\,Solv}}{E_1 - E_2} \log_{10} \frac{I_2}{I_1} \quad \ldots \quad \ldots \quad (122)$$

where $E_{O'\,Solv}$ is given by[2]

$$E_{O'\,Solv} = 0{\cdot}401 + \frac{2{\cdot}3\,RT}{4\,F} \log_{10} \frac{K_{H_2O}^4}{[H_2O]_{1M}^2\,[O_2SAT]_{T,1}} \quad \ldots \quad \ldots \quad \ldots \quad (123)$$

EVALUATION OF RATE PARAMETERS FOR BACKGROUND REACTIONS AND THE CALCULATION OF COULOMETRIC CURRENT EFFICIENCIES

As for oxidation - reduction reactions,[1] a random series of pairs of points from the voltammetric scan will permit a statistical appraisal to be made of the over-all conditional charge-transfer rate constants and charge-transfer coefficients. If the currents are confined to below the gas-saturation levels, then, unless electrodes of large area are used, the range is too restricted to afford definitive evidence of changes in k or α with current density. Experimental work in the author's laboratory has, however, shown that the pattern equations are obeyed to levels well above the gas-saturation currents, so that supersaturation of hydrogen or oxygen gas is evidently considerable. This effect, while of interest in the study of the background reactions on their own, is not important in the evaluation of current efficiencies, which will have dropped to unacceptable values before gas saturation is reached.

From a voltammetric scan of the sample or intermediate, or both, and the beginning of the first background wave, all the mass-transfer and charge-transfer kinetic parameters can be evaluated under the actual conditions of the coulometric determination, and from them the current efficiency can be calculated.[2] An example is shown in Fig. 2 for a reaction in which both k and α for the sample reaction change with current density. If the efficiency is not sufficiently high, conditions can be regulated so as to make it as high as possible.[3]

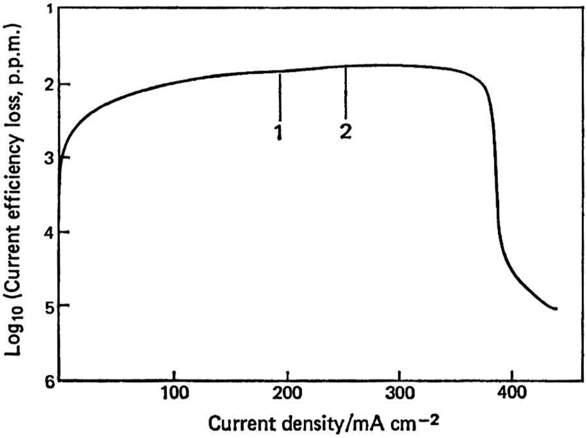

Fig. 2. Current efficiency graph for the generation of tin(II) from tin(IV) at a gold cathode in a medium of 3M sodium bromide and 0·4M perchloric acid solution, 0·2M in tin(IV). At point 1, α changes from 0·435 to 0·348, and at point 2, k changes from $5{\cdot}1 \times 10^{-9}$ to $3{\cdot}7 \times 10^{-8}$ l cm^{-2} s^{-1}

Currents for amperostatic determinations and control potentials for potentiostatic determinations can be correctly selected from an initial scan before the determination is started. A further scan during or after the determination will reveal any significant change in the kinetic parameters, and perhaps current efficiency, consequent upon a change in the condition of the electrode surface during use. Appropriate steps can be taken to repair any deterioration, either by a change in conditions or reactivation of the electrode. It is much better to make a quick voltammetric determination of kinetic parameters in this way than to depend on tabulated values, however carefully the latter have been determined, because the values needed are for the particular electrode under the particular experimental conditions in use.

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NOTE—References 1, 2 and 3 are to Parts III, I and II, respectively, of this series.

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Thermometric Determination of Acid Anhydrides in the Presence of the Parent Acids

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A thermometric method is described for the determination of some carboxylic acid anhydrides. The anhydride is added to a methanolic solution of morpholine and the unreacted morpholine is titrated with a methanolic solution of hydrochloric acid. In most instances, the presence of large amounts of the parent acid has no effect on the determination and for 0·5 mmol of anhydride the accuracy is about ±1 per cent.

ALTHOUGH some individual carboxylic anhydrides have been determined by selected methods that involve the use of particular reagents,[1,2] there are very few general methods for the determination of anhydrides. Carboxylic acid anhydrides are, in general, very reactive and are often involved in many of the reactions that are undergone by their parent acids; this fact must be taken into account in the selection of a general method as many samples of anhydrides contain appreciable amounts of the free acid, and in some instances the amount of the acid present may exceed that of the anhydride.

Hence, any reaction that is used for the determination of an anhydride must not occur to any practical extent with the free acid during the time taken for the determination.

One such reaction is the formation of an amide by the reaction of the anhydride with a weak organic base. Aniline and morpholine have been used as such bases in a titrimetric method with either a visual indicator or a potentiometric end-point determination. Johnson and Funk[3] used morpholine dissolved in methanol, added an excess of the alcoholic solution to the anhydride sample and determined the unreacted base by titration with methanolic hydrochloric acid. A visual indicator system was used to ascertain the end-point. The method has been modified[4] so that both the anhydride and the acid can be determined consecutively in the same sample. However, neither method can be used if the sample is coloured, either because of self-colour or because of the presence of coloured impurities in some of the commercial samples.

The disadvantages of using a visual or photometric indication of the end-point in the determination of coloured materials are obvious, and the problems associated with the potentiometric methods that are used mainly for covalent multicomponent systems are also well known. The advantages of thermometric methods for such systems have been previously discussed.[5]

Surprisingly, however, there has been very little reported on the thermometric or enthalpimetric determination of anhydrides. Richmond and Eggleston[6] determined the purity of acetic anhydride by measuring the heat of reaction of acetic anhydride with aniline. Toluene was used as a diluent in order that the acetic acid produced in the reaction did not react with the excess of aniline at the higher temperatures produced.

Somiya[7] titrated acetic anhydride in tetrachloroethylene with aniline in the same solvent, having previously added pyridine so as to neutralise any strong acids, which would retard the reaction if they were present.

Acetic anhydride in glacial acetic acid was determined by Greathouse, Janssen and Haydes,[8] who measured the change in temperature caused by the perchloric acid catalysed reaction between water and acetic anhydride. Angelescu and Bărbulescu[9] determined acetic anhydride in the presence of acetic acid by adding the anhydride solution to a solution of aniline in toluene and measuring the temperature change produced.

Preliminary investigations by the present authors indicated that the reaction between morpholine and hydrochloric acid in a methanolic solution could be followed thermometrically. The reaction exhibited a substantial heat rise and the subsequent titration graph had a sharp break at the equivalence point.

The aim of the present work was to establish a general method for the determination of the anhydrides of carboxylic acids, both alone and in the presence of substantial amounts of their parent acids. The proposed method and a previously published method for some anhydrides were to be compared in order to ascertain the advantages or disadvantages of the proposed method when used for the determination of anhydrides in various types of samples.

EXPERIMENTAL

APPARATUS—

Details of the apparatus have been previously described.[10,11] The titrant, thermostatically controlled, was delivered to the titrand sample by a constant-speed peristaltic pump. The reaction vessel was thermally insulated in a suitable manner and the temperature changes were recorded as the imbalance voltage from a Wheatstone bridge containing a 10 000-Ω thermistor as one of its arms. The thermistor acted as the temperature sensor.

The titrant and titrand were at approximately the same temperature, *viz.*, 25 ± 1 °C.

REAGENTS—

Tris(hydroxymethyl)aminomethane (Tris)—A 0·1 M solution in methanol was prepared by dissolving a weighed amount (1·2114 g) of Tris in methanol and diluting the mixture to 100 ml with methanol. Suitable aliquots of this solution were used in the standardisation of the hydrochloric acid by continuous thermometric titration as recommended elsewhere.[12]

Hydrochloric acid—A stock solution (nominally 1·0 M) of hydrochloric acid in methanol was made by diluting 90 ml of hydrochloric acid (sp. gr. 1·16) to 1 litre with methanol. The solution was standardised by using the standard Tris solution.

Morpholine—A 0·1 M solution of morpholine in methanol was prepared by diluting a measured amount (9·3 ml) of redistilled morpholine to 1 litre with methanol. The solution was standardised against the standardised hydrochloric acid.

METHOD—

Transfer 10·0 ml of the morpholine solution into the titration vessel and add the sample containing about 0·5 mmol of the anhydride. (Methanol or other hydroxy-solvents should not be used to transfer the anhydride because in some instances the hydroxyl compound may react with the anhydride before the latter has had sufficient time to complete its reaction with the morpholine. The reaction between the morpholine and the anhydride is, for practical purposes, immediate and quantitative, while the reaction with the hydroxy-solvent is slow. However, the latter reaction is fast enough to occur to some extent if the anhydride is dissolved in methanol and allowed to stand before it is added to the morpholine.)

Place the titration vessel in the block of insulation and allow the mixture to stand at room temperature for 5 to 10 minutes to allow complete reaction to occur between the morpholine and the anhydride and also to allow thermal equilibrium to be attained.

Titrate the unreacted morpholine with the standardised hydrochloric acid solution. The amount of acid required to react with the excess of morpholine, and thence the amount of anhydride present, is then determined from the enthalpogram.

The results for the assay of some samples of pure materials are given in Table I.

TABLE I

THERMOMETRIC TITRATIONS OF PURIFIED ANHYDRIDES

Anhydride	Amount taken/g	Amount found/g	Recovery, per cent.
Acetic anhydride	0·0534	0·0528	98·9
	0·0534	0·0528	98·9
	0·0861	0·0857	99·5
	0·0861	0·0851	98·8
		Average	99·0
Butyric anhydride	0·0767	0·0758	98·8
	0·0767	0·0758	98·8
	0·0960	0·0949	98·9
	0·0960	0·0946	98·5
		Average	98·8
Maleic anhydride	0·0775	0·0773	99·7
	0·0589	0·0591	100·3
	0·0805	0·0795	98·8
	0·0517	0·0509	98·5
		Average	99·3

COMPARISON OF THE THERMOMETRIC METHOD WITH A METHOD IN WHICH A VISUAL INDICATOR IS USED[3]—

A stock solution of the reaction mixture was prepared for each anhydride by using the following general method.

Morpholine solution (100 ml of a 0·5 M methanolic solution) was transferred to a 250-ml calibrated flask and a known amount (approximately 10 to 20 mmol) of the particular anhydride was added, and 5 to 10 minutes were allowed for the reaction to proceed to completion. The mixture was then made up to volume with methanol.

Appropriate aliquots were titrated by using either a visual indicator or a thermometric technique to indicate the equivalence point.

In order that there should be approximately the same order of precision in each method, it was necessary to take 10·0-ml aliquots for the thermometric method and 100·0-ml aliquots for the visual indicator method. The comparative results are given in Table II.

From the results, it can be seen that the thermometric method gives acceptable reproducibility and has the added advantages, when compared with the titrimetric method in which a visual indicator is used, that a smaller aliquot needs to be used in order to obtain a high precision and that it can be used in solution conditions under which the visual method fails.

TABLE II

COMPARISON OF PURITIES OF SOME ANHYDRIDES OBTAINED BY THERMOMETRIC AND VISUAL END-POINT DETERMINATIONS

Visual indicator—mixed methyl yellow - methylene blue indicator

Anhydride	Thermometric*	Titrimetric†[3]
Acetic anhydride	99·0	99·5
	99·0	98·9
Propionic anhydride	92·7	93·5
	92·7	92·5
Butyric anhydride	98·9	98·8
	99·1	98·8
Benzoic anhydride	94·7	95·0
	94·7	94·1
Phthalic anhydride	85·1	84·5
	84·5	84·5
Succinic anhydride	97·0	97·0
	98·0	97·0
Maleic anhydride	99·1	‡
	100·4	‡
	99·7	‡
Isatoic anhydride	27·1, 27·9	27·2
	26·5	29·5‡
Pyromellitic dianhydride ..	59·7, 58·8	64·3
	59·7	63·7
Tetrachlorophthalic anhydride ..	95·5	‡
	95·2	‡

* Determined on a 10·0-ml aliquot.
† Determined on a 100·0-ml aliquot.
‡ End-point difficult to ascertain.

DETERMINATION OF THE ANHYDRIDES IN THE PRESENCE OF THE PARENT ACIDS—

The effect of various amounts of the parent acids when added to the corresponding anhydride was investigated by taking 10-ml aliquots from the stock solution (prepared as previously described) and adding to these various amounts of the acid under investigation.

The over-all temperature change for the reaction mixture is somewhat less than that obtained when the anhydride alone is present, but the enthalpogram shows a much sharper break at the equivalence point and enables a more precise measurement to be made.

From the results obtained (Table III), it can be seen that more than a 20-molar excess of the parent acid can be tolerated in all the anhydrides investigated, except for maleic anhydride. For this anhydride associated with the parent acid, it appears that the formation of the amide with morpholine is prevented. The acid does not react with the morpholine, otherwise the apparent purity would be greater than 100 per cent. Addition of the acid to the anhydride - morpholine mixture also results in low values for the anhydride. The method must therefore be restricted for maleic anhydride - maleic acid mixtures to those for which the ratio of acid to anhydride does not exceed 2:1. In practice, this usually is not a severe restriction.

TABLE III

DETERMINATION OF ANHYDRIDES IN THE PRESENCE OF THEIR PARENT ACIDS

Each result is the average of at least two results that differ by not more than ±0·5 per cent. from the mean

Anhydride	Amount taken/ mmol	Molar ratio of anhydride to acid	Apparent purity of anhydride, per cent.
Acetic anhydride	0·806	Anhydride alone	100·2
		1:20	99·3
		1:65	100·2
Propionic anhydride	0·594	Anhydride alone	99·8
		1:22	100·0
		1:65	100·5
Butyric anhydride	0·465	Anhydride alone	100·0
		1:25	99·0
		1:50	100·5
		1:70	99·6
Succinic anhydride	0·596	Anhydride alone	100·0
		1:15	100·5
		1:30	99·5
Phthalic anhydride	0·589	Anhydride alone	100·0
		1:10	100·0
		1:20	99·4
		1:40*	98·2
Benzoic anhydride	0·556	Anhydride alone	100·0
		1:15	100·7
		1:30	100·0
Maleic anhydride	0·593	Anhydride alone	100·2
		1:1·5	100·7
		1:3·0	84·0
		1:6·0	80·2
		1:10·0	56·0

* Undissolved acid present.

CONCLUSION

The thermometric method for the determination of anhydrides of carboxylic acids, alone or in the presence of the parent acid, has been shown to give acceptable analytical results and has advantages over the previously proposed methods.

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The Colorimetric Determination of Pyrogallol with Sodium Metavanadate in an Acetone - Water Solution

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In the determination of pyrogallol with sodium metavanadate, a shallow S-shaped absorption curve was obtained from which two separate linear calibration graphs were established, one for the determination of the lower pyrogallol concentrations (equivalent to 0·1 to 0·3 mg of pyrogallol), the other for the higher concentrations (equivalent to 0·45 to 0·8 mg). The effect of the initial volume, time required, volume of water, metavanadate concentration and the stability of the pyrogallol have been studied. The method was also applied to some other polyhydroxyphenolic compounds for purposes of comparison. Also, the precision and the accuracy of the proposed method are compared with those obtained by the A.O.A.C. method.

As with other polyphenols, pyrogallol, which occurs in various Sudanese plants, such as henna (*Lawsonia inermis*), is characterised by giving an extensive number of colour reactions, some of which have been used for its detection.[1] Kondo[2] has reviewed some of these methods and other characteristic colour tests for pyrogallol have been demonstrated by Rossi,[3] Ekkert[4] and Liberalli.[5]

Mitchell[6] has devised a colorimetric method for the determination of pyrogallol based on the violet colour produced by iron(II) tartrate with pyrogallol, and a modification of this method[7] was established by the use of iron(II) tartrate and sodium acetate. With the latter method, between 0·5 and 3 mg of pyrogallol could be determined. Ionescu-Matiu, Popesco and Popesco[8] have also described a micro-scale method for the determination of pyrogallol with tungstophosphoric acid.

A dark blue colour produced by the reaction of vanadium with pyrogallol was used as a basis for the detection of vanadium.[9–11] As this reaction appeared to be sensitive, a detailed study was carried out in this laboratory with the aim of developing a suitable sensitive colorimetric method for the determination of pyrogallol with sodium metavanadate in an aqueous acetone solution.

Fabinyi and Szeki[12] found that pyrogallol forms condensation products with acetone. It also reacts with oxygen in aqueous or in alcoholic solution to form brown oxidation products, but Lumière and Seyewetz[13] have been able to preserve pyrogallol indefinitely by the addition of a small amount of sodium hydrogen sulphite.

EXPERIMENTAL

APPARATUS—

An E.E.L. portable colorimeter (British Patent No. 594497), with matching 8-ml E.E.L. thin-walled test-tubes and a red filter OR1, was used. A Beckman DB spectrophotometer with recording device was used.

As the coloured product obtained in this determination leaves a greenish blue stain on the flasks after evaporation of the acetone, flasks should be cleaned with chromic acid mixture followed by tap water and distilled water, and dried completely before being re-used.

Calibrated flasks used in this work were of 10-ml volume unless otherwise stated.

REAGENTS—

All chemicals were obtained from BDH Chemicals Ltd. and used without further purification.

Acetone—Analytical-reagent grade, containing 0·2 per cent. of water.

Pyrogallol—Analytical-reagent grade.

Pyrogallol standard solution—Dissolve exactly 0·05 g of pyrogallol in about 40 ml of acetone, transfer the solution to a 250-ml calibrated flask and make the volume up to the mark with acetone. This solution should be freshly prepared and used immediately.

Sodium metavanadate—Laboratory-reagent grade.

Sodium metavanadate solution—Weigh exactly 0·1 g of sodium metavanadate into a beaker, add about 20 ml of distilled water (previously boiled and cooled to room temperature), warm and stir until completely dissolved. Transfer the solution to a 50-ml calibrated flask and make the volume up to the mark with water. This solution remains stable for at least 1 month.

PREPARATION OF CALIBRATION GRAPH—

The calibration graph was prepared by transferring 0·5 to 4 ml of standard pyrogallol solution into a series of clean, dry 10-ml calibrated flasks. Then a measured volume of acetone was added; this volume should be adjusted so that after the addition of sodium metavanadate solution, the total volume in the flasks will be exactly 8 ml (0·15 ml of 0·2 per cent. sodium metavanadate solution was added). The flasks were left for 3 minutes and the solutions were then made up to the mark with acetone. After 5 minutes the greenish blue colour was read against a blank in an E.E.L. colorimeter with a red filter OR1.

RESULTS AND DISCUSSION

The method is sensitive and many factors could affect the readings obtained. Some of these factors are as follows.

(*i*) *The initial volume* (i.e., *the volume before diluting to the mark*)—Different volumes of acetone were added to flasks containing equal concentrations of pyrogallol and sodium metavanadate. The water (0·15 ml) was added to each flask in equal volumes as sodium metavanadate solution. The flasks were left for 3 minutes and the solutions were then diluted to the mark. It was observed that an 8-ml initial volume gave stable readings whereas smaller initial volumes (*e.g.*, 4 ml) led to unstable readings. This effect may have been due to the water to acetone ratio.

(*ii*) *Time of analysis*—The initial volume in each flask was fixed at 8 ml and the flasks were arranged into three groups and left for 1, 2 and 3 minutes before diluting to the mark. Lower readings at the high concentrations (equivalent to 0·5 to 0·8 mg of pyrogallol) were observed with the solutions that were left for 1 minute; identical high readings were obtained after 2 and 3 minutes.

In another experiment at two different pyrogallol concentrations (equivalent to 0·4 and 0·8 mg) the flasks, with the initial volume (8 ml), were left for 3 minutes before diluting to the mark and readings were taken after 2½, 7½, 10, 12½, 15, 17½ and 20 minutes (Fig. 1).

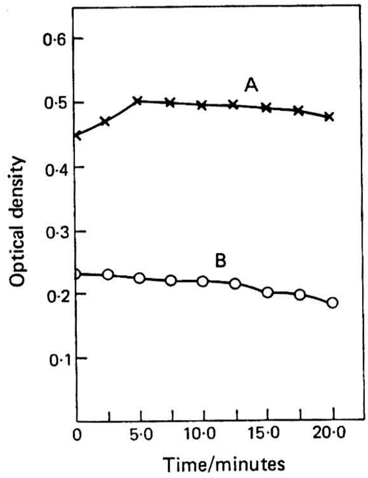

Fig. 1. Effect of time on optical density by using two different pyrogallol concentrations: A, 0·8 mg of pyrogallol present; and B, 0·4 mg of pyrogallol present

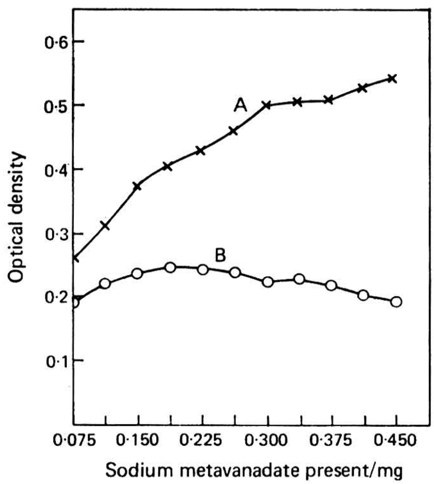

Fig. 2. Effect of different metavanadate concentrations on optical density by using two different pyrogallol concentrations: A, 0·8 mg of pyrogallol present; and B, 0·4 mg of pyrogallol present

The maximum optical density occurred at 5 minutes (with 0·8 mg of pyrogallol) and this value decreased with time. A higher reading was obtained immediately after preparation (with 0·4 mg of pyrogallol), which also decreased with time. It should be mentioned here that higher pyrogallol concentrations may require more time for the colour to develop than lower concentrations. The decrease in readings may be caused by the oxidation of the pyrogallol the colour of which, if left overnight, changes from greenish blue to brown.

(*iii*) *Sodium metavanadate concentration*—All factors affecting the readings were kept constant except the sodium metavanadate concentration, which ranged between 0·075 and 0·450 mg of sodium metavanadate in the total volume of the flasks (10 ml) when made up to the mark. These concentrations were applied with the 0·4 and 0·8-mg amounts of pyrogallol taken from the standard solution. The results obtained (Fig. 2) showed that optical density readings increased with increase in sodium metavanadate concentration when 0·8 mg of pyrogallol was used.

With 0·4 mg of pyrogallol, the increase in the readings was in direct proportion to the increase in sodium metavanadate concentration up to 0·1875 mg of sodium metavanadate and any increase over this concentration of sodium metavanadate led to a decrease in the readings.

For these two pyrogallol concentrations, the increase in the readings in relation to the increase in metavanadate concentrations could suggest that an insufficient amount had been added to the flasks; the decrease in readings in relation to the increase in the metavanadate concentrations suggests that the excess of metavanadate affects the colour produced.

(*iv*) *Volume of water*—The significance of the volume of water arises from the fact that water was used as a solvent for the sodium metavanadate. All factors affecting the reading were kept constant except for the volume of water, which ranged between 0·10 and 0·35 ml (Fig. 3).

Two different pyrogallol concentrations were used as in (*iii*). By using 0·8 mg of pyrogallol, readings increased with the increase in volume of water up to 0·2 ml and any increase of water over that limit led to a decrease in the readings. When 0·4 mg of pyrogallol was used, the decrease in the readings was proportional to the increase in the volume of water when the latter exceeded 0·125 ml.

The increase in readings with the increase in the volume of water may indicate that a specific water to acetone ratio is required for maximum colour development and this ratio varies according to the concentration of the pyrogallol. The decrease in readings with the increase in the volume of water may suggest that a higher water content in the reaction medium could facilitate the oxidation of the pyrogallol rather than the formation of the greenish blue colour.

STABILITY AND COLOUR DEVELOPMENT IN AN ACETONE - WATER MEDIUM—

Standard pyrogallol solution prepared with previously boiled and cooled water showed, after about 8 minutes, a change in colour to greenish yellow, which gradually became yellow and then brown. When the determination was carried out with the acetone completely replaced with water, a brown colour was obtained (not greenish blue), but with very high concentrations of pyrogallol a blackish colour was produced.

A standard solution of pyrogallol prepared with acetone was found to be stable for several hours after preparation, but if left overnight the colour changed to yellow and then to brown. Slightly lower readings were obtained when this solution was kept for 1 day, but the readings decreased considerably after a period of 5 days. The condensation product formed by pyrogallol with acetone does not show any difference in readings compared with acetone alone.

As an aqueous ethanolic solution of pyrogallol can be preserved indefinitely by the addition of a small amount of sodium hydrogen sulphite and because the latter is insoluble in acetone, an attempt was made to dissolve as much sodium hydrogen sulphite as possible in the acetone containing 0·2 per cent. of water. This solution was filtered and pyrogallol was added. Readings were carried out on this standard solution and they appeared to be identical with those obtained by the proposed method. The colour of this standard solution changed slightly to light brown after 2 days, which showed that the addition of sodium hydrogen sulphite could prolong the stability of the standard pyrogallol solution compared with the solution that did not contain sodium hydrogen sulphite, and indicates that the latter does not interfere in this reaction.

It was also observed that the standard pyrogallol solution was more stable in winter than in summer, probably because of the effect of temperature on the oxidation of pyrogallol.

ACETONE - METAVANADATE RELATIONSHIP—

An experiment was carried out by using only blanks (*i.e.*, without the addition of pyrogallol). These solutions were divided into two groups, the first of which was shaken every 5 minutes and the second group left without shaking. In the latter group a white precipitate formed after about 1 hour.

In another experiment sodium metavanadate was added 5, 10 and 15 minutes before the pyrogallol. A noticeable decrease in the readings that was proportional to the increase in time was observed but some differences were noticed in the duplicates. However, this effect showed that acetone reacted with some of the metavanadate.

The decrease in optical density was not observed when pyrogallol was added first, followed by sodium metavanadate. This decrease may be due to the fact that pyrogallol reacts more readily with vanadium than with acetone. Most of the sodium metavanadate appears to react with the pyrogallol, the remainder being insufficient to form a precipitate with acetone.

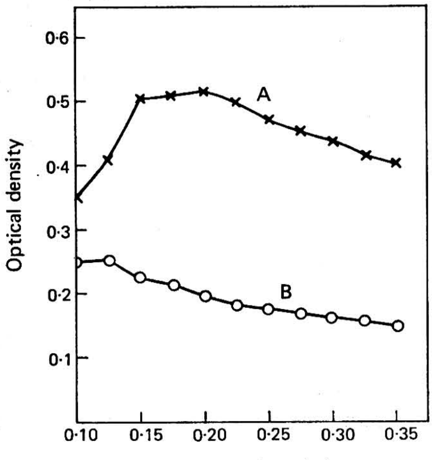

Fig. 3. Effect of volume of water on optical density by using two different pyrogallol concentrations: A, 0·8 mg of pyrogallol present; and B, 0·4 mg of pyrogallol present

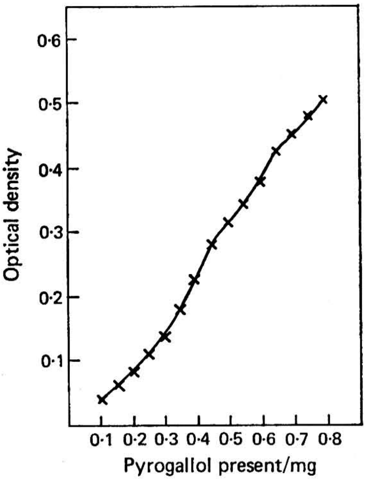

Fig. 4. Calibration graph for different concentrations of pyrogallol

APPLICATION OF THE PROCEDURE TO SOME POLYHYDROXYPHENOLIC COMPOUNDS—

The above procedure was applied to resorcinol, phloroglucinol, catechol and hydroquinone, which were tested alone and with pyrogallol. Resorcinol, phloroglucinol and hydroquinone formed colourless solutions that did not show any significant differences when compared with blanks. Catechol formed a green colour when used alone and increased the expected readings of pyrogallol by about 109 per cent. when mixed with it in equal proportions.

CALIBRATION GRAPH—

A sigmoid calibration graph was obtained over the concentration range equivalent to 0·1 to 0·8 mg of pyrogallol (Fig. 4). Statistical analyses were carried out to enable two linear calibration graphs to be established (Fig. 5) from the sigmoid curve, one of which represents the lower concentrations (equivalent to 0·1 to 0·3 mg of pyrogallol), and the other representing the higher concentrations (equivalent to 0·45 to 0·8 mg of pyrogallol). The two linear graphs were compared with that obtained by the A.O.A.C. method (Fig. 5) in which the same E.E.L. colorimeter, but with a green filter OGR1, was used.

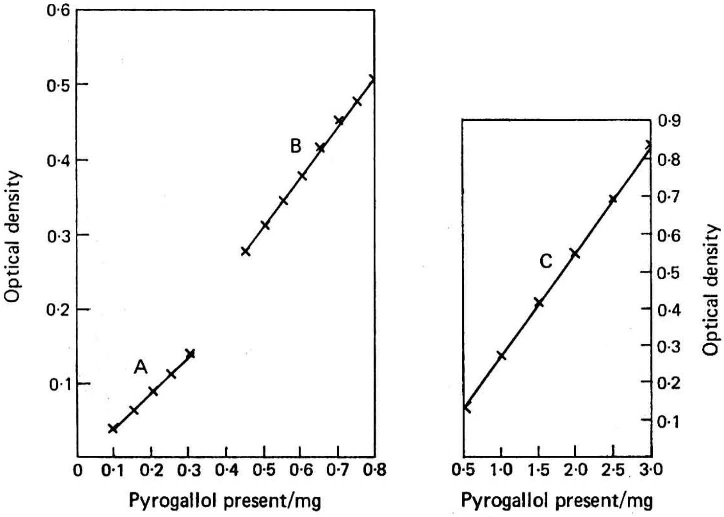

Fig. 5. Linear calibration graphs by proposed method: A, for 0·1 to 0·3 mg of pyrogallol; and B, for 0·45 to 0·8 mg of pyrogallol. C, linear calibration graph by A.O.A.C. method for 0·5 to 3·0 mg of pyrogallol:

A, $\bar{y} = 0{\cdot}0864 + 0{\cdot}502(x - 0{\cdot}2)$ ($r = 0{\cdot}9980$)
B, $\bar{y} = 0{\cdot}3953 + 0{\cdot}6602(x - 0{\cdot}625)$ ($r = 0{\cdot}9977$)
C, $\bar{y} = 0{\cdot}478 + 0{\cdot}2806(x - 0{\cdot}175)$ ($r = 0{\cdot}9999$)

PRECISION OF THE METHOD—

To determine the precision of the proposed method in standard pyrogallol solution, each amount between 0·1 and 0·8 mg of pyrogallol was determined twelve times. The worst precision obtained was ±5·00 per cent. at the lowest pyrogallol concentration (with 0·1 mg of pyrogallol). The results obtained by the proposed method were compared with those obtained by the A.O.A.C. method (Table I). Generally, better precision values were found by the A.O.A.C. method compared with the proposed method, which may have been due to the fact that acetone is a volatile solvent and some fluctuations in the readings may have occurred as a result of temperature changes at the time readings were taken.

TABLE I

PRECISION OF THE METHOD

Proposed method			A.O.A.C. method		
Pyrogallol taken/mg	Mean reading	Precision, per cent.	Pyrogallol taken/mg	Mean reading	Precision, per cent.
0·10	0·0396	±5·00	0·5	0·1283	1·41
0·15	0·0602	±2·61	1·0	0·2691	0·75
0·20	0·0836	±2·85	1·5	0·4080	0·73
0·25	0·1119	±1·81	2·0	0·5422	0·42
0·30	0·1390	±1·64	2·5	0·6909	0·81
0·35	0·1799	±1·17	3·0	0·8312	0·81
0·40	0·2258	±2·15			
0·45	0·2779	±1·23			
0·50	0·3139	±1·53			
0·55	0·3438	±1·30			
0·60	0·3778	±1·38			
0·65	0·4228	±1·91			
0·70	0·4504	±1·56			
0·75	0·4787	±0·98			
0·80	0·5030	±1·35			

ACCURACY OF THE METHOD—

The mean readings were checked on the linear calibration graphs for both the proposed and the A.O.A.C. methods. High accuracy was obtained for all the points determined, as shown in Table II.

TABLE II

ACCURACY OF THE METHOD

Proposed method			A.O.A.C. method		
Pyrogallol taken/mg	Recovered, from the linear graph/mg	Recovery, per cent.	Pyrogallol taken/mg	Recovered, from the linear graph/mg	Recovery, per cent.
0·10	0·1028	102·8	0·5	0·5050	101·0
0·15	0·1485	99·0	1·0	1·0050	100·5
0·20	0·1973	98·6	1·5	1·5050	100·3
0·25	0·2500	100·0	2·0	2·0250	101·2
0·30	0·3020	100·6	2·5	2·5050	100·2
0·45	0·4475	99·4	3·0	3·0050	100·1
0·50	0·5025	100·5			
0·55	0·5465	99·3			
0·60	0·5985	99·7			
0·65	0·6662	102·8			
0·70	0·7088	101·2			
0·75	0·7515	100·2			
0·80	0·7800	97·5			

SPECTRA—

Measurements of spectra in the visible region were made by using a Beckman DB spectrophotometer with a recording device to illustrate the wavelength of maximum absorbance. Two different concentrations were taken. The maximum absorbance for the highest pyrogallol concentration (equivalent to 0·8 mg of pyrogallol) was found to occur at wavelength 348 nm while the maximum absorbance of the lowest concentration (equivalent to 0·1 mg of pyrogallol) occurred at wavelength 356 nm (Fig. 6).

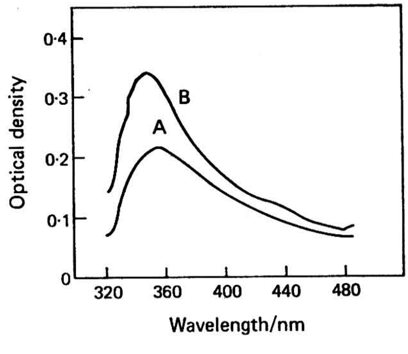

Fig. 6. Graphs of optical density *versus* wavelength: A, 5 ml of 0·02 per cent. pyrogallol and 0·375 ml of 0·2 per cent. sodium metavanadate in a 25-ml calibrated flask; and B, 10 ml of 0·02 per cent. pyrogallol and 0·375 ml of 0·2 per cent. sodium metavanadate in a 25-ml calibrated flask

CONCLUSIONS

The sigmoid calibration graph (Fig. 4) might suggest that two distinct reactions are involved, one being favoured in the higher pyrogallol concentration range and the other in the lower range. There is also some evidence to support this view in the different behaviour at the two levels as shown in both Figs. 2 and 3.

It seems that an acetone medium is more resistant to the oxidation of pyrogallol compared with an aqueous medium, which may be due to the fact that oxygen is absorbed rapidly in water, resulting instantly in the formation of the brown oxidation products. It was also observed that the greenish blue colour formed in the acetone medium is not permanently stable because with time more oxygen is absorbed and the colour changes to brown, showing that the complex or complexes formed between pyrogallol and vanadium do not protect the pyrogallol from oxidation.

The proposed method can be used to determine lower concentrations of pyrogallol than those determined by the A.O.A.C. method; also, the use of acetone renders the standard solution more stable against oxidation than the standard prepared with water. To apply this method, it is essential to prepare the extract in acetone before the determination is carried out.

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A Method for the Chemical Analysis of Chrome Ores and Chrome-bearing Refractories*

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This paper includes a detailed description of a method for the analysis of chrome ores and chrome-bearing materials; it is to be submitted to the British Standards Institution for acceptance as a standard method. The determinations include those of SiO_2, TiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Cr_2O_3, MnO, alkali-metal oxides and loss on ignition. The experimental work leading to the final method is described and tables of co-operative results obtained by the Refractories Working Group of the Analysis Committee of the British Ceramic Research Association are included.

THE problem of devising a method for the analysis of chrome ores and chrome-bearing refractories has occupied the attention of the Refractories Working Group, periodically, since its inception. In fact, its predecessor, the Analysis Sub-committee of the Refractories Testing Committee, spent much time testing methods for the determination of chromium(III) oxide and iron(III) oxide in these materials.

The first step in this programme of work was taken by the Analysis Sub-committee, which investigated a procedure for the determination of chromium devised by Bryant and Hardwick[1] and eventually published a recommended method based on this procedure.[2] The method for determining iron, which was based on a reduction followed by an oxidising titration, was approved by the Sub-committee as a potential standard, but was not published. It has since been replaced by a spectrophotometric procedure and is therefore of no concern here.

The foundation for the present work was laid in the separation method for chromium involving the use of Amberlite LA-2 liquid ion-exchange resin.[3] Most of the subsequent determinations have assumed the removal of chromium from a stock solution by this method. The first attempts in this direction were the development of a spectrophotometric method for the determination of silicon and a complexometric method for the determination of calcium.[4] These methods, together with spectrophotometric methods for determining chromium and iron, were published as a British Standard.[2]

After completing the work on the analysis of magnesites and dolomites,[5] the Working Group turned its attention to completing the programme of work on chrome-bearing materials. This paper outlines these latter activities and describes the method in detail. It should be stressed that the paper does not purport to be exhaustive; the Group, in fact, pursued many lines of fruitless enquiry, and only those which either produced a useful contribution to the solution of the problem or returned a negative answer to a clearly defined possibility are mentioned.

METHOD

This method covers the determination of loss on ignition, SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, Cr_2O_3, CaO, MgO and alkali-metal oxides in chrome ores, chrome - magnesite refractories and magnesite - chrome refractories. A schematic diagram is shown in Fig. 1.

PRINCIPLE OF THE METHOD

DETERMINATION OF LOSS ON IGNITION—

The loss on ignition is determined at 1000 °C.

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* A report prepared by the Refractories Working Group of the Analysis Committee of the British Ceramic Research Association.

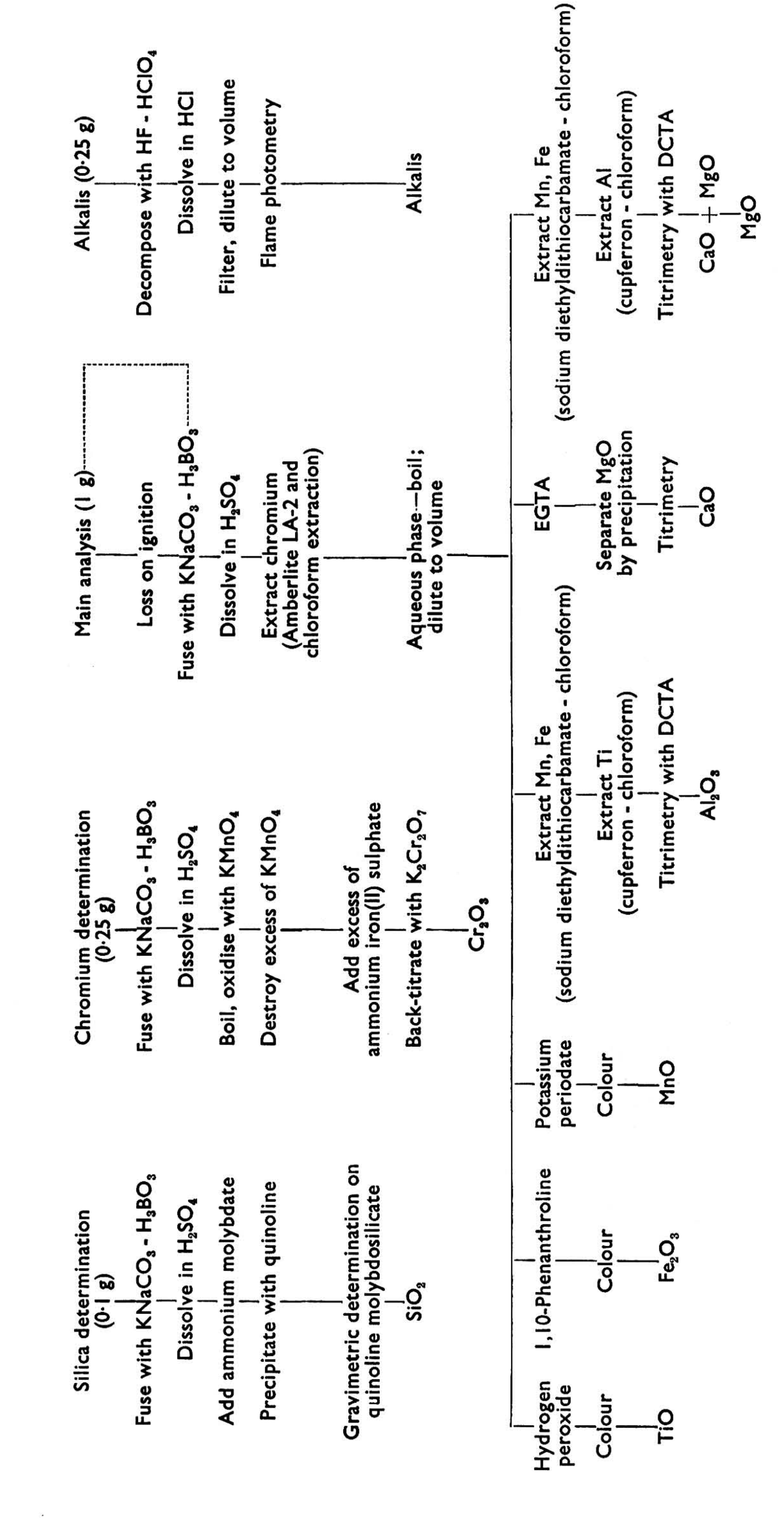

Fig. 1. Schematic diagram for the analysis of chrome ores and chrome-bearing materials

DETERMINATION OF SILICON DIOXIDE—

The sample is fused with fusion mixture - boric acid and the melt dissolved in sulphuric acid. After dilution, ammonium molybdate is added and the yellow molybdosilicic acid allowed to develop. After adjustment of the acidity, the molybdosilicic acid is precipitated by the addition of quinoline and the solution is heated to 80 °C and then cooled to below 20 °C. The precipitate is filtered on a weighed Gooch crucible, washed and dried at 150 °C in an air-oven.

DETERMINATION OF CHROMIUM(III) OXIDE—

The sample is fused with fusion mixture - boric acid and the melt dissolved in sulphuric acid. The solution is transferred to a 1-litre conical flask and boiled. Dilute potassium permanganate solution is added, so as to oxidise any reduced chromate present, until the reddish amber colour persists, and the excess of permanganate is then destroyed by boiling the solution with dilute hydrochloric acid. The solution is cooled and excess of standard ammonium iron(II) sulphate solution added, followed by phosphoric acid. The excess of ammonium iron(II) sulphate is back-titrated with standard potassium dichromate solution, with barium diphenylaminesulphonate as indicator.

DETERMINATION OF THE OXIDES OF TITANIUM(IV), IRON(III), ALUMINIUM(III), MANGANESE(II), CALCIUM AND MAGNESIUM—

The sample is fused with fusion mixture - boric acid and the melt dissolved in sulphuric acid. Chromium is then removed by extraction with Amberlite LA-2 liquid ion-exchange resin. The aqueous phase is washed by extraction with chloroform, transferred into a beaker and all traces of chloroform are removed by boiling the solution. After cooling, the solution is made up to standard volume. Aliquots of this "stock" solution are used for all of the following determinations.

Titanium dioxide is determined spectrophotometrically with hydrogen peroxide, the iron(III) oxide with 1,10-phenanthroline and the manganese(II) oxide with potassium periodate. For the aluminium(III) oxide determination, an aliquot is extracted with sodium diethyldithiocarbamate - chloroform to remove iron and manganese, followed by an extraction with cupferron - chloroform to remove titanium. The determination is completed titrimetrically by the addition of excess of diaminocyclohexanetetraacetic acid (DCTA) and back-titration with zinc, with dithizone (diphenylthiocarbazone) as indicator. Any residual chromium present in the stock solution is not titrated, as the solution is not boiled after the addition of DCTA. Calcium is determined on a measured volume of the solution to which triethanolamine is added to complex interfering elements. A known volume of standard 1,2-bis-(2-aminoethoxy)ethanetetraacetic acid (EGTA), sufficient to complex all the calcium, is then added, after which the magnesium is precipitated with potassium hydroxide. After filtration, the excess of EGTA is titrated with standard calcium solution, calcein being used as indicator. Magnesium oxide is determined titrimetrically on an aliquot of the stock solution by extraction with sodium diethyldithiocarbamate - chloroform to remove iron and manganese, followed by a buffered cupferron - chloroform solvent extraction to remove aluminium and titanium. After addition of triethanolamine, the magnesium is titrated with DCTA in a strongly ammoniacal solution containing ammonium chloride. This titration also includes the titration for calcium, which must be allowed for.

DETERMINATION OF ALKALI-METAL OXIDES—

The sample is decomposed with hydrofluoric and perchloric acids to remove the silicon. A further evaporation with perchloric acid removes traces of fluoride; the residue is dissolved in hydrochloric acid and the solution is filtered. After dilution of the solution to a standard volume, the alkali-metal oxides are determined by using a flame photometer.

REAGENTS—

Unless otherwise stated, all reagents should be of analytical-reagent grade when available, and distilled water must be used throughout the analysis.

Ammonium chloride.

Boric acid.

Ammonium iron(II) sulphate.

Fusion mixture.

Potassium periodate.

Thymolphthalein.

Acetic acid, glacial.

Amberlite LA-2 resin solution (1 + 4)—Add 50 ml of resin to 200 ml of chloroform and mix. Transfer the mixture to a 500-ml separating funnel, add 25 ml of dilute sulphuric acid (1 + 9) and shake gently (release the pressure in the funnel frequently during the first few seconds of shaking). Allow the layers to separate and run off the organic layer into a 250-ml measuring cylinder.

Ammonia solution, sp. gr. 0·88.

Ammonium acetate solution, approximately 10 *per cent.*—Dilute 140 ml of glacial acetic acid to 1700 ml with water and add carefully 140 ml of ammonia solution. Mix, cool and adjust the pH to approximately 6·0 to 6·5.

Ammonium acetate buffer solution (for aluminium determinations)—Add 120 ml of glacial acetic acid to 500 ml of water followed by 74 ml of ammonia solution. Mix, cool and dilute the solution to 1 litre.

Ammonium acetate buffer solution (for magnesium determinations)—Dilute 5 ml of ammonia solution to 100 ml with water and add 30 ml of glacial acetic acid. Adjust the solution to pH 3·8 by using a pH meter and then dilute it to 200 ml with water.

Ammonium molybdate solution, 10 *per cent.* m/V—Discard this solution after 4 weeks, or earlier if any appreciable deposit is observed.

Chloroform, B.P. grade.

Cupferron solution, 6 *per cent.* m/V—This solution must be freshly prepared.

Ethanol, 95 *per cent.*—Industrial methylated spirit.

Hydrochloric acid, sp. gr. 1·18.

Hydrofluoric acid, 40 *per cent.* m/m.

Hydrogen peroxide, 20 *volume.*

Hydroxylammonium chloride, 10 *per cent.* m/V.

Magflok, about 2 *per cent.* m/V—The resin is a thick viscous liquid and it is therefore most convenient to transfer a drop to a beaker and to weigh the amount taken. Sufficient water is then added to make up a solution about 2 per cent. *m/V*. The resin is available from Ridsdale & Co Ltd., Newham Hall, Middlesbrough, Teesside.

Magnesium sulphate solution—Dissolve 6·11 g of magnesium sulphate heptahydrate in water, filter and dilute the solution to 500 ml.

50 ml of solution ≡ approximately 0·1 g of MgO.

Naphthol green B, 0·1 *per cent.* m/V.

Nitric acid, sp. gr. 1·42.

Perchloric acid, sp. gr. 1·54.

1,10-*Phenanthroline hydrate,* 1 *per cent.* m/V—Prepare sufficient solution for immediate use at a concentration of 0·1 g of 1,10-phenanthroline hydrate per 10 ml of acetic acid (1 + 1).

Orthophosphoric acid, sp. gr. 1·75.

Potassium hydroxide solution, 25 *per cent.* m/V.

Quinoline solution, 2 *per cent.* V/V—Add 20 ml of quinoline (boiling range 235 to 239 °C) to about 800 ml of hot water acidified with 25 ml of the hydrochloric acid, stirring constantly if the mixture is cloudy. Cool, add some paper pulp and stir the mixture vigorously. Allow the mixture to settle and filter it under suction through a paper-pulp pad to remove traces of oily matter, but do not wash the pad. Dilute the filtrate to 1 litre.

Quinoline wash solution, 0·05 *per cent.* V/V—Dilute 25 ml of the quinoline solution to 1 litre.

Sodium diethyldithiocarbamate solution, 10 *per cent.* m/V—This solution must be freshly prepared.

Sodium hydroxide solution, 0·4 *per cent.* m/V.

Sulphuric acid, sp. gr. 1·84.

Triethanolamine.

STANDARD SOLUTIONS—

Calcium solution (1·0 *mg* ml^{-1} *of CaO*)—Dissolve 1·785 g of calcium carbonate (dried at 150 °C) in a slight excess of hydrochloric acid (1 + 4), boil the solution to expel carbon dioxide, cool and dilute it to 1 litre.

1,2-Diaminocyclohexanetetraacetic acid (DCTA) solution, about 0·05 M—Dissolve 18·2175 g of DCTA in 500 ml of water by the progressive addition of the minimum amount of potassium hydroxide solution (25 per cent. *m/V*). Dilute the solution to 1 litre. Standardise this solution against both standard magnesium and standard zinc solutions.

1,2-Bis-(2-aminoethoxy)ethanetetraacetic acid (EGTA), about 0·05 M—Dissolve 19·017 g of EGTA in 500 ml of water by the progressive addition of the minimum amount of potassium hydroxide solution (25 per cent. *m/V*). Dilute the solution to 1 litre. Standardise the solution against the standard calcium solution.

Ammonium iron(II) sulphate solution, about 0·05 N—Dissolve 19·6 g of ammonium iron(II) sulphate in 1 litre of diluted sulphuric acid (1 + 4). Standardise the solution against 0·05 N potassium dichromate solution.

Iron solution A (0·1 *mg ml*$^{-1}$ *of* Fe_2O_3)—Dissolve 0·0699 g of the oxide-free metal wire in a slight excess of hydrochloric acid (1 + 9); add 5 ml of hydrogen peroxide and boil the mixture for 15 minutes. Cool and dilute the solution to 1 litre.

Iron solution B (0·01 *mg ml*$^{-1}$ *of* Fe_2O_3)—Dilute 50 ml of iron solution A to 500 ml.

Lithium solution A (400 *p.p.m. of* Li_2O)—Dehydrate lithium sulphate monohydrate by heating it at 150 °C for 24 hours. Dissolve 1·4719 g of the anhydrous lithium sulphate in water and dilute the solution to 1 litre.

Lithium solution B (20 *p.p.m. of* Li_2O)—Dilute 25 ml of lithium solution A to 500 ml.

Magnesium solution (5 *mg ml*$^{-1}$ *of* MgO)—Dissolve 3·016 g of the oxide-free metal in a slight excess of hydrochloric acid (1 + 9), cool the solution and dilute it to 1 litre.

Manganese solution A (0·1 *mg ml*$^{-1}$ *of* MnO)—Dilute the calculated volume of previously standardised (about 0·1 N) potassium permanganate solution to 1 litre (with exactly 0·1N potassium permanganate solution, 70·5 ml are required).

Manganese solution B (0·01 *mg ml*$^{-1}$ *of* MnO)—Dissolve 50 ml of the manganese solution A to 500 ml.

Potassium dichromate solution, 0·05 N—Dissolve 2·4516 g of the recrystallised salt (dried at 150 °C) in water and dilute the solution to 1 litre.

Potassium permanganate solution, about 0·1 N—Dissolve about 3·2 g of potassium permanganate in 1 litre of water to obtain an approximately 0·1 N solution. Boil this solution for 5 minutes, filter it through a sintered-glass crucible of porosity grade No. 4 and cool it. Standardise the solution against sodium oxalate and store it in an amber-glass bottle.

Potassium - sodium solution A (200 *p.p.m. of* K_2O, 100 *p.p.m. of* Na_2O)—Dissolve 0·3700 g of anhydrous potassium sulphate (dried at 150 °C) and 0·2292 g of anhydrous sodium sulphate (dried at 150 °C) in water and dilute the solution to 1 litre.

Potassium - sodium solution B (10 *p.p.m. of* K_2O, 5 *p.p.m. of* Na_2O)—Dilute 25 ml of potassium - sodium solution A to 500 ml.

Titanium solution A (1·0 *mg ml*$^{-1}$ *of* TiO_2)—Ignite pure TiO_2 and then fuse 1·000 g of it with 10 g of potassium pyrosulphate. Allow the melt to cool and dissolve it, at a low temperature to prevent hydrolysis, in 200 ml of water to which 20 ml of the sulphuric acid have been cautiously added. Cool the solution and dilute it to 1 litre.

Titanium solution B (0·04 *mg ml*$^{-1}$ *of* TiO_2)—Dilute 20 ml of titanium solution A to 500 ml.

Zinc solution, 0·05 M—Dissolve 3·2685 g of the oxide-free metal in 50 ml of hydrochloric acid (1 + 4); cover the beaker with a clock-glass and allow it to stand overnight on a steam-bath. Cool the solution and dilute it to 1 litre.

INDICATORS—

Barium diphenylaminesulphonate solution, 0·3 *per cent.* m/V—Dissolve 0·3 g of barium diphenylaminesulphonate in 100 ml of warm water and cool the solution.

Bromophenol blue solution, 0·1 *per cent.* m/V—Grind 0·1 g of bromophenol blue with 1·5 ml of sodium hydroxide solution (0·4 per cent. *m/V*) and dissolve the mixture in 100 ml of water.

Calcein indicator—Mix, by grinding together, 0·2 g of calcein, 0·12 g of thymolphthalein and 20 g of potassium chloride.

Dithizone solution, 0·025 *per cent.* m/V—Dissolve 0·0125 g of dithizone in 50 ml of 95 per cent. ethanol. This solution will keep for about 1 week.

Solochrome black 6B (*also known as Eriochrome blue-black B*)—Mix, by grinding together, 0·5 g of Solochrome black 6B and 20 g of sodium chloride.

STANDARDISATIONS—

DCTA against magnesium—Transfer 50·0 ml of the standard magnesium solution (5 mg ml^{-1} of MgO) to a 500-ml conical flask. Add 100·0 ml of the DCTA solution, then 2 g of ammonium chloride and 25 ml of the ammonia solution. Titrate with the DCTA solution, with Solochrome black 6B as indicator, from red, through purple, to the last change in colour to a clear ice blue.

1 ml of 0·05 M DCTA solution ≡ 2·016 mg of MgO.

DCTA against zinc—Transfer 50·0 ml of the DCTA solution to a 500-ml conical flask and add 5 or 6 drops of the hydrochloric acid. Add a few drops of bromophenol blue indicator and then add ammonium acetate buffer solution (for aluminium determination) until the indicator turns blue, followed by an excess of 10 ml. Add a volume of 95 per cent. ethanol equal to the total volume of the existing solution, followed by 1 to 2 ml of dithizone solution (0·025 per cent. *m*/*V*), and titrate with the standard zinc solution (0·05 M) from green to the first appearance of a permanent pink colour.

1 ml of 0·05 M DCTA solution ≡ 2·55 mg of Al_2O_3.

EGTA against calcium—Transfer 50 ml of the magnesium sulphate heptahydrate solution to a 250-ml calibrated flask and add 20·0 ml of the EGTA solution. Dilute the solution to 150 ml and add potassium hydroxide solution (25 per cent. *m*/*V*) until no further precipitation occurs and then add an excess of 10 ml, followed by 10 ml of Magflok solution (2 per cent. *m*/*V*). Dilute the mixture to 250 ml, shake it and allow it to stand for about 10 minutes to settle. Filter the mixture through a dry 125-mm Whatman No. 541 filter-paper into a dry beaker. Transfer by pipette 200 ml of the filtrate into a 500-ml conical flask and add 15 ml of potassium hydroxide solution (25 per cent. *m*/*V*). Titrate with standard calcium solution (1 mg ml^{-1} of CaO), with screened calcein as indicator, to the first appearance of green fluorescence.

1 ml of 0·05 M EGTA solution ≡ 2·804 mg of CaO.

BLANK DETERMINATIONS—

Blank determinations should be carried out on all reagents in accordance with the general scheme of analysis. When carrying out the blank determination for calcium, it is necessary to add 50 ml of the magnesium sulphate heptahydrate solution before the addition of the standard EGTA solution.

PREPARATION OF THE SAMPLE—

The sample prepared for analysis should be ground to pass a 125-μm B.S. test sieve. A non-metallic (*e.g.*, 120-mesh nylon bolting cloth) sieve is preferable.

The preparation of a ground sample of chrome-bearing material is complicated by the fact that the material is often itself magnetic, so that the use of a magnet to remove iron contamination is therefore precluded. However, unless materials such as boron carbide are available, there is little alternative to completing the crushing in an iron percussion mortar. Fortunately, the iron content of these materials is so high that the iron introduced represents only a small fraction of the amount in the sample. The material is too hard, in general, to permit the use of either porcelain or agate mortars.

EXPERIMENTAL DETAILS OF THE METHOD

DETERMINATION OF LOSS ON IGNITION—

Weigh 1·000 g of the finely ground sample, previously dried at 110 °C, into a platinum crucible. Increase the temperature slowly over a period of about 20 minutes and then transfer the crucible to a furnace at 1000 °C for 30 minutes. Remove the crucible from the furnace, cool and weigh it.

DETERMINATION OF SILICON DIOXIDE—

NOTE—The determination must be carried out from the completion of the fusion to the precipitation of the quinoline molybdosilicate with no delay.

Decomposition of the sample—Weigh 0·100 g of the finely ground sample, previously dried at 110 °C, into a platinum dish; convenient dimensions are 70 mm diameter and 40 mm deep, with an effective capacity of 75 ml. Add 4 g of fusion mixture and 2 g of boric acid and mix intimately to form a charge in the centre of the dish.

Heat the dish with a bunsen or Meker burner, slowly increasing the temperature until the mixture begins to melt, and continue to heat at this temperature until melting is completed. It is important that the initial stage of the heating should be slow, as a vigorous reaction takes place on melting and spattering easily occurs. Increase the temperature further, slowly and steadily, to that of the full heat of the flame (approximately 950 °C). After maintaining this temperature for 5 minutes, swirl the contents of the dish every 2 minutes, making sure that the particles of sample on the side of the dish come into contact with hot, molten flux. Continue to heat the dish at this temperature until decomposition is completed; 15 minutes is usually sufficient. Completeness of decomposition can be checked visually by the absence of unfused material at the bottom of the melt. The type and position of the burner should be chosen so as to maintain oxidising conditions throughout the heating.

Cool, place the dish and lid in a porcelain basin so as to avoid loss of solution if frothing occurs and add 20 ml of diluted sulphuric acid (1 + 3). When dissolution is complete, transfer the solution to a 1-litre beaker, washing the dish and lid with water. Dilute the solution to approximately 400 ml with cold water.

Determination of silicon dioxide—Immediately add 50 ml of ammonium molybdate solution (10 per cent. m/V) from a pipette or burette, stirring vigorously during the addition and for 1 minute after it, and stand the solution at room temperature for 10 minutes.

Add 50 ml of the hydrochloric acid rapidly, and immediately precipitate the quinoline molybdosilicate by adding 50 ml of the quinoline solution from a burette, dropwise at first but rapidly after the formation of a permanent precipitate, stirring the solution during the addition.

Place a thermometer in the solution, heat with occasional stirring to 80 °C over a period of about 10 minutes and maintain the solution at this temperature for 5 minutes. Cool the solution, stirring it occasionally, in running water to below 20 °C and filter it through a weighed Gooch crucible with a sintered-glass mat (porosity 4), transferring the precipitate to the crucible with a jet of quinoline wash solution that has been cooled to below 20 °C.

After scrubbing out the beaker with a "policeman," wash the precipitate eight times with quinoline wash solution, care being taken not to allow the precipitate to run dry during filtration and washing.

Dry the precipitate at 150 °C to constant mass; 2 hours is usually sufficient. Cool it in a desiccator and weigh it.

Calculation—If a 0·1-g sample is taken, then

$$\text{Mass of precipitate (g)} \times 25{\cdot}65 = \text{SiO}_2 \text{ (per cent.)}$$

Correct the result for the blank determination.

DETERMINATION OF CHROMIUM(III) OXIDE—

Decomposition of the sample—Weigh 0·250 g of the finely ground sample, previously dried at 110 °C, into a platinum dish; convenient dimensions are 70 mm diameter and 40 mm deep, with an effective capacity of 75 ml.

Add 4 g of fusion mixture and 2 g of boric acid and mix intimately to form a charge in the centre of the dish.

Effect the fusion, and subsequent dissolution in 20 ml of dilute sulphuric acid (1 + 3), as described above for the determination of silicon dioxide. When decomposition is complete, transfer the solution to a 400-ml beaker and add 100 ml of dilute sulphuric acid (1 + 3).

Determination of chromium(III) oxide—Transfer the solution to a 1-litre conical flask and dilute it to about 500 ml. Heat the solution to boiling and add potassium permanganate solution (about 0·1 N) slowly, drop by drop, until the reddish amber colour of the solution persists after boiling for 5 minutes. Normally, less than 2 ml is required and it is important that a large excess of permanganate is not added.

Cool the solution slightly, add 20 ml of dilute hydrochloric acid (1 + 3), remove the excess of permanganate and any manganese(IV) oxide present by boiling the solution until it is crystal clear, then boil it for a further 15 minutes to remove all traces of chlorine.

Cool, add 50, 75 or 100 ml, as necessary, of the ammonium iron(II) sulphate solution (about 0·05 N) from a pipette and then add 25 ml of the orthophosphoric acid and 10 drops of barium diphenylaminesulphonate indicator solution. Back-titrate the excess of ammonium iron(II) sulphate with standard potassium dichromate solution (0·05 N).

Standardise the ammonium iron(II) sulphate against the standard potassium dichromate as follows. Dilute 120 ml of sulphuric acid (1 + 3) to about 500 ml with water in a 1-litre conical flask. Add 50, 75 or 100 ml, according to the volume taken in the actual determination, of the ammonium iron(II) sulphate solution (about 0·05 N) with the same pipette as that used in the determination. Add 25 ml of the orthophosphoric acid and 10 drops of barium diphenylaminesulphonate indicator solution and titrate with the standard potassium dichromate solution (0·05 N).

Calculation—If V ml is the volume of potassium dichromate solution (0·05 N) equivalent to the ammonium iron(II) sulphate added and v ml is the volume used in the back-titration, then the percentage of Cr_2O_3 is 0·5067 $(V-v)$ if exactly 0·25 g of the sample was taken.

DETERMINATION OF THE OXIDES OF TITANIUM(IV), IRON(III), ALUMINIUM(III), MANGANESE(II), CALCIUM AND MAGNESIUM—

Decomposition of the sample—Weigh 1·000 g of the finely ground sample, previously dried at 110 °C, into a platinum dish. Add 8 g of fusion mixture and 4 g of boric acid and mix thoroughly. Cover the dish with a lid.

Heat the dish with a bunsen or Meker burner, slowly increasing the temperature until the mixture begins to melt, and continue to heat at this temperature until melting is completed. It is important that the initial stage of heating should be slow, as a vigorous reaction takes place on melting and spattering easily occurs. Increase the temperature further, slowly and steadily, to that of the full heat of the flame (approximately 950 °C).

After maintaining this temperature for about 5 minutes, swirl the contents of the dish every 2 minutes, making sure that the particles of sample on the sides of the dish come into contact with hot, molten flux. If swirling is begun too early, it is difficult to detach unfused particles from the sides of the dish. Continue to heat the dish at this temperature for 45 to 60 minutes, depending on the nature of the sample. Completeness of decomposition can be checked visually by the absence of any black, unfused material at the bottom of the melt. The type and position of the burner should be chosen so as to maintain oxidising conditions throughout. If, after 60 minutes, any of the sample remains unfused, then a further 1 to 2 g of boric acid should be added.

Cool and place the dish in a porcelain basin about 5 inches in diameter (this is to avoid loss of solution if the reaction on the addition of the acid is too vigorous). Raise the lid slightly and add 35 ml of dilute sulphuric acid (1 + 3). Replace the lid and allow the reaction to proceed for a few minutes and, if necessary, complete the dissolution by warming. Transfer the solution from the dish to a 400-ml beaker, dilute it to about 100 ml and cool it.

Extraction of chromate—The separation should be carried out in diffuse light, not bright sunlight, so as to minimise reduction of chromate.

Transfer the cold solution to a 500-ml separating funnel (Squibb's type) with the minimum volume of water. The volume at this stage should not exceed about 150 ml. Add 50 ml of the Amberlite resin solution, stopper the funnel and shake it vigorously for 1 minute. Release the pressure in the funnel by carefully removing the stopper and rinse the stopper and neck of the funnel with water. Allow the layers to separate, then withdraw and discard the organic phase. Repeat the extraction with 20 ml of the Amberlite resin solution and again withdraw the organic phase.

Add 10 ml of dilute sulphuric acid (1 + 9) to the aqueous phase and repeat the extraction with a further 20 ml of the Amberlite resin solution, again discarding the organic phase.

Remove traces of resin by three successive extractions with 20-ml portions of chloroform. Transfer the aqueous phase and washings from the funnel to a beaker and boil the solution so as to remove traces of chloroform. Cool the solution, dilute it to 500 ml in a calibrated flask and mix. This solution is referred to as the "stock" solution.

DETERMINATION OF TITANIUM(IV) OXIDE—

Transfer a 20-ml aliquot of the stock solution into each of two 50-ml calibrated flasks, A and B. To each flask add 10 ml of dilute orthophosphoric acid (2 + 3) and, to flask A only, add 10 ml of hydrogen peroxide solution (20 volume). Dilute the solution in each flask to 50 ml and shake them well.

Measure the optical density of solution A against B in 40-mm cells at 398 nm, or by using a colour filter (Ilford 601) in a suitable instrument. The colour is stable from 5 minutes until 24 hours after the addition of the hydrogen peroxide solution. Determine the titanium(IV) oxide by reference to a calibration graph.

DETERMINATION OF TOTAL IRON [AS IRON(III) OXIDE]—

Dilute 25·0 ml of the stock solution to 100 ml in a calibrated flask and mix. Transfer 5·0 ml of this diluted solution to a 100-ml calibrated flask and add 2 ml of hydroxylammonium chloride solution (10 per cent. *m*/*V*) followed by 5 ml of 1,10-phenanthroline solution (1 per cent. *m*/*V*). Add ammonium acetate solution (about 10 per cent.) until a pink colour forms, then add an excess of 2 ml. Allow the solution to stand for 15 minutes, dilute it to 100 ml and mix.

Measure the optical density of the solution against water in 10-mm cells at 510 nm. The use of a filter-type colorimeter or absorptiometer is not satisfactory, a spectrophotometer being essential. The colour is stable from 15 to 75 minutes after the addition of the ammonium acetate solution. Determine the iron(III) oxide content of the solution by reference to a calibration graph.

NOTE—The dilution of the stock solution specified above will cover the range from 0 to 20 per cent. of Fe_2O_3. For iron contents considerably below 20 per cent. of Fe_2O_3, a lesser dilution of the stock solution should be made.

It is not permissible to dilute an aliquot of the solution once the colour has developed.

DETERMINATION OF MANGANESE(II) OXIDE—

Transfer a 50-ml aliquot of the stock solution to a 250-ml beaker. Add 10 ml of dilute sulphuric acid (1 + 1) and 10 ml of dilute nitric acid (1 + 1), and evaporate to strong fumes so as to destroy traces of resin.

Cool the solution, add 20 ml of the nitric acid, 10 ml of dilute orthophosphoric acid (1 + 9) and about 50 ml of water. Boil the mixture to dissolve salts and to remove nitrous fumes, filtering if necessary. Add about 0·5 g of potassium periodate, boil until the colour develops and then for a further 2 minutes. Transfer the beaker to a steam-bath for 10 minutes.

Allow the solution to cool, transfer it into a 100-ml calibrated flask, dilute it to 100 ml and mix. Measure the optical density of the solution against water in 40-mm cells at 524 nm or by using a colour filter (Ilford 604) in a suitable instrument. Determine the manganese(II) oxide content of the solution by reference to a calibration graph.

DETERMINATION OF ALUMINIUM(III) OXIDE—

Transfer a 100-ml aliquot of the stock solution to a 500-ml separating funnel (Squibb's type). Add the ammonia solution dropwise, until the solution is faintly alkaline to bromophenol blue, then just re-acidify with dilute hydrochloric acid (1 + 3) and add an excess of 4 ml.

Add 20 ml of chloroform and 10 ml of sodium diethyldithiocarbamate solution (10 per cent. *m*/*V*). Stopper the funnel and shake it vigorously. Release the pressure in the funnel by carefully removing the stopper and rinse the stopper and neck of the funnel with water. Allow the layers to separate and withdraw the chloroform layer (if an emulsion has formed it will be necessary to add a few drops of hydrochloric acid and to shake the mixture again).

Add 10-ml portions of chloroform and 5-ml portions of sodium diethyldithiocarbamate solution and repeat the extraction until a coloured precipitate (brown or pink) is no longer formed. Finally, wash the aqueous phase with 20 ml of chloroform. This separation will remove iron and manganese.

Add 25 ml of the hydrochloric acid followed by 2 to 3 ml of cupferron solution (6 per cent. *m*/*V*) and 20 ml of chloroform. Stopper the funnel and shake it vigorously. Remove the stopper and rinse the stopper and neck of the funnel with water. Allow the layers to separate and withdraw the chloroform layer. Repeat the extraction with three 10-ml portions of chloroform to remove traces of cupferron and sodium diethyldithiocarbamate.

Run the aqueous phase from the separating funnel into a 1-litre conical flask. Add a few drops of bromophenol blue indicator followed by the ammonia solution until the mixture is just alkaline. Re-acidify the mixture quickly with hydrochloric acid, add an excess of

5 or 6 drops and cool the flask in running water. The solution must be cold before the addition of DCTA or the residual chromium present in the stock solution may be complexed.

Add sufficient standard DCTA solution (about 0·05 M) to produce an excess of a few millilitres over the expected amount (1 ml of solution ≡ 1·275 per cent. of Al_2O_3). Then add ammonium acetate buffer solution (for aluminium determination) until the indicator turns blue, followed by an excess of 15 ml.

Add a volume of 95 per cent. ethanol equal to the total volume of the existing solution and 20 ml of hydroxylammonium chloride solution (10 per cent. m/V). The hydroxylammonium chloride solution is added before the dithizone indicator and prevents the latter from being decolorised by the trace amounts of cupferron present in the solution. Add 1 to 2 ml of dithizone indicator and titrate the solution with standard zinc solution (0·05 M) from green to the first appearance of a permanent pink colour. (The end-point is often improved by the addition of a small volume of naphthol green solution so as to eliminate any pink colour that may be formed in the solution when the indicator is added.)

Calculation—If the concentration of the DCTA solution is not exactly 0·05 M, calculate the equivalent volume of 0·05 M DCTA.

If V ml is the volume of DCTA solution (0·05 M) added and v ml is the volume of standard zinc solution (0·05 M) used in the back-titration, then

$$Al_2O_3 \text{ (per cent.)} = 1{\cdot}275\ (V - v)$$

DETERMINATION OF CALCIUM OXIDE—

Transfer a 100-ml aliquot of the stock solution to a 250-ml calibrated flask. Add 5 ml of dilute triethanolamine (1 + 1), 5·0 ml of standard EGTA solution (about 0·05 M) and dilute the solution to 150 ml. Add potassium hydroxide solution (25 per cent. m/V) until no further precipitation takes place and then add an excess of 10 ml, followed by 10 ml of Magflok solution (2 per cent. m/V).

Dilute the mixture to 250 ml, shake it and allow it to stand for 10 minutes to settle. Filter the mixture through a dry coarse 150-mm Whatman No. 541 filter-paper into a dry beaker. Transfer by pipette 200 ml of the filtrate into a 500-ml conical flask and add 15 ml of potassium hydroxide solution (25 per cent. m/V). Add approximately 0·03 g of screened calcein indicator and titrate the solution with standard calcium solution (1·0 mg ml^{-1} of CaO) until the first appearance of green fluorescence. The titration is best carried out in good daylight, but direct sunlight should be avoided.

Calculation—If 1 ml of EGTA solution ≡ x mg of CaO and y ml are added initially, and t ml is the back-titration with calcium solution (1 mg ml^{-1} of CaO), then

$$CaO \text{ (per cent.)} = 0{\cdot}625 \left(\frac{4}{5}xy - t\right)$$

Correct the result for the blank determination.

DETERMINATION OF MAGNESIUM OXIDE—

Transfer 100·0 ml of the stock solution to a 500-ml separating funnel and add the ammonia solution dropwise until the solution is slightly alkaline to bromophenol blue. Just re-acidify the solution with dilute hydrochloric acid (1 + 3), then add an excess of 4 ml. Add 20 ml of chloroform and 10 ml of sodium diethyldithiocarbamate solution (10 per cent. m/V). Stopper the funnel and shake it vigorously. Release the pressure in the funnel by carefully removing the stopper and rinse the stopper and neck of the funnel with water. Allow the layers to separate and withdraw the chloroform layer. (If an emulsion has formed, it will be necessary to add a few drops of hydrochloric acid and to shake the mixture again.) Add 10-ml portions of chloroform and repeat the extraction with 5-ml portions of sodium diethyldithiocarbamate solution until a coloured precipitate is no longer formed. Finally, wash the aqueous phase once with 10 ml of chloroform. This separation will remove iron and manganese.

Add dilute ammonia solution (1 + 1) dropwise until the solution is just alkaline to bromophenol blue. Just re-acidify the solution with dilute hydrochloric acid (1 + 9) and add 20 ml of ammonium acetate buffer solution (for magnesium determination). Add 20 ml of chloroform and 10 ml of cupferron solution (6 per cent. m/V). Stopper the funnel and shake it vigorously. Release the pressure in the funnel by carefully removing the stopper and rinse the stopper and neck of the funnel with water. Allow the layers to separate and withdraw the chloroform layer. Repeat the extraction with a further 10 ml of cupferron solution and finally wash the aqueous phase three times with 10-ml portions of chloroform. This separation will remove aluminium and titanium.

Transfer the aqueous layer to a 500-ml conical flask and boil off trace amounts of chloroform. Cool the solution, add 2 g of ammonium chloride and 5 ml of dilute triethanolamine (1 + 1) with swirling, followed by an appropriate known amount of standard DCTA solution (about 0·05 M). This addition is made so as to complex most of the magnesium before the solution is made alkaline, so that the tendency for magnesium hydroxide to precipitate is greatly reduced. Then add 30 ml of the ammonia solution and 5 ml of hydroxylammonium chloride solution (10 per cent. *m*/*V*) to stabilise the indicator.

Titrate the solution with the standard DCTA solution (about 0·05 M) with Solochrome black 6B indicator, from red, through purple, to the last change to a clear ice blue. This titration also includes the titration for calcium oxide in the sample, which must be allowed for.

Calculation—If the concentration of the DCTA solution is not exactly 0·05 M, calculate the equivalent volume of exactly 0·05 M DCTA solution.

If V ml is the total amount of 0·05 M DCTA added and v ml is the calculated amount of 0·05 M DCTA required to react with the calcium oxide in 0·2 g of sample, then

$$\text{MgO (per cent.)} = 1{\cdot}008\ (V - v)$$

Correct the result for the blank determination.

DETERMINATION OF ALKALI-METAL OXIDES—

Decomposition of the sample—Weigh 0·250 g of finely ground sample, previously dried at 110 °C, into a platinum basin. Add 5 ml of dilute nitric acid (1 + 1), 5 ml of the perchloric acid and about 5 ml of the hydrofluoric acid. Transfer the vessel to a sand-bath and evaporate the mixture to dryness in a fume cupboard, taking care to avoid spurting. Cool the mixture, add 5 ml of the perchloric acid and rinse the sides of the basin with water, then evaporate the mixture carefully to dryness.

To the cool, dry residue, add 20 drops of the hydrochloric acid and about 15 ml of water. Digest the mixture on a steam-bath for 10 minutes. Cool the mixture, filter it through a No. 42 Whatman filter-paper and wash the filter-paper thoroughly with cold water. Dilute the filtrate and washings to 250 ml in a calibrated flask and mix.

Determination of alkali-metal oxides—Compare the sample solution with standard solutions containing 5 p.p.m. of Na_2O, 10 p.p.m. of K_2O and 20 p.p.m. of Li_2O in a simple filter-type flame photometer. Calculate the alkali-metal oxide contents of the solution by reference to calibration graphs.

REPORTING OF RESULTS—

Results should be reported with respect to either the dried material (dried to constant weight at 110 °C), or the ignited (1000 °C) material (calculated to zero loss on ignition).

CALIBRATIONS FOR COLORIMETRIC METHODS—

Titanium(IV) oxide—Transfer in duplicate 0, 5·0, 10·0, 20·0 and 25·0-ml portions of the standard titanium solution B to 50-ml calibrated flasks. These solutions will give a calibration graph for 0 to 2·5 per cent. of TiO_2. Add to each flask 10 ml of dilute orthophosphoric acid (2 + 3) and to one of each pair only add 10 ml of hydrogen peroxide solution (20 volume). Dilute the solution in each flask to 50 ml and mix.

Measure the optical density of the pertitanic acid solutions against the appropriate control solution in 40-mm cells at 398 nm, or by using a colour filter (Ilford 601) in a suitable instrument. The colour is stable for 5 minutes to 24 hours after the addition of the hydrogen peroxide solution. From the optical densities prepare a calibration graph.

Iron(III) oxide—Transfer 0, 10·0, 20·0, 25·0, 40·0 and 50·0-ml portions of standard iron solution B to 100-ml calibrated flasks. These solutions will give a calibration graph for 0 to 20 per cent. of Fe_2O_3. Add to each flask 2 ml of hydroxylammonium chloride solution (10 per cent. *m*/*V*), 5 ml of 1,10-phenanthroline solution (10 per cent. *m*/*V*) and 2 ml of ammonium acetate solution (about 10 per cent.). Allow the solutions to stand for 15 minutes, dilute the solution in each flask to 100 ml and mix.

Measure the optical density of the solutions against water in 10-mm cells at 510 nm, or by using a colour filter (Ilford 603) in a suitable instrument. The colour is stable for 15 to 75 minutes after the addition of the ammonium acetate solution. From the optical densities prepare a calibration graph.

Manganese(II) oxide—Transfer 0, 10·0, 20·0, 25·0, 40·0 and 50·0-ml portions of the standard manganese solution B to 100-ml calibrated flasks. These solutions will give a calibration graph for 0 to 0·5 per cent. of MnO. Dilute the solution in each flask to 100 ml and mix.

Measure the optical density of the solutions against water in 40-mm cells at 524 nm, or by using a colour filter (Ilford 604) in a suitable instrument. From the optical densities prepare a calibration graph.

CALIBRATIONS FOR FLAME-PHOTOMETRIC METHODS—

The instrument is calibrated for K_2O, Na_2O and Li_2O as follows. Solutions equivalent to 20, 40, 60 and 80 per cent. of the concentration of the standard solution for each element should be sprayed and the readings recorded in the form of calibration graphs. One of the mid-points of each graph should be checked at frequent intervals to ensure the validity of the graphs.

RESULTS

Results for the complete analysis of six samples by the method described are shown in Tables I to VI.

DEVELOPMENT OF THE METHOD

DECOMPOSITION—

Many methods of decomposition have been recommended, and a number of these have been tried by the Group at various times. The use of acidic fusion with pyrosulphate has not been attempted, as the silica in the sample is not brought into solution and previous experience had shown that, not infrequently, a virtually insoluble basic chromium sulphate resulted. The methods and reagents that have been tried include the following—

(*i*) perchloric acid;
(*ii*) sodium peroxide fusions in iron or nickel crucibles;
(*iii*) sodium peroxide - sodium hydroxide fusions in iron or nickel crucibles;
(*iv*) sodium peroxide sinters; and
(*v*) sodium carbonate - borate fusions.

The first four of the above proved successful with many samples, but each failed on certain occasions. The only completely successful flux was a mixture of alkali carbonates and borates (or boric acid). Each method had the disadvantages or advantages described in the following paragraphs.

Perchloric acid—The sample is decomposed in a glass beaker by adding water and perchloric acid, covering the beaker with a clock-glass, boiling off the water and then allowing the fuming acid to reflux for as long as necessary; in difficult cases the period required may be several hours. Nitric acid is normally added at the start to minimise the continual risk of explosion.

The advantage of the method lies in the fact that no alkali salts are added during decomposition and in a number of laboratories the chromium is volatilised as chromyl chloride during the later stages of the decomposition. This latter process, however, needs considerable care and frequent attention from the analyst.

The main disadvantage is the risk of explosion, and the possible attack on the beaker used must give rise to some doubts concerning, at least, the silicon determination, particularly as the decomposition may sometimes be very prolonged. Finally, the solution obtained is not suitable for the separation of chromium with a liquid ion-exchange resin as perchlorate appears to prevent the extraction from taking place.

Sodium peroxide or sodium peroxide - sodium hydroxide fusions—The decomposition is relatively rapid, even when sodium hydroxide is used to moderate the attack on the crucible. The melts dissolve rapidly in water or acid and so it can be very convenient for determinations of single constituents, for example, of chromium. The decomposition cannot be carried out

TABLE I

RESULTS ON AN 11 CHROME - MAGNESITE REFRACTORY (IGNITED AT 1000 °C BASIS)

Laboratory	SiO_2, per cent.	TiO_2, per cent.	Al_2O_3, per cent.	Fe_2O_3, per cent.	Cr_2O_3, per cent.	MnO, per cent.	CaO, per cent.	MgO, per cent.	Na_2O, per cent.	K_2O, per cent.	Li_2O, per cent.
A	8·92	0·13	13·56	11·56	24·30	0·14	1·48	39·48	0·08	0·08	0·02
	8·94	0·13	13·60	11·59	24·26	0·14	1·46	39·54	0·07	0·08	0·02
	8·91	0·11	13·51	11·62	24·34	0·15	1·46	39·60	0·07	0·09	0·02
B	8·70	0·08	13·71	11·75	24·38	0·15	1·38	39·34	0·11	0·06	0·05
	8·75	0·08	13·67	11·85	24·40	0·13	1·46	39·25	0·11	0·06	0·05
	8·67	0·09	13·63	11·75	24·28	0·14	1·46	39·21	0·11	0·07	0·06
C	8·68	0·10	13·68	11·38	24·26	0·16	1·41	39·46	0·09	0·08	0·02
	8·70	0·11	13·48	11·51	24·16	0·16	1·37	39·54	0·09	0·08	0·02
	8·75	0·11	13·62	11·53	24·22	0·16	1·31	39·58	0·10	0·09	0·02
D	8·82	0·11	13·33	11·65	24·09	0·15	1·48	39·26	0·10	0·05	0·06
	8·91	0·12	13·52	11·90	24·18	0·15	1·50	39·34	0·10	0·05	0·06
	8·91	0·11	13·29	11·65	24·14	0·16	1·50	39·26	0·10	0·06	0·06
E	9·26	0·10	13·52	11·07	24·0–	0·16	1·50	39·6–	0·12	0·04	—
	9·07	0·08	13·32	11·07	24·0–	0·17	1·50	39·6–	0·13	0·04	—
	9·18	0·08	13·52	11·27	24·1–	0·16	1·50	39·6–	0·13	0·05	—
F	8·80	0·11	13·49	11·60	24·36	0·14	1·46	39·66	0·08	0·05	0·02
	8·89	0·11	13·54	11·66	24·32	0·14	1·48	39·69	0·08	0·05	0·02
	8·90	0·12	13·56	11·58	24·38	0·15	1·49	39·62	0·08	0·04	0·02
G	8·98	0·13	13·29	11·60	23·97	0·16	1·45	39·54	0·07	0·07	0·02
	8·85	0·12	13·26	11·45	23·82	0·16	1·44	39·75	0·07	0·06	0·02
	8·96	0·12	13·40	11·51	23·92	0·18	1·47	39·73	0·07	0·06	0·01
H	8·94	0·08	13·70	11·43	23·82	0·19	1·50	39·50	0·08	0·05	—
	8·93	0·08	13·64	11·43	23·92	0·19	1·44	39·44	0·08	0·05	—
	8·91	0·08	13·64	11·47	23·92	0·19	1·47	39·53	0·08	0·05	—
I	8·93	0·13	13·32	11·29	24·07	0·16	1·47	39·67	—	—	—
	8·94	0·13	13·49	11·29	24·07	0·17	1·50	39·62	—	—	—
	8·90	0·13	13·60	11·34	24·02	0·16	1·50	39·62	—	—	—
J	8·96	0·12	13·54	11·91	24·50	0·17	1·50	39·85	—	—	—
	8·99	0·11	13·48	11·91	24·50	0·17	1·50	39·85	—	—	—
	8·92	0·11	13·51	—	24·45	0·18	1·50	—	—	—	—
K	8·76	—	—	—	—	—	—	—	—	—	—
	8·75	—	—	—	—	—	—	—	—	—	—
	8·89	—	—	—	—	—	—	—	—	—	—
L	8·55	—	—	—	—	—	—	—	—	—	—
	8·48	—	—	—	—	—	—	—	—	—	—
	8·46	—	—	—	—	—	—	—	—	—	—
M	8·67	0·16	13·57	11·69	24·41	0·15	1·45	—	0·12	0·08	0·03
	8·72	0·15	13·52	11·69	24·18	0·15	1·45	—	0·12	0·09	0·03
	8·71	0·15	13·59	11·76	24·33	0·15	1·50	—	0·13	0·08	0·03
Mean	8·85	0·11	13·52	11·56	24·18	0·16	1·46	39·54	0·10	0·06	0·03
Standard deviation	0·17	0·02	0·13	0·22	0·20	0·02	0·04	0·17	0·02	0·02	0·02
Previously accepted result	8·72	0·11	13·62	11·78	24·23	0·16	1·44	39·89	0·10	0·06	0·04

in platinum and is thus usually performed in iron or nickel crucibles. Contamination by the elements of the crucible is pronounced so that the technique can only be used for determinations when this contamination is of no significance.

Sodium peroxide sinters—This technique, as it is normally carried out in platinum, avoids the problem of contamination, but at the cost of a considerable amount of speed and some loss of certainty of complete decomposition. The purity of sodium peroxide is suspect, as it often contains significant amounts of silicon and calcium, both of which are important minor constituents. This fact alone, apart from the other problems, makes the use of sodium peroxide unattractive.

Alkali carbonate - borate fusions—Various combinations and ratios of this flux have been tried, and the final choice rested on a mixture of potassium carbonate - sodium carbonate (fusion mixture) and boric acid in a ratio of 2:1. The ratio of total flux to sample was chosen

TABLE II

RESULTS ON AN 21A CHROME - MAGNESITE REFRACTORY (IGNITED AT 1000 °C BASIS)

Laboratory	SiO_2, per cent.	TiO_2, per cent.	Al_2O_3, per cent.	Fe_2O_3, per cent.	Cr_2O_3, per cent.	MnO, per cent.	CaO, per cent.	MgO, per cent.	Na_2O, per cent.	K_2O, per cent.	Li_2O per cent.
A	3·98	0·11	6·00	10·47	29·92	0·19	1·16	47·97	0·05	0·03	0·01
	3·95	0·10	6·00	10·50	29·94	0·18	1·15	48·04	0·06	0·03	0·01
	3·98	0·11	5·96	10·46	29·93	0·18	1·17	47·99	0·06	0·03	0·01
B	3·96	0·08	5·87	10·87	29·65	0·18	1·24	48·04	0·08	0·02	—
	4·02	0·08	5·93	10·79	29·81	0·17	1·20	—	0·08	0·02	—
	4·04	0·09	5·91	10·82	29·73	0·17	1·23	—	0·09	0·02	—
C	3·90	0·14	5·85	10·63	29·92	0·18	1·13	47·69	0·09	0·03	0·02
	3·94	0·13	5·90	10·63	29·74	0·19	1·13	47·85	0·09	0·02	0·02
	3·89	0·13	5·90	10·63	29·67	0·19	1·09	47·99	0·09	0·03	0·02
D	4·00	0·10	6·09	10·65	29·97	0·18	1·19	47·50	0·08	<0·01	0·04
	3·97	0·10	6·07	10·65	30·07	0·17	1·13	47·46	0·08	<0·01	0·04
	3·93	0·11	6·09	10·77	30·02	0·17	1·13	47·60	0·07	<0·01	0·04
E	3·69	0·12	5·95	10·59	29·62	0·16	1·28	47·95	0·08	0·02	—
	3·74	0·12	5·95	10·59	29·62	0·17	1·27	47·95	0·08	0·02	—
	3·72	0·12	5·90	10·59	29·62	0·17	1·28	47·95	0·08	0·02	—
F	3·91	0·12	5·94	10·57	29·62	0·17	1·21	47·79	0·06	0·02	0·01
	3·95	0·11	5·93	10·61	29·66	0·16	1·20	47·74	0·05	0·01	0·01
	3·96	0·11	5·90	10·56	29·60	0·18	1·18	47·73	0·05	0·02	0·01
G	3·99	0·10	5·80	10·61	29·55	0·18	1·20	47·58	0·05	0·01	0·01
	3·98	0·13	5·83	10·55	29·65	0·19	1·19	47·83	0·05	0·01	0·01
	4·01	0·08	5·81	10·48	29·59	0·19	1·20	47·77	0·05	0·01	0·01
H	3·99	0·13	6·14	10·43	29·77	0·20	1·21	47·62	0·05	0·01	—
	3·99	0·13	6·07	10·43	29·75	0·20	1·18	47·55	0·05	0·01	—
	4·01	0·13	6·07	10·47	29·67	0·20	1·27	47·58	0·06	0·02	—
I	3·97	0·15	5·73	10·36	29·69	0·19	1·20	47·84	—	—	—
	3·96	0·15	5·91	10·36	29·71	0·18	1·20	47·79	—	—	—
	3·98	0·15	5·89	10·36	29·66	0·18	1·26	47·73	—	—	—
J	3·99	0·14	5·89	10·70	29·57	0·17	1·20	47·63	—	—	—
	4·01	0·14	5·88	10·70	29·61	0·18	1·20	47·63	—	—	—
	4·02	0·14	5·87	10·70	29·61	0·16	1·20	47·31	—	—	—
K	3·97	—	—	—	—	—	—	—	—	—	—
	3·86	—	—	—	—	—	—	—	—	—	—
	3·89	—	—	—	—	—	—	—	—	—	—
L	4·11	—	—	—	—	—	—	—	—	—	—
	4·04	—	—	—	—	—	—	—	—	—	—
	4·05	—	—	—	—	—	—	—	—	—	—
M	4·08	0·14	6·01	10·59	29·76	0·17	1·22	47·50	0·09	0·02	—
	4·05	0·14	5·99	10·63	29·69	0·17	1·23	47·52	0·09	0·02	—
	3·98	0·12	6·03	10·59	29·67	0·17	1·22	47·58	0·09	0·02	—
Mean	3·97	0·12	5·94	10·59	29·73	0·18	1·20	47·73	0·07	0·02	0·02
Standard deviation	0·09	0·02	0·09	0·13	0·14	0·01	0·05	0·19	0·02	0·01	0·01
Previously accepted result	3·71	0·09	6·00	10·71	29·78	0·17	1·14	48·09	0·07	0·02	0·03

to be 12:1. Less flux can be used but an increase in the time required for fusion results; the length of time taken depends slightly on the type of sample but is controlled mainly by the amount of sample. An amount of 1 g of sample can require up to 1½ hours for fusion to be completed and 0·25 g about 30 minutes, whereas 0·1 g will decompose in about 10 minutes.

The optimum temperature of fusion is about 950 °C, and the fusion is preferably performed in a dish over a gas flame so as to permit regular swirling. Fusion in a furnace appears to be less effective and an increase in the temperature to 1200 °C again reduces the effectiveness of the flux. The use of a dish helps to prevent the hot gas from entering the fusion vessel and so creating a reducing atmosphere, which not only destroys the fusion but also may severely damage the platinum. The use of a dish also allows the lid to be placed slightly out of position so as to allow ready access of the air that is needed to oxidise the chromium to chromium(VI) without the risk of the introduction of hot flame gases.

TABLE III

RESULTS ON AN 22 PHILIPPINE CHROME ORE (IGNITED AT 1000 °C BASIS)

Laboratory	SiO_2, per cent.	TiO_2, per cent.	Al_2O_3, per cent.	Fe_2O_3, per cent.	Cr_2O_3, per cent.	MnO, per cent.	CaO, per cent.	MgO, per cent.	Na_2O, per cent.	K_2O, per cent.	Li_2O, per cent.
A	3·44	0·28	29·33	15·26	34·24	0·13	0·38	16·56	0·04	0·05	0·01
	3·44	0·27	29·34	15·26	34·19	0·13	0·39	16·56	0·04	0·05	0·01
	3·42	0·26	29·34	15·34	34·20	0·14	0·36	16·61	0·04	0·05	0·01
B	3·42	0·23	29·25	15·64	34·26	0·15	0·41	16·41	0·09	0·02	0·05
	3·51	0·24	29·19	15·57	34·35	0·15	0·39	16·37	0·09	0·02	0·05
	3·53	0·23	29·29	15·57	34·17	0·14	0·40	16·34	0·10	0·03	0·04
C	3·40	0·29	29·34	15·34	33·78	0·16	0·41	16·54	0·14	0·03	0·01
	3·41	0·31	29·26	15·34	33·52	0·16	0·41	16·53	0·14	0·03	0·01
	3·38	0·30	29·35	15·35	33·76	0·16	0·41	16·54	0·16	0·03	0·01
D	3·43	0·26	29·22	15·70	34·16	0·12	0·36	16·48	0·07	0·01	0·02
	3·36	0·25	29·48	15·95	34·10	0·14	0·42	16·38	0·07	0·01	0·02
	3·38	0·25	29·35	15·95	34·22	0·14	0·36	16·48	0·08	0·01	0·02
E	3·50	0·22	29·34	15·16	34·14	0·13	0·36	16·43	0·08	0·02	—
	3·42	0·22	29·25	15·26	34·20	0·13	0·36	16·43	0·08	0·02	—
	3·40	0·22	29·34	15·26	34·20	0·13	0·38	16·43	0·08	0·02	—
F	3·45	0·27	29·23	15·36	34·04	0·13	0·37	16·48	0·06	0·02	—
	3·43	0·25	29·28	15·36	33·98	0·12	0·38	16·48	0·06	0·02	—
	3·40	0·25	29·30	15·30	34·06	0·13	0·41	16·52	0·04	0·02	—
G	3·50	0·28	29·46	15·59	34·04	0·12	0·36	16·63	0·06	0·02	0·01
	3·48	0·27	29·41	15·50	33·94	0·13	0·35	16·57	0·06	0·02	0·01
	3·38	0·31	29·27	15·56	34·00	0·12	0·42	16·66	0·07	0·03	0·01
H	3·49	0·25	29·43	15·20	33·68	0·15	0·44	16·34	0·05	0·03	—
	3·50	0·25	29·55	15·04	33·75	0·15	0·44	16·34	0·06	0·03	—
	3·51	0·25	29·55	15·24	33·80	0·15	0·38	16·38	0·05	0·03	—
I	3·42	0·29	29·38	15·10	33·93	0·15	0·41	16·43	—	—	—
	3·46	0·29	29·23	15·10	33·78	0·15	0·41	16·43	—	—	—
	3·46	0·29	29·38	15·10	33·89	0·14	0·38	16·33	—	—	—
J	3·47	0·25	29·23	15·81	34·10	0·14	0·37	—	—	—	—
	3·46	0·26	29·36	15·81	34·10	0·14	0·38	—	—	—	—
	3·43	0·24	29·29	15·81	34·10	0·14	0·39	—	—	—	—
K	3·41	—	—	—	—	—	—	—	—	—	—
	3·46	—	—	—	—	—	—	—	—	—	—
	3·44	—	—	—	—	—	—	—	—	—	—
L	3·56	—	—	—	—	—	—	—	—	—	—
	3·46	—	—	—	—	—	—	—	—	—	—
	3·47	—	—	—	—	—	—	—	—	—	—
Mean	3·45	0·26	29·33	15·43	34·02	0·14	0·39	16·47	0·08	0·03	0·02
Standard deviation	0·05	0·03	0·09	0·26	0·20	0·01	0·02	0·09	0·03	0·01	0·01
Previously accepted result	3·33	0·24	29·38	15·59	34·25	0·14	0·39	16·66	0·07	0·03	0·02

Completeness of attack can readily be seen from the disappearance of the black particles on the base of the dish, so that the analyst can ensure that decomposition is complete in every instance. Prolonged fusion depletes the borate content of the melt so that if the rate of attack appears to be becoming very slow, the fusion can be completed by the addition of more boric acid. Dissolution of the melt is rapid, and, as it is performed in the same dish, it enables the volume of liquid to be kept to the minimum.

This flux has no great advantages, but its reliability and freedom from contamination appear to make it the best choice as an all-purpose tool.

MAIN ANALYSIS [DETERMINATION OF THE OXIDES OF IRON(III), ALUMINIUM(III), TITANIUM(IV), MANGANESE(II), CALCIUM AND MAGNESIUM]—

In the original conception of the method, it was intended that the determination of silicon and chromium would also be carried out on the main portion of the sample. As described in the appropriate sections, these determinations are now performed on separate portions of sample.

TABLE IV

RESULTS ON B.C.S. 308 GRECIAN CHROME ORE (IGNITED AT 1000 °C BASIS)

Laboratory	SiO_2, per cent.	TiO_2, per cent.	Al_2O_3, per cent.	Fe_2O_3, per cent.	Cr_2O_3, per cent.	MnO, per cent.	CaO, per cent.	MgO, per cent.	Na_2O, per cent.	K_2O, per cent.	Li_2O, per cent.
A	4·26	0·15	19·65	17·06	41·71	0·17	0·32	16·47	0·02	0·02	<0·01
	4·25	0·14	19·68	17·06	41·67	0·17	0·34	16·47	0·02	0·02	<0·01
	4·27	0·14	19·63	17·03	41·71	0·17	0·32	16·47	0·02	0·02	<0·01
B	4·42	0·13	19·46	17·24	41·83	0·16	0·31	16·50	0·03	0·01	0·06
	4·51	0·14	19·38	17·27	41·74	0·17	0·33	16·56	0·03	0·01	0·06
	4·55	0·14	19·47	17·26	41·87	0·13	0·35	16·58	0·03	0·01	0·06
C	4·40	0·15	19·79	17·29	41·74	0·17	0·37	16·31	0·04	0·04	0·02
	4·37	0·15	19·75	17·31	41·68	0·17	0·37	16·33	0·05	0·04	0·02
	4·41	0·15	19·75	17·31	41·61	0·17	0·37	16·33	0·04	0·04	0·02
D	4·33	0·16	19·48	17·21	41·65	0·15	0·36	16·53	0·05	0·01	0·03
	4·38	0·17	19·43	16·90	41·70	0·15	0·36	16·53	0·05	0·01	0·03
	4·39	0·17	19·48	17·21	41·70	0·14	0·36	16·35	0·04	0·01	0·03
E	4·30	0·15	19·4–	17·06	41·45	0·18	0·34	16·5–	0·06	0·01	—
	4·24	0·11	19·4–	17·06	41·45	0·18	0·36	16·5–	0·05	0·01	—
	4·26	0·11	19·4–	17·06	41·45	0·18	0·34	16·5–	0·05	0·01	—
F	4·31	0·09	19·75	17·10	41·77	0·16	0·35	16·52	0·03	0·01	0·01
	4·34	0·08	19·80	17·14	41·72	0·16	0·35	16·54	0·03	0·01	0·01
	4·36	0·08	19·81	17·09	41·74	0·16	0·35	16·54	0·04	0·01	0·01
G	4·28	0·17	19·75	16·87	41·72	0·16	0·33	16·06	0·03	0·02	0·01
	4·33	0·13	19·79	16·99	41·50	0·17	0·27	16·14	0·04	0·02	0·01
	4·26	0·13	19·82	16·88	41·59	0·16	0·33	16·11	0·02	0·01	0·01
H	4·43	0·10	19·87	16·78	41·59	0·17	0·41	16·30	0·03	0·02	—
	4·46	0·10	19·93	16·82	41·48	0·17	0·32	16·33	0·03	0·02	—
	4·40	0·10	19·93	16·82	41·54	0·17	0·35	16·25	0·02	0·02	—
I	4·41	0·14	19·64	16·40	41·54	0·16	0·31	16·29	—	—	—
	4·31	0·16	19·64	16·55	41·57	0·16	0·31	16·24	—	—	—
	4·32	0·16	19·69	16·55	41·54	0·16	0·34	16·34	—	—	—
J	—	0·11	19·70	—	41·66	0·16	0·31	16·09	—	—	—
	—	—	19·56	—	41·62	0·16	0·33	16·04	—	—	—
	—	—	19·70	—	41·62	—	0·32	16·04	—	—	—
K	4·29	—	—	—	—	—	—	—	—	—	—
	4·33	—	—	—	—	—	—	—	—	—	—
	4·39	—	—	—	—	—	—	—	—	—	—
L	4·50	—	—	—	—	—	—	—	—	—	—
	4·37	—	—	—	—	—	—	—	—	—	—
	4·35	—	—	—	—	—	—	—	—	—	—
Mean	4·36	0·13	19·65	17·01	41·64	0·16	0·34	16·36	0·04	0·02	0·02
Standard deviation	0·08	0·03	0·17	0·24	0·11	0·01	0·03	0·17	0·01	0·01	0·02
Previously accepted result	4·29	0·10	19·57	17·15	41·87	0·15	0·34	16·55	0·04	0·01	0·03

Separation of chromate—In the original method, this process was carried out on a 0·5-g portion of sample,[2] and the chromium was determined by a colorimetric method with EDTA after stripping the organic liquid ion-exchange phase. In the original work, apparently slightly low optical density readings for the EDTA - chromium complex were attributed to the presence of large concentrations of sulphate. More recent work[6] has shown that, in fact, the separation is light sensitive and that the reduction of chromium(VI) to chromium(III) takes place to a significant extent in all but very subdued light. This situation deteriorates with increase in the amount of sample present and cannot, apparently, be avoided if a 1-g sample is used. As it is necessary to perform six determinations on this portion of the sample, the treatment of one whole gram of sample is imperative.

It was found that even though the amount of resin used was increased, a significant amount of chromium remained unextracted. Co-operative tests in several laboratories during work on the determination of aluminium showed that the amount of residual chromium varied considerably (Table VII).

TABLE V

RESULTS ON B.C.S. 369 MAGNESITE - CHROME REFRACTORY (IGNITED AT 1000 °C BASIS)

Laboratory	SiO_2, per cent.	TiO_2, per cent.	Al_2O_3, per cent.	Fe_2O_3, per cent.	Cr_2O_3, per cent.	MnO, per cent.	CaO, per cent.	MgO, per cent.	Na_2O, per cent.	K_2O, per cent.	Li_2O, per cent.
A	2·55	0·12	14·79	10·24	17·10	0·11	1·16	53·62	0·06	0·05	0·02
	2·57	0·13	14·81	10·29	17·14	0·11	1·18	53·57	0·05	0·05	0·02
	2·56	0·13	14·77	10·24	17·15	0·11	1·19	53·57	0·05	0·05	0·02
B	2·66	0·17	14·59	10·40	17·27	0·10	1·22	53·12	0·05	0·02	0·04
	2·66	0·16	14·73	10·47	17·20	0·11	1·23	53·14	0·05	0·02	0·04
	2·65	0·14	14·70	10·46	17·03	0·12	1·22	53·33	0·05	0·02	0·04
C	2·61	0·15	14·74	10·02	17·19	0·13	1·13	53·42	0·05	0·04	0·01
	2·61	0·16	14·74	10·02	17·23	0·12	1·13	53·37	0·04	0·04	0·01
	2·58	0·15	14·74	10·02	17·26	0·12	1·16	53·29	0·05	0·04	0·01
D	2·59	0·11	14·62	10·27	17·16	0·11	1·23	53·19	0·06	0·02	0·02
	2·64	0·11	14·74	10·27	17·16	0·11	1·17	53·39	0·06	0·02	0·02
	2·64	0·12	14·57	10·42	17·11	0·12	1·23	53·39	0·06	0·02	0·02
E	2·60	0·14	14·59	10·14	17·17	0·11	1·16	53·67	0·04	0·02	—
	2·61	0·14	14·64	10·14	17·17	0·13	1·18	53·57	0·04	0·02	—
	2·57	0·14	14·54	10·14	17·17	0·13	1·18	53·57	0·04	0·02	—
F	2·54	0·13	14·80	10·18	17·16	0·11	1·15	53·41	0·04	0·02	0·02
	2·50	0·13	14·84	10·20	17·20	0·11	1·14	53·36	1·03	0·03	0·01
	2·55	0·14	14·86	10·16	17·21	0·11	1·16	53·37	0·04	0·02	0·02
G	2·56	0·14	14·63	10·20	17·10	0·09	1·11	53·69	0·03	0·02	0·01
	2·57	0·16	14·52	10·27	17·07	0·10	1·13	53·71	0·03	0·02	0·01
	2·58	0·14	14·59	10·24	17·00	0·09	1·18	53·73	0·03	0·02	0·01
H	2·54	0·10	14·69	10·10	17·12	0·13	1·16	53·01	0·03	0·02	—
	2·56	0·11	14·75	10·02	17·01	0·13	1·22	53·12	0·03	0·02	—
	2·59	0·11	14·75	10·18	17·14	0·13	1·19	53·14	0·02	0·01	—
I	2·62	0·13	14·85	9·97	17·02	0·12	1·25	53·17	—	—	—
	2·66	0·14	14·79	9·97	17·02	0·12	1·25	53·17	—	—	—
	2·67	0·13	14·86	9·97	17·08	0·12	1·22	53·22	—	—	—
J	2·60	—	14·72	—	17·06	—	1·16	—	—	—	—
	2·59	—	14·72	—	17·07	—	1·20	—	—	—	—
	2·59	—	14·76	—	17·10	—	1·18	—	—	—	—
K	2·60	—	—	—	—	—	—	—	—	—	—
	2·63	—	—	—	—	—	—	—	—	—	—
	2·66	—	—	—	—	—	—	—	—	—	—
L	2·68	—	—	—	—	—	—	—	—	—	—
	2·58	—	—	—	—	—	—	—	—	—	—
	2·50	—	—	—	—	—	—	—	—	—	—
Mean	2·60	0·13	14·71	10·19	17·13	0·11	1·18	53·38	0·04	0·03	0·02
Standard deviation	0·05	0·02	0·10	0·15	0·07	0·01	0·04	0·21	0·01	0·01	0·01
Previously accepted result	2·58	0·14	14·73	10·34	17·18	0·12	1·17	53·5	0·05	0·03	0·03

These results clearly indicated that although the results obtained during the development of the method of B.S. 1902 : Part 2C were excellent for the determination of chromium, there must be a considerable degree of unreliability. These good results may be due partly to the fact that the original work was carried out in the winter when light levels could be expected to be less significant. In addition, the calibration for the colorimetric determination of chromium would have been carried out at almost the same time as the results were obtained on the samples, and as the calibration includes a separation with a liquid ion-exchange resin, the errors might well have cancelled each other out.

At this stage it became clear that preference should be given to the titrimetric method for the determination of chromium, based on that of Bryant and Hardwick.[1] However, it was agreed that the separation of chromium by liquid ion exchange should be retained for the removal of this element prior to other determinations.

During the work on the determination of aluminium mentioned above, on occasions a brown precipitate had been observed at the interface of the aqueous and organic phases during the chromium separation process. This precipitate was subsequently found to contain

TABLE VI

RESULTS ON B.C.S. 370 MAGNESITE - CHROME REFRACTORY (IGNITED AT 1000 °C BASIS)

Laboratory	SiO_2, per cent.	TiO_2, per cent.	Al_2O_3, per cent.	Fe_2O_3, per cent.	Cr_2O_3, per cent.	MnO, per cent.	CaO, per cent.	MgO, per cent.	Na_2O, per cent.	K_2O, per cent.	Li_2O, per cent.
A	2·95	0·12	12·22	7·03	13·61	0·11	1·58	61·93	0·04	0·04	0·01
	2·94	0·12	12·24	7·07	13·61	0·11	1·57	61·96	0·05	0·04	0·01
	2·93	0·12	12·24	7·09	13·54	0·11	1·57	62·01	0·04	0·04	0·01
B	3·05	0·13	12·14	7·32	13·44	0·13	1·57	61·54	0·05	0·02	0·03
	3·05	0·13	12·23	7·32	13·24	0·13	1·53	61·73	0·05	0·02	0·03
	3·12	0·14	12·20	7·35	13·42	0·13	1·52	61·72	0·05	0·02	0·03
C	2·99	0·13	12·46	7·17	13·22	0·13	1·56	61·70	0·04	0·04	0·01
	2·98	0·15	12·53	7·17	13·25	0·13	1·59	61·68	0·05	0·04	0·01
	2·99	0·13	12·45	7·05	13·16	0·13	1·59	61·68	0·04	0·04	0·01
D	3·09	0·15	12·21	7·28	13·40	0·12	1·50	61·72	0·06	0·02	0·04
	3·02	0·13	12·21	7·43	13·45	0·13	1·56	61·82	0·06	0·02	0·04
	3·09	0·15	12·09	7·43	13·40	0·12	1·56	61·92	0·06	0·02	0·04
E	3·04	0·12	12·22	7·21	13·28	0·11	1·56	62·05	0·04	0·02	—
	3·04	0·10	12·22	7·21	13·30	0·11	1·58	62·24	0·04	0·02	—
	3·02	0·10	12·22	7·21	13·30	0·11	1·58	62·24	0·04	0·02	—
F	2·95	0·09	12·36	7·17	13·39	0·12	1·56	62·08	0·05	0·02	0·02
	2·97	0·10	12·38	7·14	13·44	0·12	1·57	61·98	0·05	0·01	0·02
	2·99	0·10	12·35	7·11	13·40	0·11	1·58	62·08	0·05	0·02	0·02
G	3·05	0·07	12·26	7·21	13·42	0·10	1·49	61·94	0·03	0·03	0·01
	2·99	0·09	12·37	7·27	13·44	0·10	1·48	62·03	0·04	0·02	0·02
	2·99	0·11	12·26	7·20	13·43	0·10	1·55	62·11	0·04	0·02	0·01
H	3·04	0·08	12·33	7·10	13·24	0·13	1·59	61·53	0·04	0·02	—
	3·02	0·09	12·40	7·12	13·11	0·13	1·63	61·59	0·04	0·02	—
	3·04	0·08	12·40	7·16	13·16	0·13	1·59	61·60	0·04	0·02	—
I	3·04	0·10	12·32	6·97	13·33	0·12	1·68	61·79	—	—	—
	3·03	0·08	12·32	7·02	13·28	0·12	1·65	61·79	—	—	—
	3·06	0·10	12·19	7·02	13·43	0·12	1·68	61·84	—	—	—
J	3·10	—	12·23	—	13·41	—	1·63	61·51	—	—	—
	3·01	—	12·21	—	13·41	—	1·60	61·54	—	—	—
	3·17	—	12·21	—	13·42	—	1·58	—	—	—	—
K	3·08	—	—	—	—	—	—	—	—	—	—
	3·04	—	—	—	—	—	—	—	—	—	—
	3·08	—	—	—	—	—	—	—	—	—	—
L	3·07	—	—	—	—	—	—	—	—	—	—
	3·00	—	—	—	—	—	—	—	—	—	—
	3·02	—	—	—	—	—	—	—	—	—	—
Mean	3·03	0·11	12·28	7·18	13·36	0·12	1·58	61·84	0·05	0·03	0·02
Standard deviation	0·05	0·02	0·10	0·12	0·13	0·01	0·05	0·22	0·01	0·01	0·01
Previously accepted result	3·01	0·12	12·25	7·24	13·34	0·12	1·54	61·8–	0·06	0·03	0·03

iron and was presumably iron(III) hydroxide produced by the intimate contact of the iron-bearing aqueous and only slightly acidic solution with the strongly alkaline resin. This, again, appeared to be a phenomenon caused mainly by the changes in the process required so as to handle a larger amount of sample.

In view of the decision not to determine chromium in the organic phase obtained in the separation, it was thought possible that the extraction conditions could be altered in such a way as to prevent the loss of iron without substantially increasing the amount of chromium reduced and so retained in the aqueous solution. From previous experience, it was known that an increase in acidity prevented loss of iron, but at the same time caused an increase in the amount of chromium that remained in the aqueous phase.

Experiments were therefore carried out to discover if there was, in fact, a range of acidities over which iron could be retained quantitatively without too great an increase in the reduction of chromate. Dichromate solutions (equivalent to 40 per cent. of Cr_2O_3 on a 1-g sample), and containing 8 g of $KNaCO_3$, 4 g of H_3BO_3 and the equivalent of 5 per cent. of Fe_2O_3 at various acidities were taken through the liquid ion-exchange process in the normal

TABLE VII

RESIDUAL CHROMIUM(III) OXIDE (PER CENT.) LEFT AFTER EXTRACTION WITH LIQUID ION-EXCHANGE RESIN

Laboratory	Chrome - magnesite AN 21A (Cr_2O_3 = 30 per cent.)	Chrome ore AN 22 (Cr_2O_3 = 34 per cent.)
1	0·39	0·27
	0·35	0·17
	0·45	0·21
2	0·13	0·15
	0·10	0·22
	0·15	0·29
3	0·40	0·25
	0·54	0·19
	0·40	0·12
4	0·24	0·32
	0·28	0·37
	0·28	0·38

manner. In these experiments, however, the resin, previously stripped with sodium hydroxide, had been subsequently shaken with dilute sulphuric acid so as to prevent the organic phase from being too alkaline. After carrying out the separation process, iron and residual chromium were determined on the aqueous phase. The volumes of acid used ranged from 10 to 25 ml of sulphuric acid (1 + 1), of which the flux would consume about 7·5 ml, leaving excess volumes from 2·5 to 17·5 ml. Fig. 2 shows the results of these experiments.

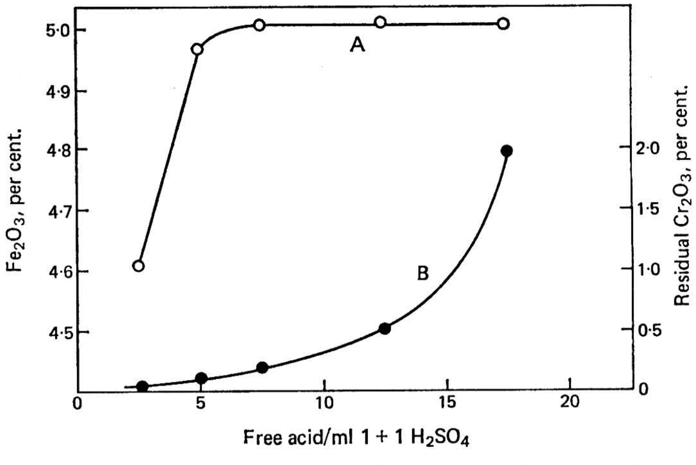

Fig. 2. Percentage of iron(III) oxide (A) and chromium(III) oxide (B) in the aqueous phase at various acidities in resin separation

It is clear from the results that all of the iron is retained at acidities equivalent to more than 7·5 ml of free acid and that up to 12·5 ml of free acid can be tolerated before the residual chromium level rises to more than 0·5 per cent. of Cr_2O_3, this being the maximum amount that was considered permissible. Therefore, the amount of acid used for dissolving a melt containing 1 g of sample and a flux of 8 g of fusion mixture and 4 g of boric acid must lie between 15 and 20 ml of sulphuric acid (1 + 1).

Determination of iron(III) oxide—In the method described in B.S. 1902 : Part 2C, a separate sample is used for the determination of iron, but following the work on the separation of chromium it was decided to carry out the determination on an aliquot of the aqueous phase. This procedure avoids the risk of interference from chromium and the need for a separate decomposition of at least 0·1 g to provide 0·005 g of sample for the actual determination.

No difficulty was experienced with the colorimetric determination itself, but two aspects required attention. The iron content is higher than in most refractory materials, and in many chrome-bearing materials it may be regarded as being a major constituent. This fact necessitated the use of a spectrophotometer rather than a colorimeter in order to achieve the desired accuracy. For the same reason, a preliminary dilution stage is included in the method in order to permit the use of adequately sized aliquots commensurate with the accuracy desired.

Determination of titanium(IV) oxide—The hydrogen peroxide method for the determination of titanium presented no difficulties. It was appreciated that the sensitivity of the procedure is not as high as would normally be desired and that as a result the analytical reproducibility is less than the optimum. However, there is no apparent technological significance in minor changes in titanium content, so that the standard achieved by the results is acceptable. Any abnormal titanium content can be detected without difficulty.

Determination of manganese(II) oxide—Similar considerations apply as for titanium, in that the main concern is to detect large abnormalities in manganese contents. The applicability of the periodate oxidation method was not in doubt, and the results showed satisfactory precision.

Determination of the oxides of calcium and magnesium—Methods developed for the determination of calcium and magnesium in magnesites and dolomites[6] should be equally applicable to the solution after the removal of chromium. The differences are the greater contents of iron and aluminium and a possibly lower level of magnesium. In the determination of calcium, the iron and aluminium are adequately complexed with triethanolamine. With magnesium, sodium diethyldithiocarbamate effectively removes the iron, and cupferron used in only slightly acidic solutions removes the aluminium. The final titrations can then be performed without difficulty.

Determination of aluminium(III) oxide—The separation of iron and manganese is accomplished with sodium diethyldithiocarbamate, and of titanium with cupferron. The chromium content of the solution after altering the acidity at which the separation of chromium is conducted is higher than that which could be accepted if it were to interfere. In the original method, in which the final titration was performed with EDTA, it was necessary to carry out a separate determination of the chromium in order to allow for its stoicheiometric interference. The work on the titration of aluminium with DCTA[7] indicated that the final titration could be carried out without interference from chromium. The final tables of results show that this was correct, and that the reproducibility of the results was very good, particularly in view of the complexity of the matrix.

DETERMINATION OF ALKALI-METAL OXIDES—

Alkali-metal oxides are determined in the usual manner except that the amount of perchloric acid is greatly increased so as to increase the degree of attack. However, as a result of the investigation into interferences in the determination of alkali-metal oxides,[8] the use of nitric and sulphuric acids is to be preferred. However, the technological requirement is again for the detection of large abnormalities; apart from this, the interferences tend to be proportional to the amount present, and as this is generally less than 0·1 per cent., the errors introduced by the use of perchloric acid are negligible.

DETERMINATION OF SILICON DIOXIDE—

It was expected that the method described in B.S. 1902 : Part 2C would be directly applicable. However, preliminary results when using a 1-g sample indicated that it was not. At the 3 per cent. level, results were up to 1 per cent. low when the separation was carried out by the revised procedure. The use of the original procedure, but with a 1-g sample, did not produce correct results. It was observed, on occasions, that slight precipitation of silicic acid occurred in the calibrated flask after the solution had been allowed to stand overnight.

Several other methods for the determination of silica were tried, including the following—

(*i*) coagulation with polyethylene oxide resins;
(*ii*) fuming with perchloric acid;
(*iii*) fusion followed by fuming with perchloric acid;

(*iv*) determination as yellow molybdosilicate after the removal of chromium;
(*v*) fusion followed by determination as molybdenum blue; and
(*vi*) fusion followed by gravimetric determination as quinoline molybdosilicate.

Coagulation with polyethylene oxide resins—The sample was fused and dissolved in the usual manner, after which the solution was evaporated for about 30 minutes. After the addition of paper pulp, the precipitate was coagulated and filtered off.

Filtration was generally slow and it was impossible to wash the precipitate free from chromium. Manipulation was difficult and the method was thought not to be practicable.

Fuming with perchloric acid—Decomposition of the sample and dehydration of silicon dioxide were both carried out with perchloric acid. The method could have the advantage that, by adding sodium chloride, most of the chromium could be removed by volatilisation as chromyl chloride.

Silicon dioxide in B.C.S. 370 magnesite - chrome refractory was determined in three laboratories by this method (Table VIII).

TABLE VIII

RESULTS FOR THE DETERMINATION OF SILICON DIOXIDE IN B.C.S. 370 MAGNESITE - CHROME REFRACTORY BY DECOMPOSITION AND FUMING WITH PERCHLORIC ACID

Laboratory	Main SiO_2, per cent.	Residual* SiO_2, per cent.	Total SiO_2, per cent.
1	2·95	0·15	3·10
	2·85	0·20	3·05
	3·00	0·08	3·08
2	—	—	3·06
	—	—	3·08
3	2·96	—	—
	2·96	—	—
	2·98	—	—

* Molybdenum-blue determination.

Two of the three laboratories did not consider the method to be satisfactory. Large volumes (40 ml) of perchloric acid were involved and decomposition took up to 8 hours. Laboratory 1 found it necessary to make repeated attempts to obtain three concordant results. For these reasons, this method was not used in further work.

Fusion followed by fuming with perchloric acid—The sample was fused with sodium carbonate and boric acid and the melt was dissolved in perchloric acid and then dehydrated by fuming with perchloric acid. The silicon that remained in solution was determined as molybdenum blue. The length of time required for the decomposition is considerably less than that for the perchloric acid decomposition procedure. However, more perchloric acid must be used so as to prevent the mixture from solidifying and spattering during the fuming stage. The results obtained in three laboratories are shown in Table IX.

The precipitated silicon dioxide was stained with chromium even after prolonged washing. In terms of the manipulations required, the method was difficult, as was the situation with both of the above methods, and did not commend itself to the members of the Working Group. Also, all three of these methods are dependent on a gravimetric figure obtained by direct weighing, and whereas the required accuracy was achieved in the analysis of magnesites and dolomites by increasing the sample mass to 5 g, the difficulty of decomposing these materials rendered such a procedure inadmissible in this instance. The Group therefore considered it doubtful that the required degree of accuracy could be achieved by any of these three methods, even if the manipulative problems could be overcome, and efforts were concentrated on the three methods discussed below.

Determination as yellow molybdosilicate after the removal of chromium—This method is basically the same as that described in B.S. 1902 : Part 2C, whereby the sample is fused with fusion mixture and boric acid, the melt dissolved in sulphuric acid, chromate removed

TABLE IX

RESULTS FOR THE DETERMINATION OF SILICON DIOXIDE IN B.C.S. 370 MAGNESITE - CHROME REFRACTORY BY FUSION FOLLOWED BY PERCHLORIC ACID DEHYDRATION AND DETERMINATION OF RESIDUAL SILICON AS MOLYBDENUM BLUE

Laboratory	Main SiO_2, per cent.	Residual SiO_2, per cent.	Total SiO_2, per cent.
1	2·88	0·07	2·95
	2·90	0·08	2·98
2	—	—	3·05
	—	—	3·03
	—	—	3·02
3	2·84	0·20	3·04
	2·82	0·16	2·98
	2·88	0·10	2·98
3	—	—	3·16*
	—	—	3·06*
	—	—	2·96*

* By double dehydration.

by solvent extraction with a liquid ion-exchange resin and the silicon in solution is determined as yellow molybdosilicate.

Preliminary results obtained at the British Ceramic Research Association had indicated that low results were obtained and that precipitation of silicic acid frequently occurred. Members of the Group, while preparing solutions for an investigation into the determination of magnesium, agreed to carry out, in addition, determinations of silicon by this method (Table X).

TABLE X

DETERMINATION OF SILICON DIOXIDE IN SAMPLES AN 22 AND AN 23 BY FUSION, REMOVAL OF CHROMIUM AND DETERMINATION OF SILICON DIOXIDE AS YELLOW MOLYBDOSILICATE

	SiO_2 content, per cent.	
Laboratory	AN 22	AN 23
1	3·18	3·49
	3·31	3·50
	3·28	3·09
2	1·10	2·85
	1·37	2·58
	1·25	2·71
	2·25	1·08
	2·39	1·20
	2·87	1·64
	1·91	2·63
3	2·78	3·08
	2·94	2·94
	3·02	2·94
4	4·18	2·54
	3·79	2·18
	3·75	1·86
	3·18	4·21
	2·86	4·22
	3·89	3·04
5	2·92	2·67
	2·40	3·70
	2·97*	2·90*
	2·42*	3·77*
6	2·92	3·38
	2·83	3·20
	2·92	3·30
	3·07	3·15
7	3·33	1·80
	3·48	1·93
	3·28	1·76
8	3·26	3·51
	3·28	3·47
	3·28	3·55
9	3·32	3·40
	3·36	3·56
	3·29	3·42
10	3·38	3·54
	3·40	3·50
	3·36	3·50

* Measured on fresh aliquots of stock solution after 3 days.

These results showed quite clearly the unreliability of the method. The final breakdown of the procedure caused the Group to consider techniques that would demand the use of a separate decomposition of the sample. Although every effort had been made to avoid this necessity, none of the methods tried was really successful. The following two methods require separate decompositions of the sample.

Fusion followed by determination as molybdenum blue—The sample was fused with fusion mixture and boric acid, the melt dissolved in sulphuric acid, the solution made up to volume and an aliquot used for the determination of silicon by a molybdenum-blue method. Manipulation was simple, the time required for a determination was small and, if the results were satisfactory, the method would be ideal. Three laboratories produced results, which are shown in Table XI.

TABLE XI

RESULTS FOR THE DETERMINATION OF SILICON DIOXIDE IN B.C.S. 370 MAGNESITE - CHROME REFRACTORY BY FUSION FOLLOWED BY DETERMINATION AS MOLYBDENUM BLUE

Laboratory	SiO_2 found, per cent.
1	3·17
	3·19
2	2·91
	2·91
	2·91
3	3·35
	3·26
	3·28

It was suspected that the difficulty of retaining silicon in the correct form during the relatively slow dissolution could result in errors, but the three laboratories concerned were satisfied with the method, so the whole Group investigated the procedure in more detail. The results are given in Table XII, and are discussed in greater detail later.

Fusion followed by gravimetric determination as quinoline molybdosilicate[9]—The sample was fused with potassium carbonate - sodium carbonate (fusion mixture) and boric acid, the melt dissolved in sulphuric acid and ammonium molybdate added to form yellow molybdosilicic acid. After increasing the acidity so as to prevent the precipitation of quinoline molybdate, quinoline is added to precipitate quinoline molybdosilicate. After digesting and cooling, the precipitate is filtered off in a sintered glass crucible, dried and weighed.

Preliminary results obtained at the British Ceramic Research Association on B.C.S. 308 Grecian chrome ore were 4·31, 4·31, 4·28, 4·25, 4·33 and 4·32 per cent. of SiO_2, compared with the accepted value of 4·29 per cent. These results were so promising that the whole Group agreed to give the method a more comprehensive trial, the results of which are shown in Table XII.

The results seem to indicate that both methods yield reasonably satisfactory results, with rather better reproducibility for the gravimetric method. Laboratory 8 reported that many variable results had been obtained by the colorimetric method, none of which could be quoted in a table. The general opinion was that even if the difficulties that gave rise to the variability could be overcome, the nature of the method was such that it was not suitable for a standard method, except as a last resort.

There was general satisfaction with the quinoline molybdosilicate gravimetric method. The results were generally of a standard that would be technologically acceptable, and, from the analyst's point of view, the method seemed to offer no difficulties and manipulation was easy. One of the main advantages was the very small conversion factor, which, even if relatively small amounts of sample were taken, seemed to offer good reproducibility.

It was decided, therefore, to carry out determinations of silicon on six 0·25-g samples, two each of chrome ore, chrome - magnesite refractory and magnesite - chrome refractory. The results are shown in Table XIII.

It was clear from the results on sample AN 11, which has a high silicon content, that the method was unsuccessful. Although AN 11 is an abnormal sample in that the silicon content would be unacceptable at present in this class of material, nevertheless, the failure to obtain satisfactory results was disconcerting. It was concluded that at this level of silicon, some of the silicon could be lost in a form that did not react with molybdate. In the procedure used for aluminosilicates,[9] this silicon, if any, is recovered by making the solution strongly alkaline with sodium hydroxide and then acidic. However, the aliquot used and the ratio of silicon to aluminium, iron, etc., in aluminosilicates permits this recovery to be achieved, but when an attempt was made to apply this procedure to chrome-bearing materials the amount of precipitate formed was excessive and it could not be redissolved in any reasonable amount of acid. In any event, the voluminous R_2O_3 precipitate would inevitably "sweep out" a proportion of the silicon. In order to avoid this precipitation, several complexing agents, including EDTA, were tried, but either obvious difficulties arose or the results were clearly low.

TABLE XII

RESULTS FOR THE DETERMINATION OF SILICON DIOXIDE IN B.C.S. 308 AND B.C.S. 370 SAMPLES BY QUINOLINE MOLYBDOSILICATE AND MOLYBDENUM-BLUE METHODS

	SiO_2, per cent.			
	B.C.S. 308 (accepted SiO_2 = 4·29 per cent.)		B.C.S. 370 (accepted SiO_2 = 3·01 per cent.)	
Laboratory	Quinoline molybdosilicate method	Molybdenum-blue method	Quinoline molybdosilicate method	Molybdenum-blue method
1	4·36	4·11	3·04	3·05
	4·33	4·09	3·05	3·09
	4·35	4·14	3·03	3·06
2	4·40	4·38	3·17	3·10
	4·34	4·41	3·13	3·15
	4·33	4·26	3·13	3·08
3	4·24	4·42	3·10	3·15
	4·24	4·59	3·17	3·02
	4·22	4·59	3·01	3·18
4	4·33	4·41	3·03	3·06
	4·34	4·40	3·00	3·04
	4·31	4·40	3·02	3·04
5	4·25	4·32	3·02	2·89
	4·30	4·37	3·02	2·89
	4·29	4·37	3·01	2·89
6	4·33	4·25	3·04	2·94
	4·31	4·25	3·02	2·98
	4·32	4·25	3·01	2·89
7	4·37	4·26	3·03	3·02
	4·40	4·22	3·01	3·00
	4·23	4·30	3·01	2·96
8	4·30	Unsatisfactory	3·08	Unsatisfactory
	4·36		3·01	
	4·29		3·08	
9	4·20	—	2·97	—
	4·23	—	3·04	—
Mean	4·31	4·32	3·05	3·02
Standard deviation . .	0·06	0·13	0·05	0·09
Coefficient of variation	1·29	3·08	1·73	2·99

Finally, in view of the success of the method on the other five samples, the experiment on AN 11 was repeated, but with only a 0·1-g sample. Co-operative results, which are included in Table I, gave a mean value of 8·72 per cent. of SiO_2 with a standard deviation of 0·17 per cent.

Rather than use a variable amount of sample, the work on the other five samples was repeated with 0·1-g samples. The results were of the same order of accuracy as with the larger amount and are included in Tables I to VI. This method was then accepted as being suitable.

DISCUSSION OF THE RESULTS

Although some of the above procedures are not elegant and leave the fastidious analyst with a desire for improvement, these methods give considerable improvements in speed and accuracy over the classical method. The matrix of these materials is complex and chromium is not readily removed. Methods of the type described are as advanced as modern analytical chemistry permits when the type of instrumentation available has to be restricted.

TABLE XIII

RESULTS OF THE DETERMINATION OF SILICON DIOXIDE BY THE QUINOLINE MOLYBDOSILICATE METHOD ON A 0·25-g SAMPLE

	SiO_2, per cent.					
Laboratory	B.C.S. 308	B.C.S. 369	B.C.S. 370	AN 11	AN 21A	AN 22
1	4·29	2·56	2·97	8·48	3·89	3·32
	4·31	2·57	2·96	6·38	3·90	3·40
	4·30	2·55	2·96	6·77	3·93	3·36
2	4·38	2·66	3·05	8·70	3·99	3·44
	4·32	2·66	3·05	8·75	3·97	3·43
	4·38	2·65	3·12	8·67	3·97	3·46
3	4·29	2·60	3·01	5·60	3·89	3·40
	4·26	2·53	3·01	5·55	3·92	3·40
	4·28	2·53	3·02	5·50	3·93	3·45
4	4·46	2·59	2·90	7·82	3·46	3·50
	4·46	2·57	2·83	7·83	3·37	3·55
	4·45	2·62	2·85	7·93	3·25	3·55
5	4·24	2·57	2·98	8·84	3·94	3·44
	4·27	2·53	3·05	9·01	3·82	3·41
	4·22	2·47	2·90	8·91	3·76	3·30
6	4·30	2·56	3·02	9·49	4·04	3·85
	4·34	2·58	3·04	9·29	4·04	3·89
	4·27	2·56	3·01	9·41	4·05	3·84
7	4·32	2·53	3·05	—	—	—
	4·29	2·54	3·07	—	—	—
	4·30	2·52	3·05	—	—	—
8	4·33	2·54	2·99	4·63	3·95	3·45
	4·34	2·55	3·01	6·67	3·96	3·44
	4·31	2·55	3·02	7·98	—	3·41
Mean	4·30	2·57	3·01	7·85	3·94	3·43
Standard deviation ..	0·04	0·05	0·05	1·42	0·08	0·07
Previously accepted result	4·29	2·58	3·01	8·72	3·71	3·33

The standard of the results achieves that required for normal technological purposes, either control or referee. Determinations such as those for titanium and manganese could conceivably be improved, at the cost of more difficult procedures, but the present inter-laboratory results are more than adequate. Results for the more important minor constituents silicon and calcium are also adequate; the determination of silicon is a matter of experience and continual use of the method seems to improve the quality of the results, whereas the results for calcium are remarkably good in view of the nature of the matrix. It is probable that the use of atomic-absorption techniques will result in improvements in the determination of calcium, particularly with regard to speed.

Few materials have four significant major constituents and although the standard deviations of the results for iron, chromium and magnesium tend to be worse than those for silicon and aluminium in aluminosilicates, this is hardly surprising. The results are, however, two or three times better than those which can be achieved by means of the classical method, and are accomplished in a much shorter time.

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The Quantitative Separation of Chromium(VI) from Other Elements with a Strongly Basic Anion-exchange Resin

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Previous work has shown that chromium(VI) on a strongly basic exchange resin in sulphuric acid solution cannot be quantitatively separated from other metal ions because of partial reduction of the chromium(VI) to chromium(III). The present investigations have demonstrated the complete retention of chromium(VI) by the resin in alkaline solutions, thus permitting the separation of chromium from many elements, which can be precipitated as hydroxides, and also from amphoteric elements, which can be eluted from the resin with alkaline solutions. Finally, chromium(VI) can be quantitatively removed from the resin with 8 to 10 per cent. sodium carbonate solution or, more satisfactorily, with an aqueous solution of a mixture of sodium hydrogen carbonate and sodium carbonate.

THE exchange properties of chromium(VI) in the multi-component system chromium(III) - vanadium(V) - molybdenum(VI) - tungsten(VI) in sulphuric acid - hydrogen peroxide solutions have been studied by Strelow and Bothma,[1] who found that sulphuric acid facilitated the partial reduction of chromium(VI) to chromium(III) by the resin. The procedure is therefore unsuitable for the quantitative separation of chromium(VI) from other elements, as was pointed out by these workers.

The present investigations were carried out by using 2 to 5 per cent. sodium hydroxide solution from which chromium(VI) was adsorbed by the resin. Amphoteric oxides, such as aluminium oxide, dissolved in the same solution were not retained by the resin and therefore separation of aluminium(III) from chromium(VI) was possible.

Recently attempts have been made to take advantage of the ion-exchange behaviour of the chromium(III) - chromium(VI) system in chromatographic separations. Steuter and Freeman[2] reported an efficient method that involved the oxidation of chromium(III) to chromium(VI) to effect rapid desorption of chromium(III) from a cation-exchange resin. The method now reported has many advantages over that proposed by Steuter and Freeman, the most important being that it permits quantitative separation of chromium from basic and amphoteric oxides. Elements that form hydroxides that are insoluble in alkaline solutions can be removed prior to the ion-exchange step by filtration of the hydroxide precipitates. In this way chromium can be separated from a wide range of elements.

EXPERIMENTAL

REAGENTS—

Amberlite resin, IRA-400, in the chloride form—Analytical grade, as supplied by Rohm & Haas Company, Philadelphia, U.S.A.

Potassium chromium sulphate, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$—Not less than 98 per cent. pure, supplied by B.D.H. Ltd., Poole.

Potassium aluminium sulphate, $K_2SO_4.Al_2(SO_4)_3.24H_2O$—Supplied by May & Baker Ltd., Dagenham.

PROCEDURE—

To mixtures of various volumes of a solution containing 10 mg ml^{-1} of aluminium and a solution containing 10 mg ml^{-1} of chromium, to cover the ranges of these elements shown in Table I, a warm mixture of 50 ml of 10 per cent. sodium hydroxide solution and 2 ml of 30 per cent. hydrogen peroxide solution was added so as to oxidise the chromium(III) to chromium(VI). After the chromium hydroxide formed had dissolved and the oxidation of chromium(III) was complete the solution was boiled until the colour changed from red-orange to yellow and the excess of peroxide was destroyed. Distilled water (300 ml) was added and the ion-exchange separation of aluminium from chromium was effected on the resulting solution.

Separation of aluminium(III) from chromium(VI)—The ion-exchange column (1 cm × 15 cm) was packed with the wet resin (15 ml). (The volume of the resin submerged under distilled water was measured in a measuring cylinder.) The column was then made ready for use by passing through it 100 ml of aqueous 0·5 per cent. sodium hydroxide solution. The solution containing aluminate and chromate ions was passed through the column at the rate of 56 drops per minute (5 ml min^{-1}). The column was finally stripped of aluminium by passing through it 400 ml of 2 per cent. sodium hydroxide solution, and to the collected aluminium fraction dilute hydrochloric acid was added until the precipitate of aluminium hydroxide formed just re-dissolved. The solution was then concentrated by evaporation and suitable aliquots of the concentrate were taken for the determination of aluminium.

Elution of chromium(VI) with 10 per cent. aqueous sodium carbonate solution—Chromium(VI), free from aluminium, was eluted from the resin with a 10 per cent. aqueous solution of sodium carbonate decahydrate. With an elution rate of 2 ml min^{-1}, 1½ litres of the solution were required for removal of 100 mg of chromium from the resin. The solution obtained was concentrated by evaporation and the concentrate was used for the determination of chromium.

Elution with a solution of a sodium carbonate - sodium hydrogen carbonate mixture—In a separate experiment a mixture of 100 ml of 10 per cent. aqueous sodium carbonate solution and 250 ml of a saturated solution of sodium hydrogen carbonate was used, which completely eluted 100 mg of chromium. The eluate was evaporated to about 180 ml, the separation of crystalline sodium hydrogen carbonate being prevented by the addition of 6 N sulphuric acid.

RESULTS AND DISCUSSION

Aluminium in the aluminium fraction was determined by titration with EDTA,[3] and chromium(VI) was determined in acidic solution by addition of potassium iodide and titration with standard sodium thiosulphate solution.[4] The results of the aluminium and chromium determinations are summarised in Table I.

TABLE I

ANALYTICAL RESULTS FOR THE ION-EXCHANGE SEPARATION OF CHROMIUM(VI) AND ALUMINIUM(III)

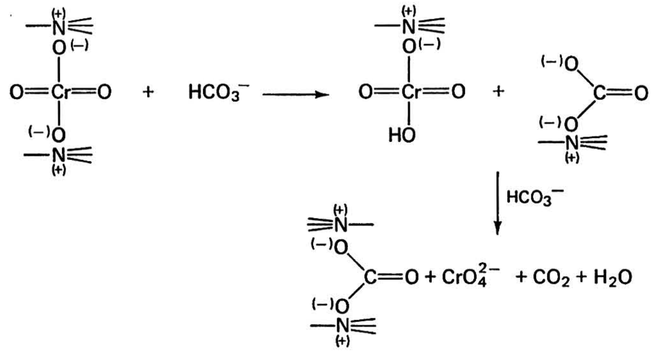
	Aluminium		Chromium	
Experiment	Amount taken/mg	Amount found in aluminium fraction/mg	Amount taken/mg	Amount found in chromium fraction/mg
1	158·40	158·20	100·00	99·80
2	140·00	140·20	50·00	50·10
3	100·00	100·30	60·00	60·00
4	99·70	99·90	75·00	74·80
5	79·00	79·20	81·10	81·00
6	60·00	60·05	73·10	72·95
7	55·00	54·90	62·50	62·46
8	49·10	49·05	52·20	52·25

The above results show that in alkaline solution there is no reduction of chromium(VI) by the resin. Large volumes of sodium carbonate solution are generally required for the complete elution of chromate from the resin. When the solution obtained is evaporated so as to reduce the volume, the crystallisation of large amounts of sodium carbonate creates difficulties in the subsequent determination of chromate.

Sodium hydrogen carbonate solution was found to be more efficient for the elution of chromate ions but then evolution of carbon dioxide occurs in the resin bed, which restricts the smooth flow of the solution through the column. This effect can, however, be suppressed by the addition of a small amount of sodium carbonate to the sodium hydrogen carbonate solution.

The elution of chromium(VI) appears not to depend directly on the carbonate concentration, which is shown by the fact that solutions of sodium carbonate and solutions of sodium hydrogen carbonate to which a small amount of sodium carbonate has been added do not exhibit the same efficiency of elution for chromium(VI), even when the carbonate is maintained at the same concentration in both solutions. It is hoped that the elucidation of the mechanism of this exchange reaction will be the subject of a further paper.

The displacement of chromium(VI) by carbonate ions in the resin bed can be represented by the following reactions—



The increased efficiency of elution of sodium hydrogen carbonate solution compared with sodium carbonate solution containing the same carbonate concentration supports this interpretation. Further, the evolution of carbon dioxide in the resin bed when chromate is eluted with a solution of sodium hydrogen carbonate alone can be accounted for.

Other potential applications of this method of separation are to minerals such as chrome-iron ore, in which chromium and aluminium exist as oxides, and to certain alloys containing chromium together with elements that form amphoteric oxides, which can be fused with sodium peroxide prior to separation by the above method.

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An Automated Method for the Determination of Lead in Calcareous Materials Utilising Liquid Ion Exchange

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An automated method for the determination of lead in calcium carbonate, lime and limestone with the Technicon AutoAnalyzer is described. The method is based on the extraction of lead from an acidic chloride solution of the sample with a long-chain amine liquid ion exchanger, followed by re-extraction into an ammonia - ammonium citrate buffer at pH 9. Finally, the lead is extracted as the lead - dithizone complex into chloroform and the optical density of the complex measured at 510 nm. The separation of lead prior to formation of the lead - dithizone complex results in low background and blank readings. Lead levels of 0 to 20 p.p.m. can be determined at a rate of twenty samples per hour. Other trace metals which occur in calcareous materials do not interfere.

CALCIUM carbonate conforming to the requirements of the British Pharmacopoeia[1] must contain less than 20 p.p.m. of lead. Previously, lead has been determined in these laboratories according to the British Pharmacopoeia test, which is based on the visual comparison of lead sulphide in the sample solution with limiting standard solutions. The large number of samples encountered in quality control made it desirable to develop an automated method for carrying out lead determinations.

A Technicon AutoAnalyzer method, based on the British Pharmacopoeia method, was developed but was found to be insufficiently sensitive. However, automated methods for lead determination based on a dithizone (diphenylthiocarbazone) extraction have been described.[2,3] Sebborn[3] noticed that the peak heights obtained by direct extraction of the lead - dithizone complex from the sample solution resulted in high results and poor precision. He ascribed these findings to a salt effect and overcame the problem by running a wash solution with a composition identical with that of the sample solutions. We found that, while running such a wash solution removed the apparent blank reading and produced more accurate results, the precision at low levels of lead still remained poor, because small changes in the salt concentration of the samples, which could sometimes occur during the routine preparation of sample solutions, resulted in a fluctuation in peak height.

Methods based on the direct extraction of lead from calcium solutions by dithizone were therefore abandoned. In order to overcome these problems of direct extraction, methods of separating the lead efficiently from the calcium solutions prior to the dithizone extraction stage were investigated. Separation of lead from calcium as the diethyldithiocarbamate complex was attempted but it was found to be impracticable to back-extract the lead into a suitable solution for direct measurement of the lead as the dithizone complex, owing to the high stability of lead diethyldithiocarbamate.

Liquid ion-exchange resins have been used to extract lead from aqueous radium solution.[4]

Recently, Delves, Shepherd and Vinter[5] have shown that the extraction efficiency for lead extracted from hydrochloric acid solution reaches a maximum of 84 per cent. for a 2 M hydrochloric acid concentration. These workers used tri(6-methylheptyl)amine in 4-methylpentan-2-one. Experiments involving the use of Amberlite LA-1 (as a 15 per cent. *V*/*V* solution in heptane), with various calcium and hydrochloric acid concentrations over a range of total chloride concentrations from 0·5 to 2·0 M, showed that the extraction efficiency did not vary significantly over such a range of total chloride concentrations. The results are shown in Table I. With a 2:1 ratio of aqueous phase to organic phase, a single 1-minute extraction was used and the lead was back-extracted into 5 M nitric acid. A 25-μg amount of lead was added to each sample prior to the extraction and the recovered lead was determined by the method reported by Richardson.[6]

Concentrations of total chloride in excess of 2 M were not studied as Delves, Shepherd and Vinter[5] have shown that lead extraction efficiencies in the tri(6-methylheptyl)amine -

hydrochloric acid system begin to diminish above 2 M. It was found convenient to use a sample solution that was 0·5 M with respect to calcium and 0·5 M with respect to hydrochloric acid because a solution of this composition is used for other automated tests in these laboratories.

TABLE I

VARIATION OF EXTRACTION EFFICIENCY WITH CHLORIDE CONCENTRATION

Chloride concentration from $CaCl_2$/M	Chloride concentration from HCl/M	Lead extracted, per cent.
0·5	0	50
0·5	0·5	55
1·0	0	40
0	1·0	44
0	1·5	40
1·5	0	60
0·75	0·75	44
1·0	1·0	58

AUTOMATED METHOD

The flow scheme of the manifold is shown in Fig. 1. A solution of the samples is segmented and extracted with a 15 per cent. *V*/*V* solution of Amberlite LA-1 liquid ion-exchange resin in heptane in a mixing coil. After phase separation the lower aqueous layer is rejected and the resin passed through the platinum tube of an A6 connector into an ammonia - ammonium citrate buffer stream. The lead is back-extracted into the buffer and the stream is again phase separated. The resin is collected for regeneration.

The aqueous phase is segmented and extracted with a 0·001 per cent. *m*/*V* solution of dithizone in chloroform in a mixing coil and phase separated in a B0 phase separator on the colorimeter module. The separator is connected by a short J-shaped glass tube of 1·5-mm bore to the Technicon flow cell. The optical density of the lead - dithizone complex is measured at a wavelength of 510 nm at ×4 range expansion.

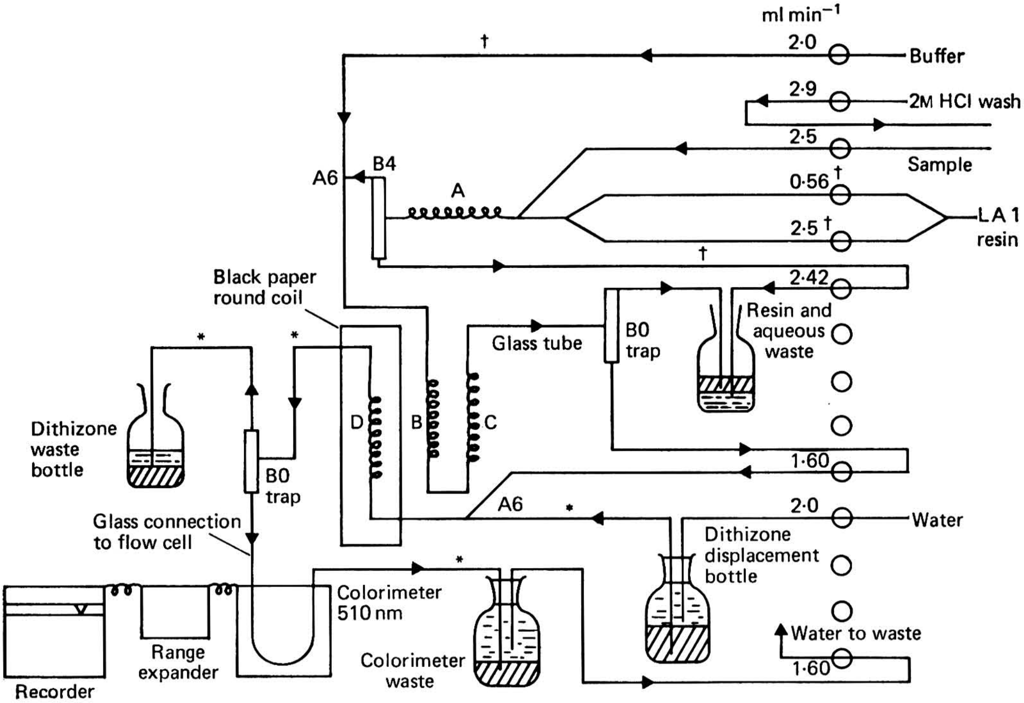

Fig. 1. Flow scheme of the manifold. A, B, C and D are double mixing coils; * Acidflex tubing; † Solvaflex tubing

The sampling rate is twenty samples per hour with 1 minute aspiration and 2 minutes for washing; this gives well shaped peaks although a very slight base-line drift is evident. A sample cup containing 1·5 M hydrochloric acid is placed after the last standard to avoid sample cross-contamination.

REAGENTS—

All reagents should be of analytical-reagent grade, except where indicated. Distilled water should be used throughout.

Dithizone, AnalaR grade—Prepare a stock solution of dithizone (Hopkin & Williams) at a concentration of 0·01 per cent. *m*/*V* in chloroform. Store this solution in a darkened bottle at 0 °C and prepare it fresh weekly. From this solution, prepare the working solution by diluting the stock solution ten-fold immediately before use. Do not store this dilute solution.

Liquid ion-exchange resin, Amberlite LA-1, 15 *per cent.* V/V *in heptane*—The resin is converted to the chloride form before use by using the resin regeneration procedure.

Hydrochloric acid, 2 M—Dilute from B.D.H. Aristar grade.

Hydrochloric acid, 4 M—Dilute from B.D.H. Aristar grade.

Hydrochloric acid, 5 M—Dilute from AnalaR grade.

Sodium hydroxide, 4 M.

Nitric acid, 4 M.

Ammonia buffer—Dissolve 100 g of triammonium citrate and 2 g of hydroxylammonium chloride in about 600 ml of water, then add 160 ml of ammonia solution (sp. gr. 0·880) followed by 2·5 g of potassium cyanide (low in lead). Finally, dilute to 1 litre with water. Prepare the buffer solution fresh daily. (Waste solutions containing cyanide should be treated with an excess of sodium hypochlorite and allowed to stand for 24 hours before disposal.)

Standard lead solution—Weigh 1·60 g of lead nitrate, dissolve it in water and add 10 ml of concentrated nitric acid. Dilute the solution to 1 litre.

1 ml of solution ≡ 1000 μg of lead.

Standard lead working solution—Dilute 10 ml of the 1000 μg ml^{-1} solution to 1 litre with water. Prepare this solution fresh daily.

1 ml of solution ≡ 10 μg of lead.

RESIN REGENERATION PROCEDURE—

To regenerate about 800 ml of resin solution, transfer the used resin - aqueous waste mixture to a 1-litre separating funnel and run off the lower aqueous layer. Add 100 ml of 4 M nitric acid to the resin and shake the funnel for about 30 s, allow the layers to separate and then discard the lower layer. Repeat the operation with a further 100 ml of nitric acid. A dark amber lower layer, formed during the regeneration, is the nitrate form of the resin, which is less soluble in heptane than the free amine.

Shake the contents of the funnel with two separate 100-ml portions of 4 M sodium hydroxide solution. After discarding the aqueous layer, shake the heptane layer with two separate 100-ml portions of 4 M hydrochloric acid, separating the aqueous layer each time. Finally, extract with two separate 100-ml portions of 2 M hydrochloric acid. After allowing the layers to separate, transfer the resin - heptane layer to an amber bottle.

PREPARATION OF LEAD STANDARD SOLUTIONS—

Weigh 10 ± 0·01 g of a sample of calcium carbonate known to have a lead content of less than 1 p.p.m. into each of three 250-ml beakers and add 60 ml of 5 M hydrochloric acid. Boil the mixture to expel carbon dioxide and transfer each of the solutions to a 200-ml calibrated flask. Add 5·0, 10·0 and 20·0 ml of 10 μg ml^{-1} lead solution to successive flasks, diluting to the mark with water. These solutions provide calibrating standards representing 5, 10 and 20 p.p.m. of lead in the original calcium carbonate.

PREPARATION OF SAMPLES—

Calcium carbonate—Dissolve 5 ± 0·01 g of sample in 30 ml of 5 M hydrochloric acid, diluted from AnalaR acid, boil to expel carbon dioxide from the solution, and dilute to 100 ml with water.

Calcium oxide—Add water cautiously to 2·8 ± 0·01 g of lime until it is completely slaked, then add 30 ml of 5 M hydrochloric acid, warm the solution to dissolve the solids and dilute to 100 ml. When testing for lead in calcium oxide it is normal practice to express the result in parts per million of lead per mole of calcium carbonate. If this practice is adopted, no adjustment of the composition of the standard solutions is required.

Limestone—Dissolve 5 ± 0·1 g of limestone in 5 M hydrochloric acid, boil the solution to expel carbon dioxide and filter it to remove any extraneous matter. Dilute the solution to 100 ml.

DISCUSSION OF THE AUTOMATED METHOD

RESIN EXTRACTION STEP—

A Technicon double mixing coil was used for the extraction of lead into the resin. A resin concentration of 15 per cent. *V/V* in heptane was found to give satisfactory extraction efficiencies. An A6 connector was used to increase the extraction efficiency by injecting the resin into the sample stream in small droplets.

BACK-EXTRACTION STEP—

The extraction of lead from resin solutions was investigated. Dilute nitric, perchloric and acetic acids, ammonia - ammonium acetate and ammonia - ammonium citrate solutions were found to be equally effective in extracting the lead. However, the use of acids caused interference, owing to salt formation in the subsequent buffering step. Ammonia - ammonium citrate solution was chosen because it also functions as a buffer for the dithizone extraction stage. Hydroxylammonium chloride added to the buffer reduces iron(III) to the iron(II) state; iron(III) interferes by oxidising the dithizone. Potassium cyanide is added to prevent interference by iron, copper, zinc and cadmium.[7]

DITHIZONE EXTRACTION STEP—

The buffer stream is extracted with a solution of dithizone in chloroform. The buffer is passed into a double mixing coil through an A6 connector to provide good mixing of the two phases. The coil is shaded from direct sunlight to prevent decomposition of the dithizone.

INTERFERENCES—

Of the following metals, known to be extracted by long-chain amines from dilute chloride solution: cadmium, lead, zinc, bismuth and, to a lesser extent, iron and copper,[5,8] only bismuth interferes in the dithizone determination of lead. The interference of bismuth is minimised if the pH of the buffer solution is controlled between 8·7 and 9·0.[2]

PHASE SEPARATION—

After the resin extraction stage, a Technicon B4 separator is used. The separated resin is passed through an A6 connector into the back-extraction coil.

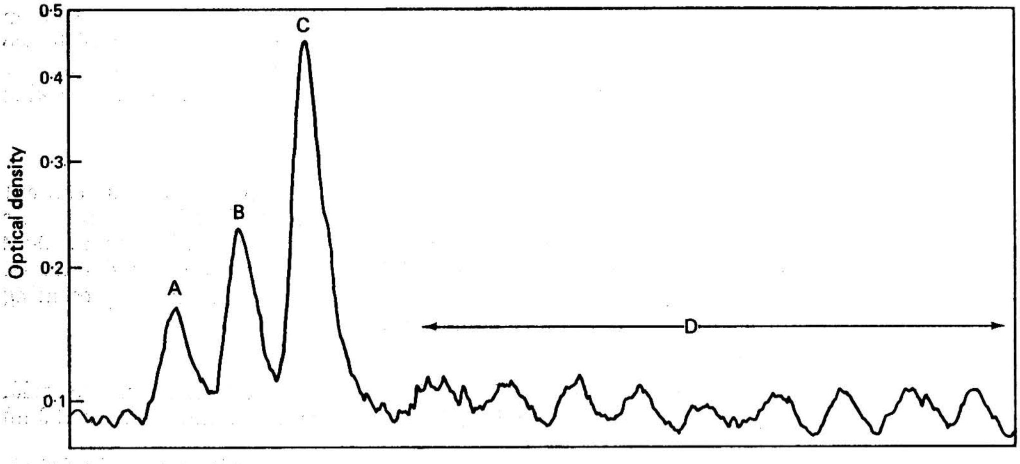

Fig. 2. Typical recorder trace: A, 5 p.p.m. standard; B, 10 p.p.m. standard; C, 20 p.p.m. standard; and D, samples

The chloroform phase is separated in a B0 separator placed on top of the Technicon Type N colorimeter module, with a 15-mm flow cell. Acidflex tubing is used for the connections. The phase separator - flow cell assembly is flushed through, just prior to use, with about 5 ml of methylated spirit delivered from a syringe, in order to remove traces of water that would cause a noisy recorder trace. In order to prevent water from entering the flow cell when starting a run, its outlet is clamped off from the flow cell waste displacement bottle until a steady bubble pattern has been established.

REGENERATION OF RESIN—

It was found that the resin solution could be regenerated and re-used repeatedly with only a very gradual decrease in activity. The height of the standard peaks can be taken as a measure of resin activity.

The use of double mixing coils, instead of glass-beaded extraction coils, reduced the noise level; a high noise level can cause difficulties when a large number of solvent-extraction steps are used. The use of double mixing coils in place of glass-beaded extraction coils did not significantly decrease the extraction efficiency, provided that the sample stream was injected as small droplets through an A6 connector. A typical recorder trace is shown in Fig. 2.

PRECISION—

To evaluate the precision of the method, the lead content of three solutions was determined eleven times, and the standard deviation (σ) and coefficient of variation were calculated. The results obtained are shown in Table II.

TABLE II

DETERMINATION OF THE LEAD CONTENT OF THREE SOLUTIONS

Solution	Mean lead content, p.p.m.	Standard deviation, σ	Coefficient of variation, per cent.
A	5	0·49	9·8
B	10	0·55	5·5
C	20	0·90	4·5

A comparison of results obtained with the cathode-ray polarograph and the AutoAnalyzer is shown in Table III. The polarographic method is that of Richardson.[6]

TABLE III

COMPARISON OF RESULTS OBTAINED BY THE AUTOANALYZER AND POLAROGRAPHIC METHODS

	Lead, p.p.m.	
	AutoAnalyzer method	Polarographic method
Limestone	11	14
	10	12·2
	19	21
Calcium carbonate	5	7·7
	2	2·0
	2	2·0
	2	2·0
	2	2·0
	2	2·0

The authors thank the Board of Directors of John & E. Sturge Limited for permission to publish this paper.

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A Rapid Method for the Extraction and Determination of Iron(II) in Silicate Rocks and Minerals

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A rapid method for the efficient extraction of iron(II) from rocks and minerals is described. With this method oxidation is minimised and batch working is possible. The silicate is decomposed in sealed plastics bottles and the iron(II) determined titrimetrically by redox titration or, for small amounts of minerals, colorimetrically by means of 2,2′-bipyridyl.

RESULTS obtained by various laboratories for determinations of iron(II) oxide on various standards show a relative spread of greater than 10 per cent. As these results were in general obtained by similar procedures based on redox titration, a series of experiments were carried out to establish the main causes of error. In addition, the possibility of speeding up the techniques was studied. The principal errors in the usual procedures are considered to be failure to extract all of the iron from the sample and oxidation during the extraction process, although reduction may occur if organic compounds or sulphides are present. Tests showed that there is little to choose between the various titrants and indicators that are commonly used. We used 0·05 N cerium(IV) sulphate (prepared by precipitation of the hydroxide from cerium(IV) ammonium nitrate and dissolution of the hydroxide in sulphuric acid) as the titrant and *N*-phenylanthranilic acid (*o*-phenylaminobenzoic acid) as the indicator. Further trials, analogous to those made by Neuerburg and reported by Peck,[1] confirmed that the use of de-gassed boric acid solution was not necessary as virtually identical results were obtained in experiments with saturated boric acid solution prepared by different procedures. The addition of phosphoric acid to the boric acid medium was also found to produce no measurable difference in titration values.

EXPERIMENTAL

An attempt was made to determine the rate of extraction of iron(II) and to establish the conditions required for minimum oxidation to occur. The trials were based on 0·250-g portions of Queen Mary College standard dolerite I_3, for which E. Engleman (United States Geological Survey, personal communication) obtained a value of 10·04 per cent. of iron(II) oxide. This result was later found to be one of the highest values so far reported from a number of laboratories. In preliminary tests, the iron was extracted from the sample in covered platinum crucibles, maintained at 100 °C, with 5 ml of 50 per cent. *V*/*V* sulphuric acid and 5 ml of 40 per cent. hydrofluoric acid as the solvent. The amount of iron extracted under these conditions was found to be proportional to the logarithm of the time required. When the maximum concentration of iron(II) in the solution had been reached, further heating slowly produced oxidation (Curve E, Fig. 1). These experiments gave a value of 9·85 per cent. of iron(II) oxide for sample I_3. Samples of this rock that had been boiled rapidly in the same solvent gave a value of 9·80 per cent. of iron(II) oxide. The iron was completely extracted from the samples after boiling them for 5 to 10 minutes or after maintaining them at 100 °C for 10 to 25 minutes, the period of time required depending mainly on the amount of iron present. The tests made at 100 °C indicated that the rate of extraction was slow during the initial stages of warming the mixture. Pre-mixing the acids increased the initial rate of extraction and increased the percentage of iron(II) found. The use of 40 per cent. *m*/*V* hydrofluoric acid pre-mixed with sulphuric acid (sp. gr. 1·84) produced the maximum rate of extraction and the amount of iron(II) found for I_3 became 10·09 per cent. (see also Peck[1]).

Tests were then made to investigate the improvement that was possible if the samples were sealed in an inert atmosphere during extraction. Polythene, polycarbonate and polypropylene vessels of various sizes were tried with various mixtures of sulphuric acid and hydrofluoric acid as solvents and air, steam and carbon dioxide atmospheres. The most satisfactory vessels were found to be strong 60-ml wide-mouthed polypropylene bottles with screw-caps, but 25-ml polycarbonate screw-capped capsules were found to be useful in the analysis of small amounts of minerals. These capsules have the advantage that they can be heated in a small domestic pressure-cooker and hence at temperatures above 100 °C. Poor reproducibility was found when carbon dioxide or nitrogen was used as the atmosphere, and with air and a cold mixture of acids low results were obtained. However, the addition of a hot mixture of acids (equal volumes of concentrated sulphuric acid and 40 per cent. *m*/*V* hydrofluoric acid) to the sample produced a violent reaction and copious vapour, and this vapour was found to provide the most effective atmosphere. The iron from sample I_3 was completely extracted in less than 10 minutes with this reagent and no oxidation was detected after heating mixtures on a water-bath for 90 minutes. The bottles can be used repeatedly without distortion. Gases leak from them only extremely slowly and the rapid dissociation of the silicates at this relatively low temperature is presumably due to the increased vapour pressure within them. As the samples can be heated by this means for more than 1 hour without oxidation, the method is suitable for batch working. About twelve samples can be analysed in 1 hour, the number being limited by the period of time required for weighing and titrating.

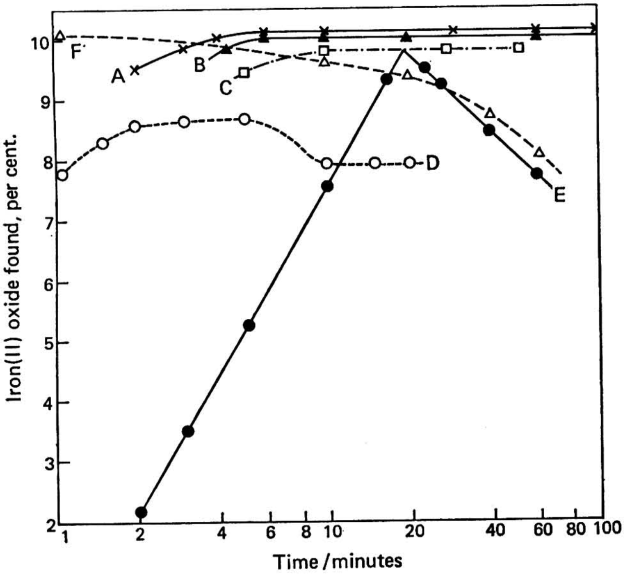

Fig. 1. Extraction of iron(II) from rocks under differing conditions. All results apply to the rock sample I_3. The conditions were as follows: A, pre-mixed hot concentrated sulphuric acid and hydrofluoric acid; B, nitrogen and hot pre-mixed concentrated sulphuric acid and hydrofluoric acid; C, nitrogen and cold 50 per cent. *V*/*V* sulphuric acid and hydrofluoric acid; D, cold 50 per cent. *V*/*V* sulphuric acid and hydrofluoric acid; E, cold 50 per cent. *V*/*V* sulphuric acid and hydrofluoric acid added, then maintained at 100 °C in platinum crucibles; and F, reagents as for A but applied after grinding dry for various periods of time

PREPARATION OF ROCK SAMPLES—

There is little doubt that one of the largest sources of error in the determination of iron(II) oxide is the preparation of the sample before extraction. The rock used in the above tests was analysed to determine iron(II) oxide after additional grinding with an agate pestle and mortar for periods of up to 100 minutes. After grinding for 20 minutes, the observed amount of iron(II) oxide had decreased by more than 0·5 per cent. and this rate of oxidation was maintained throughout the grinding period (Curve F, Fig. 1). Grinding the powder in the same apparatus for 10 minutes but with continuous moistening with acetone produced a sufficiently fine grain size and no detectable oxidation.

RESULTS

The extraction procedure was applied to four separate samples of I_3 by two analysts on different occasions. The mean of forty-two determinations was 10·10 per cent. of iron(II) oxide and the standard deviation (without culling) was 0·02 per cent. The means found for each sample bottle were within one standard deviation of the mean of all results. The technique was applied to several other standards and the results in Table I show that the results obtained by the suggested procedure are generally higher than the published mean values. The procedure was checked independently by Mr. C. G. Elliott of the British Museum (Natural History) and some of the results that he obtained are given in Table I. As the suggested extraction procedure can be extended to periods of more than 1 hour, the possibility of applying the method to the analysis of resistant silicate minerals was investigated. A garnet that had been digested for up to 90 minutes showed maximum extraction after about 30 minutes. The iron(II) oxide content found was 34·5 per cent. compared with a total iron content of 36·4 per cent. expressed as iron(II). Staurolite was, however, only slightly attacked. It was found that the amount of garnet taken had to be reduced to about 50 mg for the best results to be obtained and further tests were carried out to establish the optimum amount of sample required for normal rocks. When the amount of sample taken for I_3 was increased, the consistency of the results was satisfactory for up to 300 mg of sample but the use of larger amounts led to a slight but systematic reduction in the percentage of iron(II) oxide found, which decreased to 9·86 per cent. when the amount of sample used was 500 mg. For the analysis of rocks that contain about 1 per cent. of iron(II) oxide, a suitable amount of sample seems to be about 500 to 600 mg.

TABLE I

COMPARISON OF RESULTS OBTAINED BY THE SUGGESTED PROCEDURE WITH PREVIOUS RESULTS

Rock	Previous mean	This method A	This method B	U.S. Geological Survey
I_3	9·62[b]	10·10 (42)[a]	10·12 (5)	10·04[a]
I_1	0·15[b]	0·22 (6)	—	0·22[a]
M_2	6·02[b]	6·28 (3)	—	6·41[a]
M_3	3·13[b]	3·44 (5)	—	3·38[a]
W1	8·72[c]	8·83 (3)	8·82 (2)	—
BR	6·56[d]	6·66 (3)	—	6·68[e]
BCRI	8·91[f]	8·96 (3)	8·96 (2)	—
DTSI	6·79[f]	7·06 (2)	7·04 (2)	—
PCCI	4·94[f]	4·86 (3)	4·51 (2)	—

Rock standards I_3, I_1, M_2 and M_3 can be obtained from Dr. A. B. Poole, Geology Department, Queen Mary College, Mile End Road, London, E.1.

A, Results obtained by the authors by the method described in this paper; and B, results obtained by C. G. Elliott of the British Museum (Natural History) by the same method. Elliott found sample I_3 to contain 10·00 per cent. of iron(II) oxide by the procedures that are usually used at the British Museum. For columns A and B the numbers in brackets are the numbers of determinations carried out.

[a] Results obtained by Engleman, U.S. Geological Survey.
[b] Mean of results submitted by several laboratories.
[c] Recommended value.[2]
[d] Recommended value.[3]
[e] Cited by Roubault, de la Roche and Govindaraju.[3]
[f] Recommended value.[4]

RECOMMENDED PROCEDURE

Weigh accurately about 0·250 g of each sample powder (100 mesh) into 60-ml polypropylene bottles. Mix equal volumes of 40 per cent. *m/V* hydrofluoric acid and concentrated sulphuric acid in a polypropylene beaker and, after allowing a few seconds for the temperature of the acid mixture to increase, add 10 ml of the hot mixture to each sample with a polypropylene measuring cylinder. A violent reaction between the acids and silicate produces copious vapour and the vessel should be tightly sealed when this vapour appears in the neck of the bottle. Float the bottles, upright or slightly tilted, in boiling water; the bottle should be immersed only to a depth of about 15 mm. After 10 minutes (longer if resistant minerals are present), remove one vessel from the water-bath. Cool it quickly, fill it with saturated boric acid solution and decant the solution into a 400-ml titration vessel. Wash the bottle with saturated boric acid solution so as to bring the total volume to 200 ml. Titrate the solution with standardised 0·05 N cerium(IV) sulphate solution from a 10-ml burette with *N*-phenylanthranilic acid as the indicator until one drop produces a faint pink colour that persists for 30 s. Repeat the procedure from "After 10 minutes . . ." for the remaining samples.

The scale of the extraction procedure can be reduced by using 25-ml vessels and reducing the volume of the mixed acids to 2 ml. The amount of sample taken should be adjusted so that it contains not more than about 500 μg of iron(II) oxide. After heating the sample for a few minutes, add 10 ml of 50 per cent. *m*/*V* aqueous beryllium sulphate solution. Transfer the mixture into a 100-ml calibrated flask containing 25 ml of 50 per cent. *m*/*V* aqueous ammonium acetate solution, 5 ml of a 0·1 per cent. *m*/*V* aqueous solution of 2,2′-bipyridyl and a few drops of 0·2 M hydrochloric acid. Standardise by treating a known mineral as above.

The authors are grateful to Dr. A. B. Poole for information on standard rocks I_3, I_1, M_2 and M_3, and to Mr. C. G. Elliott for subjecting the method to a thorough independent test.

CAUTION—

When hydrofluoric acid and concentrated sulphuric acid are mixed hydrogen fluoride vapour is produced, and the process must therefore be carried out with care in a suitable fume cupboard and protective clothing should be worn. In addition, the use of beryllium sulphate to complex excess of fluoride is hazardous and at no stage in the above procedures should pipettes be used orally. Care should be taken in the disposal of the finished solutions.

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Determination of Silica in Silicate Materials by an X-ray Fluorescence (Standardised Inert Dilution) Method

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An X-ray fluorescence standardised inert dilution method has been developed for the determination of silica in quartz-sand, glass and cement-clinker samples.

By using the fused sample technique, the method can be applied satisfactorily (standard deviation 0·7 per cent.) to the rapid routine determination of silica.

The results for determinations of silica in quartz sand are compared with those obtained by four different chemical methods.

VARIOUS chemical methods for the determination of silica, such as those by Hillebrand; Longuet and Burglen; Brabson; Armand and Berthoux; Wilson; and Sajo, are known.[1,2] However, there is no rapid and accurate method that could be used for the routine determination of silica in both the glass and the cement industries. Apart from the above chemical methods, the traditional X-ray fluorescence methods can be used.[3–9] The usual X-ray fluorescence method requires the construction of calibration graphs for each material, which is time consuming, and the results may have considerable errors,[9–11] especially when there are large matrix variations in the samples.

In this paper, results are reported for the determination of silica obtained by using a fairly new and versatile X-ray fluorescence method[12] and are compared with those obtained by four well known[13–16] chemical methods.

GRAVIMETRIC AND TITRIMETRIC CHEMICAL METHODS

REAGENTS—

All chemicals were of analytical-reagent grade.

Ammonium molybdate solution, 10 *per cent.* m/m.

Quinoline solutions, 2 *and* 0·05 *per cent.* m/m.

Thymol blue indicator solution.

Cresol red - thymol blue indicator solution.

The above four solutions were prepared as described by Wilson.[16]

Gelatin solution, 3 *per cent.* m/m.[17]

PROCEDURES—

The following four methods for the determination of silica were compared by using quartz-sand samples: the classical gravimetric method, involving double dehydration with hydrochloric acid[18]; precipitation of silica with a 3 per cent. *m/m* gelatin - hydrochloric acid solution (Longuet and Burglen method) as described by Voinovitch[17]; gravimetric determination as quinoline molybdosilicate (Armand and Berthoux method) as described by Wilson and Wilson[19]; and the titrimetric determination of quinoline molybdosilicate precipitate as described by Wilson.[16]

Modifications—In order to obtain reproducible results, the following modifications were made to the gravimetric determination of the molybdosilicate complex precipitated with quinoline.[19] Firstly, before the complex was formed, a more precise pH adjustment was made by using dilute hydrochloric acid (1 + 1 *V/V*) instead of the concentrated acid (this was also carried out by the Wilson technique), and secondly, a blank was run simultaneously with the sample.

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STANDARDISED INERT DILUTION METHOD

MATERIALS—

All chemicals were of analytical-reagent grade. Samples of quartz sand, cement clinker and soda-lime - magnesia silica glass (No. 0 and No. 2) were used. The compositions of the relevant matrices, in per cent. *m/m*, were as follows—

Cement clinker—CaO, 65·4; MgO, 3·7; Fe_2O_3, 2·6; Al_2O_3, 7·6; and Mn_2O_3, 0·02.
Glass No. 0—CaO, 8; MgO, 3; Fe_2O_3, 0·25; Al_2O_3, 1·50; B_2O_3, 0·70; and $Na_2O + SO_3$, 15.
Glass No. 2—CaO, 7·6; MgO, 3·5; Fe_2O_3, 0·15; Al_2O_3, 2·40; B_2O_3, 0·90; and Na_2O, 14·5.

INSTRUMENTAL CONDITIONS—

A Philips PW 1540/00 vacuum spectrograph was used with a gypsum analysing crystal and a wide-aperture collimator. A tungsten X-ray tube was operated at 40 kV and 20 mA. A flow-proportional counter with a pulse-height analyser was used with a constant channel width of 32 V. The pulse height was slightly variable with time (29 to 32 V) and was checked every 20 minutes. The background angles (55·30° and 56·60°) were chosen after slow X-ray scanning over a small range in the vicinity of the silicon Kα line. An alumina pellet containing 5 per cent. *m/m* of iron(III) oxide was used in order to search for possible interference of the iron Kβ line (fourth order). The silicon pellet (Philips PW 1049) normally used for calibration of the diffractometer was used as the external reference standard in all measurements.

SAMPLE PREPARATION—

Both powdered and fused samples were prepared from each material.

Powdered samples—For the diluted samples, 37·5 per cent. *m/m* of alumina was used as diluent, so as to obtain a good intensity reduction. Starch (25 per cent. *m/m*) was used as plasticiser and binder for both diluted and concentrated samples. Alumina, starch and the sample material were ground separately in an agate mill, sieved (325 mesh) and dehydrated in a drying oven at 110 °C. The dehydrated alumina (for diluted samples), starch and the sample material were quickly weighed and then mixed in an agate mill for 20 minutes. The mixture was placed inside a steel ring, the diameter of which fitted the sample holder, and compressed at 1 kg cm^{-2} with a hydraulic press for 1 minute. The surface of the steel compression cylinder was highly polished so as to avoid the production of any surface imperfections on the pellet. The smoothness of the surface of the pellets was checked under a microscope.

Fused samples—Dehydrated borax was used as a flux and as a diluent for the samples. The following additions of borax were made: 66·67 per cent. *m/m* for concentrated quartz samples, 80 per cent. *m/m* for dilute quartz samples and 66·67 per cent. *m/m* for dilute glass samples and for dilute cement-clinker samples. The original glasses No. 0 and No. 2 were cut so as to fit inside the sample holder, polished as described below and used as concentrated samples. The preparation of the discs of concentrated cement clinker was not feasible because of the high melting-point of this material, and a pellet of pure cement clinker was used as the concentrated sample. The preparation of lower melting-point mixtures to be used as concentrated samples was abandoned because of the large counting error involved with the further diluted sample.

The ground sample and the dehydrated borax were weighed in the indicated proportions and fused together, following the procedure described by Vera,[12] and circular discs weighing about 12 g were obtained. The discs were then ground with 50, 100, 180 and 220-grit abrasive paper, following a wet polish with 240, 320, 400 and 600-grit abrasive paper (No. 30–5160) and a careful wash with distilled water. Finally, they were polished with metallographic alumina powder No. 2, on a rotatory polisher, and washed. No appreciable contamination by alumina was observed under the microscope. However, it would be safer to use diamond paste so as to prevent contamination in the final polishing stage. Some substantial reduction of the preparation time may be made possible by omitting some of the intermediate grinding and polishing stages.

COUNTING—

Three concentrated and three diluted pellets made from quartz sand, cement clinker and glass were counted. Also, a number of pellets made from quartz (washed and calcined, reagent grade) were counted in order to obtain the value for the characteristic constant for powdered samples.

Three concentrated and three diluted discs from each material, except the concentrated cement-clinker samples, were counted.

Seven measurements of the silicon Kα radiation were made from each pellet or disc, and corrected for background. The average of twenty-one measurements was then considered for each type of sample.

The number of counts chosen in each instance is shown in Table I.

TABLE I

NUMBER OF COUNTS (N_{peak}) CHOSEN FOR EACH TYPE OF SAMPLE IN THE SILICON Kα LINE

The $N_{\text{background}}$ value was 8000, and N_{peak} for the silicon standard was 256000

	N_{peak}		
		Fused samples	
Material	Powdered samples	Dilute	Concentrated
Quartz sand	128000	32000	16000
Quartz	128000	—	—
Glass No. 0..	128000	128000	32000
Glass No. 2..	128000	128000	32000
Cement clinker	32000	—	16000

OUTLINE OF THE STANDARDISED INERT DILUTION METHOD—

Only two measurements are needed for each sample, that is, one for the concentrated sample and one for the sample diluted with a known percentage of an appropriate inert diluent. An external reference standard is used so as to minimise instrumental variations

A characteristic constant for each element, standard and diluent must be determined. The results should be independent of the matrix.

The fundamental equation for standardised inert dilution—

$$W_j = C_j \times D(X) \times R(I) \quad \ldots \quad (1)$$

gives the sample concentration W_j of the element j, in terms of a constant C_j, and the dilution factor $D(X)$ and the intensity ratio $R(I)$, which are defined as

$$R(I) = \frac{r \times r'}{r - r'} = \frac{I \times I'}{I_s(I - I')} \quad \ldots \quad (2)$$

$$r = \frac{I}{I_s} \quad \ldots \quad (3)$$

$$r' = \frac{I'}{I_s} \quad \ldots \quad (4)$$

$$D(X) = \frac{1 - X}{X} \quad \ldots \quad (5)$$

where I and I' are the X-ray intensities of the silicon Kα line, corrected for background, from the concentrated and diluted samples, respectively; I_s is the corresponding intensity for the reference standard (background corrections are not needed for the reference standard, as they are taken into account in the constant C_j); and X is the mass fraction of the concentrate in the diluted sample.[12]

Calculations—For powdered samples, the constant C_j was calculated from equation (1) by measuring the intensities of three diluted and three concentrated pellets prepared from pure quartz (99·36 per cent. *m*/*m* in silica, after the Hillebrand method). The average values of r and r' were 0·4111 and 0·1388, respectively. The value of $D(X)$ was chosen as 1. A value of 47·41 per cent. was obtained for the constant C_j.

Intensity averages were used for calculating the concentrations of the samples.

For fused samples, the constant C_j was calculated by applying the least-squares method to ten measurements on quartz sand and glass. The value of $D(X)$ was chosen as 2. A value of 308·6 per cent. was obtained for C_j.

A rough estimation of the theoretical errors in the standardised inert dilution method gave optimum results for intensity reductions of about 50 per cent. in the diluted sample. Too high dilutions increase the relative errors in the intensity I' (numerator), while too low dilutions produce high relative errors in the difference $I - I'$ (denominator). This criterion was used in the choice of $D(X)$. A more detailed study on errors will be described in future publications.

RESULTS AND DISCUSSION

CHEMICAL METHODS—

The Armand and Berthoux and Wilson techniques, as described by Wilson and Wilson,[19] were modified by us in such a way that all the silica reacts with molybdate to form β-molybdosilicic acid at pH 1·5. The unmodified technique[19] gave results with an error of 3 to 4 per cent., probably because of incomplete reaction between silica and molybdate.[20] The large deviations in the results obtained by Voinovitch[17] with the Armand and Berthoux method (−5·12 to +5·65 per cent.) and with the Wilson method (−6 to +3·15 per cent.) are probably caused by the low pH of the solution during the formation of the β-molybdosilicate complex.

Table II shows the results obtained with the four chemical methods. It is clear that so far as precision, accuracy and the analyst's time are concerned, the modified quinoline-precipitation method is the most suitable. Moreover, it can be applied satisfactorily to the analysis of cement clinker[2] and glass.[21]

TABLE II

DETERMINATION OF SILICA IN QUARTZ SAND BY DIFFERENT CHEMICAL METHODS

		Silica			Time required/ hours	
Technique	Number of experiments	Mean, per cent.	Standard deviation, per cent.	Mean error, per cent.	Total	By analyst*
Classical gravimetric	5	99·27	0·11	0·00†	15·0	6·0
Longuet and Burglen	5	99·35	0·14	0·08	7·5	4·5
Quinoline precipitation (with modifications)‡	21	99·27	0·20	0·00	4·5	2·5
Wilson (with modifications)	11	99·03	0·17	0·24	3·5	3·5

* The analyst's time is the difference between the total time required for one determination and the evaporation *plus* drying times.

† By definition.

‡ A blank was run simultaneously with the sample.

It is well known[22] that the presence of 5 per cent. or more of iron(III) oxide introduces errors into the quinoline-precipitation method. Therefore, in applying this method, we decided to evaluate the above error by determining the silica contents in five quartz samples that were prepared to contain 5 per cent. of iron(III) oxide. The results were found to be affected by a mean error and a standard deviation of −0·72 per cent. and 0·18 per cent., respectively.

X-RAY FLUORESCENCE METHODS—

Results for the determination of silica by means of X-ray fluorescence methods for both powdered and fused samples are summarised in Table III. The values in columns B, C and E were obtained by applying the direct relationship

$$W = W_{\mathrm{q}} \times \frac{r}{r_{\mathrm{q}}}$$

where W and r are the silica concentration and measured intensity ratio, respectively, of the sample, and W_{q} and r_{q} are those of pure quartz samples.

Powdered samples—The results in columns B, C and D in Table III show that values closer to the true value occur as one proceeds from B to D. Better results were obtained with dilute samples (column C) than with concentrated samples (column B): this fact could be explained by the occurrence of a smaller matrix effect in the dilute samples. Moreover, the further improvement that was obtained when standardised inert dilution calculations were applied (column D) may well be attributed to the use of the constant C_j, which helps to eliminate the matrix effect.

The results obtained for cement-clinker samples are subject to larger errors than those for glass samples, irrespective of the method used. These errors are probably due to the large particle-size effect that arises from the highly variable absorption coefficient of calcium and iron-rich matrices.

TABLE III

COMPARISON OF SILICA DETERMINATIONS BY CLASSICAL CHEMICAL AND X-RAY FLUORESCENCE METHODS

All results are given in per cent.

Material	Classical chemical method (true value)	Powdered samples			Fused samples		
		By direct proportion		Standardised inert dilution method*	Direct proportion with dilute sample	Standardised inert dilution method†	
		Concentrated sample	Dilute sample			Mean	Mean error
	A	B	C	D	E	F	G
Quartz sand ..	99·27	98·27	98·85	99·15	—	99·78	+0·51
Glass No. 0 ..	71·60	52·40	56·94	59·61	66·22	71·15	−0·45
Glass No. 2 ..	71·20	50·28	53·40	55·16	65·63	71·01	−0·19
Cement clinker..	20·91	13·59	13·71	13·77	20·11	21·69(‡)	+0·78

* The total time required for the determination of silica in each material was 1·0 hour.

† The time required for the preparation of the discs is 50 minutes and for counting, 40 minutes.

‡ The concentrated sample was a pellet (see sample preparation).

Fused samples—The poor analytical results obtained for the determination of silica in powdered samples are caused by both particle-size and matrix effects. Therefore, if the particle-size effect is eliminated by fusing the samples, an improvement in the results would be expected. This improvement is shown in column E and is particularly noticeable for cement-clinker samples. Nevertheless, acceptable results are not obtained until the matrix effect is also eliminated by applying the standardised inert dilution method to fused samples (column F).

Iron does not interfere in the determination of silica by means of the standardised inert dilution fused-sample method when pulse-height discrimination and adequate background angles are used.

The time required for the standardised inert dilution method in fused samples (1½ hours) is shorter than that for any of the chemical methods studied. Another important advantage of the former method is that the same disc can be used to determine other elements under consideration.

In general, the accuracy (column G) and the precision achieved (standard deviation 0·70 per cent.; $n = 10$) with the standardised inert dilution fused-sample method are fairly acceptable for the rapid routine analysis of materials with a silica content of 20 to 99 per cent., such as cement clinker, glass and quartz sand.

The authors acknowledge the help of Prof. L. Balabanoff with problems associated with the chemical techniques and Dr. S. Patel for helpful criticism of the text.

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Book Reviews

PRINCIPLES OF ACTIVATION ANALYSIS. By PAUL KRUGER. Pp. xii + 522. New York, London, Sydney and Toronto: Wiley-Interscience. 1971. Price £11·75.

The contents of this book fall into three parts. The initial chapters give a general account of radiochemistry along traditional lines: nuclear structure, radioactive decay, radioactivation theory, interaction of radiation with matter, detectors, statistics, etc. The second part is devoted to a comprehensive account of activation analysis, including radiochemical and instrumental activation analysis, non-neutron methods, gamma-spectrometry and the applications of computers. A very full account is given of the limitations of activation analysis in a chapter that includes an account of methods, *e.g.*, variable-energy activation analysis, that are aimed to overcome these limitations.

The last part of the book consists of a chapter on applications, which includes a salutary comparison of the method with other techniques of trace analysis and a discussion on how to decide whether activation analysis is *the* method for a specific purpose. The applications discussed include those to cosmology, geochemistry and the life sciences and industrial uses such as the determination of oxygen in metals, well-logging and the uses of stable isotopes as tracers with subsequent determination by activation analysis.

The literature covered is mainly pre-1965, although reference to more recent papers is given in the applications chapter, including mention of recent work on moon rocks. The references are given as footnotes, which tends to limit their number, but each chapter is followed by a very complete bibliography. A number of practical problems are given at the end of each chapter.

The sections of the book dealing with chemical separations are probably the least satisfactory. Thus there is no mention of complexing agents in cation exchange, anion-exchange separation of metals or reversed-phase chromatography. Automatic separation is restricted to two papers, given in some detail, from the 1965 Modern Trends in Activation Analysis Symposium.

There are some typographical errors, although few would mislead the reader. The reference to Zenon with its symbol Zn (page 189) is curious. In some instances there are errors of omission. A formula for the number of plates in an ion-exchange column omits the definition of one of the symbols although this is required to be calculated in a question at the end of the chapter. In a table (page 208) giving the position of subsidiary peaks in a pulse-height spectrum, α (*i.e.*, $h\nu/m_0c^2$) is not defined. The line width of a peak in a germanium detector spectrum is calculated without mention of the Fano factor.

The style of writing is very clear and the book is well produced. It is long, and this is reflected in the price. Many tables are reproduced from the literature and some of these could have been omitted or curtailed, *e.g.*, there are several pages of tables of results of analyses of rocks, trace elements in water, etc., that go beyond "principles."

D. I. COOMBER

MASS SPECTROMETRY: TECHNIQUES AND APPLICATIONS. Edited by GEORGE W. A. MILNE. Pp. xii + 521. New York, London, Sydney and Toronto: Wiley-Interscience. 1971. Price £11·75.

Dr. Milne has edited a substantial book on mass spectrometry that comprises a series of specialist articles written by authors drawn from the younger mass spectroscopists, as the editor himself points out. The work includes the following chapters: Automatic Acquisition and Processing of Mass Spectral Data; Photographic Techniques in Organic High-resolution Mass Spectrometry; The Electrical Recording of Magnetically scanned High-resolution Mass Spectra; Computer-assisted Interpretation of Mass Spectra; Gas Chromatography - Mass Spectrometry; An Application of Artificial Intelligence to the Interpretation of Mass Spectra; Newer Ionisation Techniques; Mass Spectral Studies Employing Stable Isotopes in Chemistry and Biochemistry; Mass Spectrometry in Peptide Chemistry; The Application of Mass Spectrometry to Problems in Medicine and Biochemistry; Mechanism Studies of Fragmentation Pathways; and Some Aspects of Metastable Transitions. Each chapter is accompanied by an often extensive bibliography and in addition there are two extensive indexes at the end of the volume.

With such wide coverage as that given here, it is rather difficult to criticise the book in detail, but the reviewer, whose interests are rather different, does regret the absence of any discussion of organometallic compounds as well as the virtual neglect of the quasi-equilibrium theory, of which there is but the merest mention. In contrast, there are separate chapters in this book that cover much the same ground and could possibly have been merged. Possibly, although the title does not disclose the fact, the whole work is directed more towards medical and biochemical interests than being intended as a comprehensive review of the state of the art.

This book is fairly free from mistakes, misprints and technical jargon, an increasing hazard in modern works, and the editor is to be congratulated upon this. There is, however, some confusion of ideas, as for instance, with the units used in magnetically scanned instruments.

The book is well produced with clear diagrams and a legible text, as one has come to expect from the known high standards of the publishers.

The careful reader will find within much that is stimulating and instructive. R. I. REED

ANALYTICAL SEPARATIONS AND DETERMINATIONS: A TEXTBOOK IN QUANTITATIVE ANALYSIS. By C. T. KENNER. Pp. xx + 395. New York: The Macmillan Co.; London: Collier-Macmillan Ltd. 1972. Price £5 (hard-back); £2·75 (soft-back).

One is hesitant before reviewing an undergraduate-level text written for a specific market in an internationally circulated journal, as comments may not be relevant to many readers.

This particular text differs from most at this level in that it omits detail for individual experiments, these being the subject of a parallel volume. Despite the title, the contents are mainly classical: theory of weighing, stoicheiometry, theory of titrimetric and gravimetric analysis, colorimetry, chromatography and ion exchange. I have grave doubts on the value of describing the Duboscq colorimeter and spending ten pages in explaining equal-arm balances and weighing by swings in 1972.

Numerical problems are given for each area discussed and a valuable feature for students are the many examples that are worked out in full. In these days of rising book prices, there must be some cheaper way to ensure that students have logarithm tables than to print a set in each class text. In addition, is it necessary to spend eight pages explaining their use?

Having been critical of certain of the contents, one must point out that this book gives an excellent exposition for undergraduates of inorganic classical analytical chemistry, the basis of much experimental work, which it is hoped they will meet later in their courses. The book will therefore be useful to teachers in preparing courses and as a class text in a modular scheme that contains an appropriate module. D. THORBURN BURNS

COLORIMETRIC METHODS OF ANALYSIS, INCLUDING PHOTOMETRIC AND FLUOROMETRIC METHODS. By FOSTER DEE SNELL and CORNELIA T. SNELL. Volume IVAAA. Pp. xiv + 351. New York, Cincinnati, Toronto, London and Melbourne: Van Nostrand Reinhold Co. 1971. Price £11·25.

To state that this book follows the excellent and well known line already established in the series of volumes on colorimetric methods of analysis is but to state the anticipated. Nevertheless, the authors are to be congratulated yet again on publishing a further volume in this series. The present volume deals with enzymes, antibiotics and related compounds, haemoglobin and related compounds and natural pigments. The volume is the modern extension of Chapters 14, 15 and 16 in the fourth volume of the series and deals with the currently available methods such as spectrophotometry and spectrofluorimetry, which are widely used in the determination of the above substances.

The arrangement of the material is such that the worker can readily find information, both by using the extensive subject index and by reading the detailed "procedures" for the desired analyte. There is a wealth of reference to the original literature, but the authors ensure, by their diligent and detailed approach, that there will be few occasions when it is vital to consult the source; their work will in most instances give all that is necessary.

A comparison of this supplementary volume and the original volume reveals how extensive is the work that has been reported on these series of compounds—it also reveals the need for the publication of the supplement. L. S. BARK

CALCULATIONS IN ADVANCED CHEMISTRY. By P. J. F. GRIFFITHS and J. D. R. THOMAS. Second Edition. Pp. viii + 271. London: Edward Arnold. 1971. Price £1·75.

This edition represents an updating of a book which is already a success. The original aim was to provide an illustration by means of typical worked examples of the calculations encountered in the study of advanced physical chemistry. To all students it represented the means whereby they could study privately the problems that they were likely to meet in their examinations and their unqualified verdict must rest on the great number of copies of this book in the possession of students. The passage of time has meant that the recommendations of the Symbols Committee of the Royal Society must be taken into account with particular reference to the introduction of SI units. These amendments have been introduced and there seems no reason why this edition should not be as great a success as the first edition. The success of the book is to be found in no small measure in the number of worked examples. The printing is clear and the arrangement straightforward. The introduction of a chapter on statistical treatment of data is welcome, and perhaps it could be followed by a greater awareness of this kind of treatment in many of the B.Sc. courses in which it is often sadly neglected. D. DOLLIMORE

TRANSFER COEFFICIENTS IN ELECTROCHEMICAL KINETICS. By J. P. BRENET and K. TRAORE. Pp. xiv + 158. London and New York: Academic Press. 1971. Price £3·50; $10.50.

This is a useful but very specialised book intended primarily for research workers in the field of electrochemical kinetics. As such, it will be of little interest to most analytical chemists. The concept of the transfer coefficient is reviewed and developed in the light of current theories of electron transfer reactions at electrode surfaces. J. M. OTTAWAY

LA CHIMIE EN SOLVANTS NON-AQUEUX. By BERNARD TRÉMILLON. Pp. 240. Paris: Presses Universitaires de France. 1971. Price 18F.

This is a very useful book, dealing with the general chemistry of non-aqueous solvents. It deals with the problem in a very interesting manner, as it concerns itself not only with the type of solvent but also with the types of reaction that occur. In the first chapter solutes and solvents are discussed; this chapter gives good coverage not only of molecular solvents with which many of us deal, such as water, alcohols and hydrocarbons, but also of those eutectics which may be used as solvents. There is very good coverage of the use and application of molten salts, in which the solvent may be regarded as being ionised to a very large extent. Although there is but a passing mention of liquid metals, it is sufficient to bring to mind the fact that there are large commercial plants in which liquid metals are used as coolants and heat exchangers, and that the chemistry of many of these liquids is sometimes unexpected by those who instinctively think of aqueous solution chemistry.

The other four chapters deal with various aspects of chemistry such as acid - base reactions, redox chemistry, ion exchange and lastly the correlation of properties in different solvents.

This book is not aimed at the analytical chemist, but is designed more especially for the physical - inorganic chemist. Nevertheless, it is a most interesting book and the applications of its contents to problems in analytical chemistry are numerous.

The range of all chemistry will be much increased by an improved understanding of solvent systems other than water, and this book will undoubtedly help in this increase. L. S. BARK

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In the determination of pyrogallol with sodium metavanadate, a shallow S-shaped absorption curve was obtained from which two separate linear calibration graphs were established, one for the determination of the lower pyrogallol concentrations (equivalent to 0·1 to 0·3 mg of pyrogallol), the other for the higher concentrations (equivalent to 0·45 to 0·8 mg). The effect of the initial volume, time required, volume of water, metavanadate concentration and the stability of the pyrogallol have been studied. The method was also applied to some other polyhydroxyphenolic compounds for purposes of comparison. Also, the precision and the accuracy of the proposed method are compared with those obtained by the A.O.A.C. method.

A. M. ABDEL HAMID

Agricultural Research Corporation, Hudeiba Research Station, Biochemistry Section, P.O. Box No. 31, Ed-Dammer, Sudan.

Analyst, 1972, **97**, 787–793.

A Method for the Chemical Analysis of Chrome Ores and Chrome-bearing Refractories

This paper includes a detailed description of a method for the analysis of chrome ores and chrome-bearing materials; it is to be submitted to the British Standards Institution for acceptance as a standard method. The determinations include those of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Cr_2O_3, MnO, alkali-metal oxides and loss on ignition. The experimental work leading to the final method is described and tables of co-operative results obtained by the Refractories Working Group of the Analysis Committee of the British Ceramic Research Association are included.

H. BENNETT and R. A. REED

The British Ceramic Research Association, Queens Road, Penkhull, Stoke-on-Trent, ST4 7LQ.

Analyst, 1972, **97**, 794–819.

The Quantitative Separation of Chromium(VI) from Other Elements with a Strongly Basic Anion-exchange Resin

Previous work has shown that chromium(VI) on a strongly basic exchange resin in sulphuric acid solution cannot be quantitatively separated from other metal ions because of partial reduction of the chromium(VI) to chromium(III). The present investigations have demonstrated the complete retention of chromium(VI) by the resin in alkaline solutions, thus permitting the separation of chromium from many elements, which can be precipitated as hydroxides, and also from amphoteric elements, which can be eluted from the resin with alkaline solutions. Finally, chromium(VI) can be quantitatively removed from the resin with 8 to 10 per cent. sodium carbonate solution or, more satisfactorily, with an aqueous solution of a mixture of sodium hydrogen carbonate and sodium carbonate.

A. M. MULOKOZI

Department of Chemistry, University of Dar es Salaam, Dar es Salaam, Tanzania.

Analyst, 1972, **97**, 820–822.

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An Automated Method for the Determination of Lead in Calcareous Materials Utilising Liquid Ion Exchange

An automated method for the determination of lead in calcium carbonate, lime and limestone with the Technicon AutoAnalyzer is described. The method is based on the extraction of lead from an acidic chloride solution of the sample with a long-chain amine liquid ion exchanger, followed by re-extraction into an ammonia - ammonium citrate buffer at pH 9. Finally, the lead is extracted as the lead - dithizone complex into chloroform and the optical density of the complex measured at 510 nm. The separation of lead prior to formation of the lead - dithizone complex results in low background and blank readings. Lead levels of 0 to 20 p.p.m. can be determined at a rate of twenty samples per hour. Other trace metals which occur in calcareous materials do not interfere.

F. J. BANO and R. J. CROSSLAND

John & E. Sturge Limited, Lifford Chemical Works, Kings Norton, Birmingham, B30 3JW.

Analyst, 1972, **97**, 823–827.

A Rapid Method for the Extraction and Determination of Iron(II) in Silicate Rocks and Minerals

A rapid method for the efficient extraction of iron(II) from rocks and minerals is described. With this method oxidation is minimised and batch working is possible. The silicate is decomposed in sealed plastics bottles and the iron(II) determined titrimetrically by redox titration or, for small amounts of minerals, colorimetrically by means of 2,2′-bipyridyl.

W. J. FRENCH and S. J. ADAMS

Queen Mary College, Mile End Road, London, E.1.

Analyst, 1972, **97**, 828–831.

Determination of Silica in Silicate Materials by an X-ray Fluorescence (Standardised Inert Dilution) Method

An X-ray fluorescence standardised inert dilution method has been developed for the determination of silica in quartz-sand, glass and cement-clinker samples.

By using the fused sample technique, the method can be applied satisfactorily (standard deviation 0·7 per cent.) to the rapid routine determination of silica.

The results for determinations of silica in quartz sand are compared with those obtained by four different chemical methods.

M. CAMPOS and R. VERA

Instituto Central de Química, Instituto Central de Física, Universidad de Concepción, Concepción, Chile.

Analyst, 1972, **97**, 832–837.

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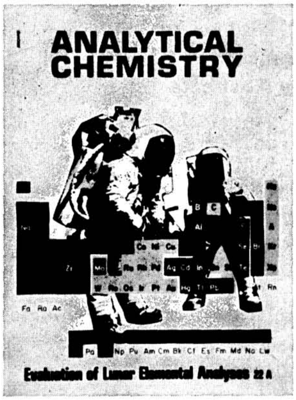
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