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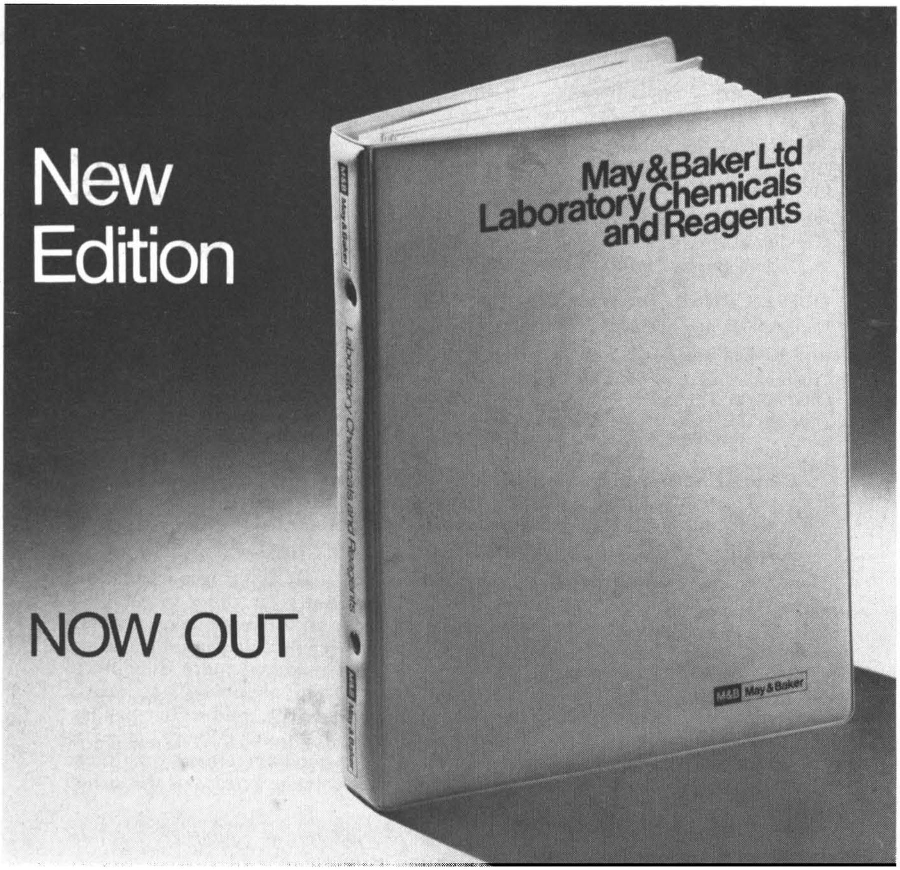
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Summaries of Papers in this Issue

Modified Oscillating Mirror Rapid Scanning Spectrometer as a Detector for Simultaneous Multi-element Determination

An oscillating mirror rapid scanning spectrometer has been modified to improve its light throughput and resolution. Results of the application of this spectrometer to simultaneous microwave-induced atomic-emission spectrometry and simultaneous carbon furnace atomic-absorption spectrometry are given.

Keywords: *Oscillating mirror rapid scanning spectrometer; microwave-induced atomic-emission spectrometry; carbon furnace atomic-absorption spectrometry; multi-element determination*

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Analyst, 1978, **103**, 113–121.

Determination of Lead in Plastic Containers for Pharmaceutical Products by Atomic-absorption Spectrophotometry Using a Carbon Rod Atomiser

A method is described for the determination of lead in a variety of plastic pharmaceutical containers by direct solid-sample analysis using a carbon rod atomiser. The recovery of added standard is measured in order to establish suitable assay conditions for each type of plastic. In the absence of recovery tests, low results for lead in the presence of plastics can result from mechanical loss during ashing or because the lead has been rendered more difficult to atomise. The amounts of lead found ranged from about 0.03 to nearly 1 p.p.m., with a mean relative standard deviation of 15%, and were considerably less than the British Pharmacopoeia limit of 50 p.p.m. Where comparative tests were possible, results are shown to be in good agreement with those obtained by measuring lead in a chelate - organic solvent extract of wet-ashed plastic.

Keywords: *Lead determination; plastic pharmaceutical containers; atomic-absorption spectrophotometry; carbon rod atomisation*

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Analyst, 1978, **103**, 122–127.

Infrared Determination of Quartz, Kaolin, Corundum, Silicon Carbide and Orthoclase in Respirable Dust from Grinding Wheels

A method is proposed for the solid-state, quantitative, infrared determination of the common components found in respirable dust from grinding wheels. The entire spectral region, 1 300–300 cm^{-1}, is used and the masses of components are computed by the least-squares method. The practical detection limit is 20 μg and the working range extends up to 600 μg, which is sufficient for this type of sample. Known synthetic mixtures yielded mean recoveries of 92–108%, depending on the component under consideration, the relative standard deviations being of the order of 5–18%.

Keywords: *Multi-component quantitative determination; infrared spectroscopy; respirable grinding wheel dust*

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Analyst, 1978, **103**, 128–133.

Determination of Nickel, Cobalt and Copper by Direct Photometric Titration with Cyanide

Nickel(II), cobalt(II) and copper(II) at the 0.1 M level are titrated photometrically with cyanide in ammoniacal solution. The nickel - cyanide reaction shows reproducible 1:4 stoicheiometry and can be used for titration. The reaction with cobalt shows firm 1:5 stoicheiometry but is complicated by formation of oxygen-containing species. The reaction with copper shows uncertain stoicheiometry of about 1:4. In the nickel titration zinc does not interfere but cobalt and copper add on, both showing 1:4 metal - cyanide stoicheiometry.

Keywords: *Nickel determination*; *cobalt determination*; *copper determination*; *photometric determination*; *cyanide*

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Analyst, 1978, **103**, 134–139.

Biacetyl Bis(4-phenyl-3-thiosemicarbazone) as a Reagent for the Spectrophotometric Determination of Copper

The synthesis, characteristics and analytical applications of biacetyl bis(4-phenyl-3-thiosemicarbazone) (BBPT) are described. The reaction between copper(II) and BBPT has been studied by spectrophotometry. The reddish orange 1:1 copper - BBPT complex ($\epsilon = 12.7 \times 10^3$ l mol^{-1} cm^{-1} at 485 nm and 8.2×10^3 l mol^{-1} cm^{-1} at 530 nm) is formed at pH 1.8–11.9, in a solution containing 60% *V/V* of dimethylformamide. The effect of interferences was studied. A rapid and simple method for the spectrophotometric determination of copper in a white metal, in blende and in a waste water has been devised. The method is compared with others proposed for the spectrophotometric determination of copper with thiosemicarbazone reagents.

Keywords: *Biacetyl bis*(*4-phenyl-3-thiosemicarbazone*) *reagent*; *copper determination*; *spectrophotometry*

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Analyst, 1978, **103**, 140–148.

Potentiometric Determination of Copper in Palm Oil with a Copper(II) Ion-selective Electrode

The applicability of a copper(II) ion-selective electrode for the determination of the copper content of crude and hydrogenated palm oils was investigated. Dry ashing was used for destroying the organic matrix and a porcelain crucible was used as container. The recovery of copper in dry ashing and the leaching of copper from the internal glazing of a porcelain crucible were investigated. A complexing antioxidant buffer was used in order to minimise the interfering effect of iron(III) on the determination of copper(II). A direct potentiometric method can be applied to determine the copper content of palm oil at a concentration higher than 10 μg kg^{-1} in the presence of 30 mg kg^{-1} of iron.

Keywords: *Copper determination*; *palm oil*; *direct potentiometry*; *copper*(*II*) *ion-selective electrode*

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Analyst, 1978, **103**, 149–155.

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The Analyst

Modified Oscillating Mirror Rapid Scanning Spectrometer as a Detector for Simultaneous Multi-element Determination

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An oscillating mirror rapid scanning spectrometer has been modified to improve its light throughput and resolution. Results of the application of this spectrometer to simultaneous microwave-induced atomic-emission spectrometry and simultaneous carbon furnace atomic-absorption spectrometry are given.

Keywords: *Oscillating mirror rapid scanning spectrometer; microwave-induced atomic-emission spectrometry; carbon furnace atomic-absorption spectrometry; multi-element determination*

An oscillating mirror rapid scanning spectrometer[1] can be classified as a sequential linear scan spectrometer.[2] The oscillating galvanometer provides a scanning wavelength window and each spectral element is detected in rapid sequence by a single photomultiplier tube. In a preliminary evaluation[3] of this type of spectrometer as applied to simultaneous multi-element emission spectrometry, it was found that its photomultiplier detection system and wide optical range would make it suitable as a multi-element detector. However, modifications were needed in order to improve the optical throughput and resolution. This paper describes the modified rapid scanning spectrometer (RSS) and its application to simultaneous atomic-emission spectrometry using the microwave-induced plasma (MIP) as the source and to simultaneous carbon furnace atomic-absorption spectrometry.

Experimental

Apparatus

Detection system

Basically, the detection system, consisting of the Harrick Rapid Scan Spectrometer (Model RSS-B), the RSS signal processing module, the Nicolet NMR-80 minicomputer with the FT-74 software package, was similar to that described previously.[3]

In order to avoid a lengthy re-alignment of the optics from one application of the RSS to the next, the instrument being also used extensively in other projects as a dual-beam spectrophotometer with a xenon arc lamp source, two modifications of the optical layout of the Model RSS-B described by Denton *et al.*[4] were made. Firstly, a telescope entrance lens (5 cm focal length, 2.5 cm diameter), aligned with the entrance slit (S_1) and the first spherical mirror (SM_1), was added with the first plane mirror removed, and secondly, a 1P28 photomultiplier tube was inserted immediately after the exit slit. Fig. 1 is a diagram of the modified optical layout and indicates that only the optical T was found to be necessary for atomic spectrometry. A photomultiplier power supply (MPI Model MP-1031) and a laboratory-constructed signal amplifier were used. By using the 1P28 photomultiplier tube and the separate amplifier, the signal to noise ratio was improved. (The amplifier circuit supplied by the manufacturer contained a pre-amplifier section and a log amplifier section. Only the output of the pre-amplifier section was displayed in the preliminary study.[3]) This

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improvement of the signal to noise ratio permitted the slit widths to be reduced, resulting in better resolution. Slit widths of 0.06 and 0.18 mm for entrance and exit slits, respectively, were used in the present emission studies.

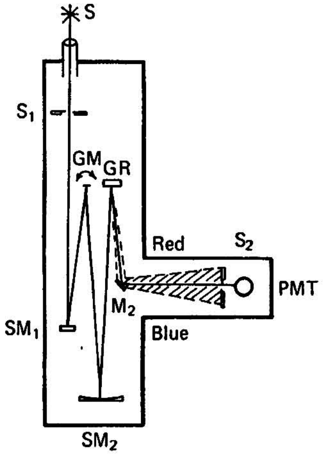

Fig. 1. Diagram of modified optical layout of Harrick RSS-B rapid scan spectrometer as used for trace metal emission work: S is the emission source; S_1, the entrance slit; SM_1, the first spherical mirror; GM, the galvanometer mirror; SM_2, the second spherical mirror; GR, the grating; M_2, the flat mirror; S_2, the exit slit; and PMT, the photomultiplier tube.

In order to evaluate the performance of the RSS with optical components other than those supplied by the manufacturer, other sources including a copper hollow-cathode lamp (Tekmar), a zinc, cadmium, lead and copper multi-element hollow-cathode lamp (Tekmar) and a low-pressure mercury vapour lamp were utilised for well defined spectral lines. The hollow-cathode lamps were powdered by a d.c. supply (Model GPS-2, Barnes Engineering Co.) and both lamps were operated at 8 mA. Before spectra were recorded following a change of an optical component, the optical alignment was optimised.

To improve the resolution, the grating supplied by the manufacturer, which was ruled at 300 lines mm^{-1} and blazed at 300 nm, was replaced with one ruled at 1 200 lines mm^{-1} and blazed at 250 nm. A comparison of the two gratings is made in Table I. In order to enhance the sensitivity by increasing the light throughput, and to improve the resolution by illuminating more lines of the grating, the galvanometer mirror (4.8 mm diameter) was replaced by a larger mirror (8.9 mm diameter) after a study of various galvanometer mirror sizes with respect to repetition rate. To fill the larger mirror with radiation, a larger first spherical mirror (SM_1) was installed. An ultraviolet sapphire hemicylinder, 20 × 25 mm with a 10-mm radius, fitted in well with the use of the 8.9 mm diameter galvanometer mirror.

In the preliminary study,[3] the minicomputer determined the repetition rate of the RSS. However, it was found that identical spectra could be stored in different 1K memory locations and coincide more precisely (permitting exact subtraction of background) if the galvanometer mirror oscillated continuously. A square-wave generator (Model 126C, Exact Electronics Inc.) was then used to trigger each scan of the galvanometer mirror and each sweep of the minicomputer. Thus, while the RSS collected spectral information continuously, the minicomputer stored data only upon command.

Carbon cup vaporisation assembly - MIP system

The carbon cup vaporisation assembly and the procedure for introducing analyte into the

MIP has been described previously.[5] The set power level of the microwave generator was 50 W direct and 0.5 W reflected, while the optimum flow-rate of argon was 600 ml min^{-1}.

Desolvation apparatus - MIP system

This system was similar to that described by Margoshes and Veillon[6] and modified by Skogerboe and Coleman,[7] except the microwave cavity was an Evenson ¼-wave cavity.[8] Small droplets of water splashed into the side-arm below the condenser that led to the quartz tube and extinguished the plasma. A piece of PTFE tape was suspended in front of the side-arm opening in order to minimise this interruption of the signal. The microwave power was 90 W direct and 0.5 W reflected. The flow-rate of argon was 800 ml min^{-1} and the solution aspiration rate was 2.2 ml min^{-1}.

Carbon furnace atomic-absorption system

Radiation from the zinc, cadmium, lead and copper multi-element hollow-cathode lamp operated at 8 mA was passed through the carbon rod atomiser (Model 63, Varian Techtron) and then detected by the RSS. The atomisation temperature was chosen to be the optimum for the determination of copper with a corresponding flow-rate of argon of 4 l min^{-1}.

Reagents

Aqueous standards pipetted into the carbon cup or carbon rod were diluted from stock solutions, which were either Fisher atomic-absorption standards or solutions prepared by dissolving pure metals or laboratory-reagent grade salts in an acid and diluting the solution with de-ionised water. Solutions aspirated into the desolvation apparatus were made 0.1 N in hydrochloric acid. All other reagents were of ACS reagent grade.

Data Acquisition

As in the preliminary study,[3] the difference between the signal observed for the sample and that observed for the solvent was used as a direct measure of the emission (absorption for the carbon furnace atomic-absorption system) of the elements.

For a determination using the carbon cup vaporisation assembly - MIP and the carbon furnace atomic-absorption systems, a 130-nm wavelength window was observed by the RSS with a repetition rate of 73 Hz. For both systems, the minicomputer accumulated data only when the transient signals were detected by the RSS. For the emission system, 200 spectra were accumulated, while for the carbon furnace atomic-absorption system, 140 spectra were accumulated.

For a determination involving the use of the desolvation apparatus - MIP system, an 80-nm wavelength window was observed by the RSS with a repetition rate of 20 Hz and 500 spectra were accumulated after aspiration of the sample solution.

Results and Discussion

Evaluation of Modified RSS

Grating

The use of a more finely ruled grating in the RSS results in a compromise between increased resolution and reduced maximum wavelength window size as the angular displacement (excursion) of the galvanometer mirror needs to be greater to display the same wavelength window size than that with less spectral dispersion. Table I lists the maximum wavelength

TABLE I

COMPARISON OF PERFORMANCE OF THE RSS WITH MOUNTING OF DIFFERENT GRATINGS

	300 lines mm^{-1} grating	1 200 lines mm^{-1} grating
Maximum wavelength window size/nm	500*	170†
Line half-width of Cu 324.8-nm line/nm‡	1.9	0.4

* Limited by spectral response of 1P28 photomultiplier.
† Limited by size of second spherical mirror (see Fig. 1).
‡ Wavelength window size 17 nm.

window size and line half-width observed when the 300 and the 1 200 lines mm^{-1} gratings were mounted with all other components unchanged. The improvement in resolution was substantial as the line half-width (full width at half maximum height) of the copper 324.8-nm line decreased from 1.9 to 0.4 nm.

Fig. 2 shows the same 17-nm window of the radiation from the copper hollow-cathode lamp, which includes the 324.8- and 327.4-nm lines recorded after optical components were changed. A comparison of spectra (*a*) and (*b*) indicates the enchancement of resolution with a more finely ruled grating mounted in the RSS. However, the maximum possible wavelength window decreased from 500 to 170 nm. With the 300 lines mm^{-1} grating mounted in the RSS, the maximum wavelength window size was determined by the spectral response of the photomultiplier tube. For example, with the photomultiplier tube supplied by the manufacturer (RCA C31025Q), the maximum wavelength window is 730 nm, while with the 1P28, the maximum width is 500 nm. The spherical mirror, SM_2, limits the maximum wavelength window size with the 1 200 lines mm^{-1} grating mounted in the RSS. Any greater angular displacement (excursion) of the galvanometer mirror does not result in an increase in wavelength window because the path of the light beam produced by the oscillating mirror is greater than the width of SM_2.

Galvanometer mirror size

The use of the 4.8 mm diameter galvanometer mirror supplied by the manufacturer provided a repetition rate fast enough to permit a sufficient accumulation of transient signals.[3] In order to select the size of a larger mirror that would increase the light throughput and resolution, but still provide a reasonable repetition rate, the performance of several galvanometer mirrors was studied by mounting these on the same optical scanner (General Scanning, Model 0612). For example, the use of a 12.7 mm square galvanometer mirror (area 161.3 mm^2), which increased the light throughput markedly, decreased the repetition rate to 16 Hz (at a scanning rate of 41 Hz) with the wavelength window of 50 nm. (Any subsequent reference to wavelength window size implies that the 1 200 lines mm^{-1} grating was mounted in the RSS.) Any faster repetition rate caused significant distortion of the spectrum displayed. This decrease in repetition rate is due, in part, to the unfavourable ratio of mirror inertia to scanner armature inertia.[9] The time required for the mirror to come to rest after each scan is much greater than that required for a smaller mirror and there is much more inertia to overcome at the beginning of each scan. The maximum repetition rate would decrease still further if the wavelength window size were increased because the rate of angular displacement would be larger. This increased rate provides greater momentum to reverse as the mirror re-sets after the scan is completed and more time is required to bring to rest the resulting increased surface distortions of the mirror. However, in applications that need only a slower repetition rate (less than 20 Hz), but high light throughput, the use of a larger galvanometer mirror can be an important modification

TABLE II

COMPARISON OF PERFORMANCE OF THE RSS WITH MOUNTING OF DIFFERENT GALVANOMETER MIRRORS

	4.8 mm diameter mirror (area 18.1 mm^2)	8.9 mm diameter mirror (area 62.2 mm^2)
Maximum repetition rate/Hz*	73	20
Scan rate at maximum repetition rate/Hz	101	50.5
Relative intensity of Cu 324.8-nm line	1	3.1
Line half-width of Cu 324.8-nm line†	0.4	0.3
Linearity of scan (correlation coefficient of wavelength *versus* position plot‡)	0.999 4	0.999 4

* Wavelength window size 130 nm.
† Wavelength window size 17 nm.
‡ Thirteen emission lines of radiation from a low-pressure mercury vapour lamp.

to the RSS-B spectrometer. It was not possible to utilise a larger optical scanner without totally rebuilding the RSS-B. By use of a different monochromator, much larger optical scanners and corresponding mirrors (*e.g.*, an 875-mm^2 mirror such as are found on General Scanning 300 Series models[9]) could be employed.

An 8.9 mm diameter galvanometer mirror was chosen as a compromise between increased light throughput and repetition rate for the RSS-B spectrometer. Table II gives a comparison of the performance of the RSS when the 4.8 mm diameter and 8.9 mm diameter mirrors are mounted in the RSS with all other optical components unchanged. The light throughput was increased by a factor of 3.1 even though the actual observation time (scan period multiplied by the repetition rate) was decreased and the resolution of the RSS increased. A comparison of spectra (*b*) and (*c*) in Fig. 2 indicates the improvement of the spectral output of the RSS with the use of the larger galvanometer mirror. Spectrum (*c*) has been attenuated by a factor of two for display purposes. The maximum repetition rate was reduced to 20 Hz with a wavelength window of 130 nm, compared with 73 Hz for the same wavelength window width with the smaller mirror mounted in the RSS. With the Model 0612 optical scanner, the larger mirror is best utilised in applications in which the observed signals are continuous so that a more favourable signal to noise ratio is obtained. It should be indicated at this point that even with the larger mirror mounted, the grating was severely under-illuminated, which appears not to be a drawback in other applications[1,4] but needs to be improved for future atomic-emission work, probably by building a new instrument.

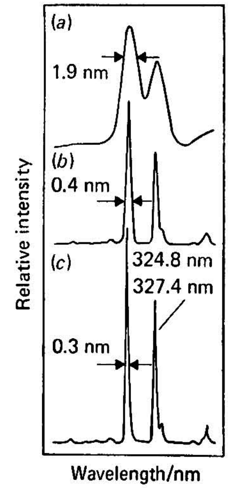

Fig. 2. Identical wavelength windows (width 17 nm) of the emission of a copper hollow-cathode lamp. Slit widths: entrance 0.06 mm, exit 0.18 mm. Display attenuation: (*a*), 16 000 counts cm^{-1}; (*b*), 16 000 counts cm^{-1}; (*c*), 32 000 counts cm^{-1}. Optical components mounted in the RSS: (*a*), 4.8 mm diameter galvanometer mirror, 300 lines mm^{-1} grating; (*b*), 4.8 mm diameter galvanometer mirror, 1 200 lines mm^{-1} grating; (*c*), 8.9 mm diameter galvanometer mirror, 1 200 lines mm^{-1} grating.

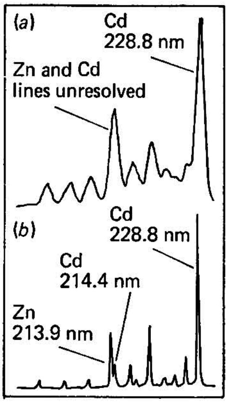

Fig. 3. Identical wavelength windows (width 35 nm) of the emission of a zinc, cadmium, lead and copper hollow-cathode lamp. Slit widths: entrance 0.06 mm, exit 0.18 mm. Optical components mounted in the RSS: (*a*), 4.8 mm diameter galvanometer mirror, 300 lines mm^{-1} grating; (*b*), 8.9 mm diameter galvanometer mirror, 1 200 lines mm^{-1} grating.

In the preliminary study of the RSS,[3] it was noted that zinc and cadmium could not be determined simultaneously as the zinc 213.9-nm and cadmium 214.4-nm lines were unresolved. By mounting the 8.9 mm diameter galvanometer mirror and the 1 200 lines mm^{-1} grating in the RSS, these two lines can be resolved. Fig. 3 gives a comparison of the same 35-nm window of radiation from a zinc, cadmium, lead and copper multi-element hollow-cathode lamp recorded with different optical components mounted in the RSS. An increase in the wavelength window size decreases the resolution because fewer data points per nanometer are accumulated. The maximum wavelength window size that can be used for multi-element determinations while still resolving the zinc 213.9- and cadmium 214.4-nm lines according to the Rayleigh criterion of resolution was 80 nm.

Atomic-emission and -absorption Spectrometry

After modifying the RSS spectrometer as described above, it was again evaluated as a detector in simultaneous multi-element determinations. Both the transient signals produced by the carbon cup vaporisation assembly - MIP system and the carbon furnace atomic-absorption system, and the continuous signals produced by the desolvation apparatus - MIP system, were observed. In order to obtain an enhanced signal to noise ratio, the 4.8 mm diameter galvanometer mirror was mounted in the RSS for the detection of the transient signals, although the 8.9 mm diameter mirror was mounted for the detection of continuous signals.

Table III lists the limits of detection for the three systems. These limits are not as low as it is possible to achieve with the MIP, as Skogerboe and Coleman indicate.[10] It is likely that these high limits result from the low duty cycle (see below) as well as from the rather limited optical throughput available with the RSS-B. With the carbon cup vaporisation assembly - MIP system, bismuth, cadmium, manganese, lead, magnesium and copper were determined simultaneously; Fig. 4 shows a typical background-corrected emission spectrum of this determination. Of note is the resolution of the manganese triplet that appeared as one peak in an identical wavelength window recorded in the preliminary study.[3] As a result of the intensity and randomness of the argon background, its subtraction was not precise. Zinc was determined separately owing to the spectral overlap of the zinc 213.9- and cadmium 214.4-nm lines. Typical analytical graphs for this system are shown in Figs. 5 and 6. Two sets of units are given in the abscissae as the system is mass sensitive. In this study, the sample volume used was 5 μl. The linear range is approximately one order of magnitude. This range is more compressed than is desirable; however, that is to be expected when the limited optical throughput of the system, which in part leads to higher detection limits than might otherwise be possible, is considered. Indeed, scanners capable of supporting mirrors greater than ten times the largest area that we could mount in the RSS-B are readily available with sufficient frequency response (see above). In order to utilise such scanners, however, a different instrument is required as size restrictions in the RSS-B prohibit further modification.

The onset of self-absorption gives rise to a slope of about 0.5 at higher concentrations. This is not unexpected, particularly with the carbon cup experiments where the particle density in the transient pulse is likely to be high enough to give rise to this phenomenon.

TABLE III

LIMITS OF DETECTION* (p.p.m.)

Element	Wavelength/nm	Carbon cup vaporisation assembly - MIP†	Desolvation apparatus - MIP	Carbon furnace atomic absorption†
Zn	213.9	0.1	0.07	—
Bi	223.1	0.2	0.7	—
Cd	228.8	0.03	0.02	0.000 3
Mn	257.6	0.04	0.04	—
Pb	283.3	0.2	—	0.007
Mg	285.2	0.06	0.02	—
Cu	324.8	0.05	0.09	0.005

* Defined as that concentration which produces a net signal twice the standard deviation of the background signal.

† Sample volume 5 μl.

Unquestionably, the MIP is capable of providing lower detection limits and extended linear ranges.[10] Nevertheless, the limits of detection for the carbon cup vaporisation system and the desolvation system are in the sub-parts per million range and are mutually comparable. These detection limits are surprising in view of the low duty cycle for the analytical line (line sampling time). For example, consider a typical carbon cup experiment with a 130-nm window, a repetition rate of 73 Hz and a scanning rate of 101 Hz. Also, assume that the maximum residence time for cadmium in the plasma is 1 s and that 0.5 nm represents the cadmium "slice" of the 130-nm total. Based on the repetition and scanning rates, 73 spectra are taken per second with the total time per 130-nm spectrum given as 0.0099 s (1/101). Thus, in the residence time of 1 s, a total of 0.73 s is spent in sampling the 130-nm window giving 2.8 ms "on time" for the cadmium line. Thus, while the detection levels for direct-reading plasma emission spectrographs are less, the observation time per analytical line is at least 1 000 times greater.

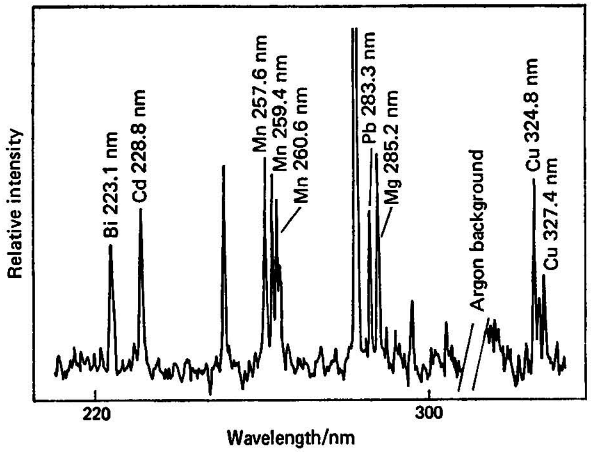

Fig. 4. Typical background-corrected emission spectrum obtained for a simultaneous determination of bismuth, cadmium, manganese, lead, magnesium and copper using the carbon cup vaporisation assembly - MIP system.

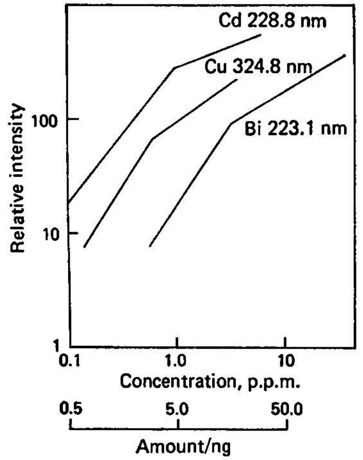

Fig. 5. Log - log plots of analytical graphs for cadmium, copper and bismuth obtained using the carbon cup vaporisation assembly - MIP system.

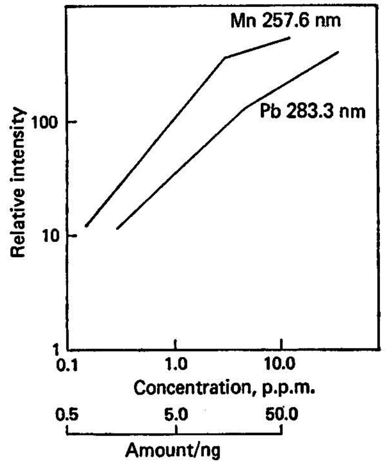

Fig. 6. Log - log plots of analytical graphs for manganese and lead obtained using the carbon cup vaporisation assembly - MIP system.

As the larger mirror was mounted for determination using the desolvation apparatus - MIP system, zinc and cadmium were determined simultaneously in an 80-nm window that also includes bismuth, manganese and magnesium. The emission of lead at low concentration levels was obscured by background emission. Copper was determined in a separate window. Typical analytical graphs for this system are shown in Figs. 7 and 8. The linear range is also approximately one order of magnitude for this system.

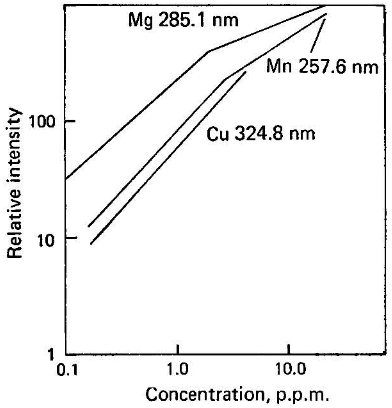

Fig. 7. Log - log plots of analytical graphs for magnesium, manganese and copper obtained using the desolvation assembly - MIP system.

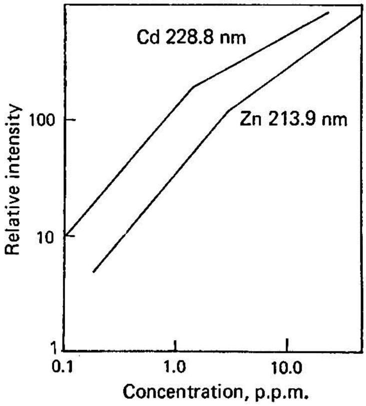

Fig. 8. Log - log plots of analytical graphs for cadmium and zinc obtained using the desolvation assembly - MIP system.

Cadmium, lead and copper were determined simultaneously by using the carbon furnace atomic-absorption system. No data were obtained for zinc owing to the presence of zinc in the de-ionised water and the problems associated with it for furnace atomic-absorption determination.[11] However, the determination of zinc is sensitive, being in the parts per 10^9 range. As is to be expected, considering the sensitivity of the carbon furnace atomic-absorption method, the limits of detection for this system are superior to those for the two emission systems. However, the linear range is narrow, especially for cadmium, making an optimum dilution difficult when working with complex samples.

Matrix Effects

In order to study possible matrix effects for the carbon cup experiment, 500 ng of sodium (5 μl of a 100 p.p.m. sodium solution from a stock solution of sodium nitrate) were vaporised into the plasma. As the sodium passed through the plasma the intense orange emission was noted, but the plasma appeared to be stable. The direct power increased only slightly and the reflected power did not change. After several vaporisations, the quartz tube above the plasma was coated with a white residue. Table IV gives the limits of detection of cadmium, manganese, magnesium, copper and zinc in 100 p.p.m. solutions of a sodium salt. There was little difference between these values in comparison with the limits of detection in aqueous solutions (Table III). As can be seen, the concentration of the matrix element is usually more than 1 000 times that of the analyte and in one instance about 5 000 times. Five microlitres of a 1 000 p.p.m. solution of sodium were injected into the cup and 5 000 ng of sodium were vaporised into the plasma, causing the plasma to contract appreciably. Also, there was a considerable memory effect as the sodium signal persisted for several minutes. However, casual observations indicate that it may be possible to tune the MIP with a continuous flow of sodium salt solution comparable with the amount that passes through the plasma upon vaporisation of 5 000 ng of sodium in a carbon cup. Tuning the MIP to the matrix is very important in sustaining a plasma.

Skogerboe and Coleman aspirated solutions containing 1 000 p.p.m. of sodium into a desolvation - MIP system without extinguishing the plasma.[7] However, when a 1 000 p.p.m. sodium solution was aspirated in the desolvation apparatus described above, it was not possible to sustain a plasma, although it must be mentioned that the tuner had been

TABLE IV

LIMITS OF DETECTION* (p.p.m.) IN THE PRESENCE OF A MATRIX ELEMENT (100 p.p.m. OF SODIUM)

Element	Wavelength/nm	Carbon cup vaporisation assembly - MIP	Desolvation apparatus - MIP
Zn†	213.9	0.1	0.4
Cd	228.8	0.04	0.06
Mn	257.6	0.02	0.2
Mg	285.2	0.1	0.3
Cu†	324.8	0.1	0.2

* Defined as that concentration which results in a net signal twice the standard deviation of the background.

† Zinc determined separately in the carbon cup experiment; copper determined separately in the desolvation experiment.

rebuilt in our laboratories and was not operating completely satisfactorily. A plasma was sustained with a 100 p.p.m. solution of sodium aspirating into the desolvation apparatus after the aspiration rate had been decreased to 0.9 ml $\min^{-1}$ and the argon flow-rate increased to 1.9 l $\min^{-1}$. With the aspiration of the 100 p.p.m. sodium solution into the desolvation apparatus the entrance lens became coated with salt, because the stream of gas leaving the quartz tube is directed at the lens. Limits of detection for zinc, cadmium, manganese, magnesium and copper in a 100 p.p.m. solution are also given in Table IV. The higher detection limits in solution in 0.1 N hydrochloric acid in the presence of the 100 p.p.m. solution of sodium as compared with those in just the 0.1 N hydrochloric acid (Table III) are attributed to the reduction in transport efficiency in the presence of sodium,[7] to changes in the plasma energy characteristics as a result of the large excess of sodium[7] and, to a large extent, the decrease in the aspiration rate.

Conclusions

Each of the three systems has distinct advantages. The carbon cup vaporisation assembly - MIP system has the potential for simultaneous determination when sample volume is critical. The desolvation apparatus - MIP system offers the advantage of observation of a continuous signal. For example, in this study, the larger mirror could only be mounted in the RSS for the detection of a continuous signal. The carbon furnace atomic-absorption system gives superior sensitivity of detection, but is limited by the availability of multi-element sources of radiation.

This study indicates that rapid scanning spectrometry may provide a useful detector for simultaneous atomic spectrometry. However, future work must increase the light throughput still further in order to lower the limits of detection, thereby increasing the linear range and fulfilling the capabilities of the MIP.[10] Also, more fully illuminated optics will enhance the resolution still further. The general concept of an oscillating mirror rapid scanning spectrometer with photomultiplier detection may well provide an answer to the growing need for an inexpensive detector for simultaneous multi-element determinations.

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Determination of Lead in Plastic Containers for Pharmaceutical Products by Atomic-absorption Spectrophotometry Using a Carbon Rod Atomiser

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A method is described for the determination of lead in a variety of plastic pharmaceutical containers by direct solid-sample analysis using a carbon rod atomiser. The recovery of added standard is measured in order to establish suitable assay conditions for each type of plastic. In the absence of recovery tests, low results for lead in the presence of plastics can result from mechanical loss during ashing or because the lead has been rendered more difficult to atomise. The amounts of lead found ranged from about 0.03 to nearly 1 p.p.m., with a mean relative standard deviation of 15%, and were considerably less than the British Pharmacopoeia limit of 50 p.p.m. Where comparative tests were possible, results are shown to be in good agreement with those obtained by measuring lead in a chelate - organic solvent extract of wet-ashed plastic.

Keywords: *Lead determination*; *plastic pharmaceutical containers*; *atomic-absorption spectrophotometry*; *carbon rod atomisation*

The extent to which pharmaceutical products are liable to be contaminated with lead from plastic containers is difficult to define, and comparatively little information is available concerning the content of lead in different plastic materials. In view of its physiologically harmful nature, however, the need to limit the occurrence of lead as an impurity is recognised and the British Pharmacopoeia[1] specifies that the heavy metal content of certain plastic containers for pharmaceutical use should not exceed the equivalent of 50 p.p.m. of lead.

The determination of lead in plastics by use of flame atomic absorption generally requires a preliminary ashing procedure, owing to the relative insolubility of plastics in most solvents. Two publications[2,3] by a Sub-Committee of the Analytical Methods Committee recommend wet oxidation with 50% hydrogen peroxide in the presence of hot concentrated sulphuric acid, although the recovery of lead from plastics following the wet-oxidation procedure has not been reported. The direct aspiration of aqueous solutions after ashing does not usually provide sufficient sensitivity,[4] and the lead is therefore complexed with a suitable organic reagent[4,5] in order to effect its extraction into a small volume of organic solvent that can be aspirated into the flame.

In some instances, procedures can be made less time consuming by dissolving the plastic directly in an organic solvent. Musha *et al.*[6] have used dimethylacetamide as a solvent for poly(vinyl chloride) that is suitable for direct aspiration into the flame. However, Olivier[7] has compared the different methods of sample preparation and reported that detection limits for lead, when 2% solutions of plastics are aspirated into a flame, are low (10 p.p.m.), while at higher concentrations the viscosity of the solution prevents efficient aspiration. As a consequence of this, it appeared that the direct analysis of solid samples of plastic using an electrothermal atomiser would be the most convenient procedure. Robinson *et al.*[8] have reported briefly on the determination of lead in polyethylene using a "hollow-T" atomiser. The purpose of this work has been to investigate this electrothermal atomisation method further, using a carbon rod atomiser, and to apply the method to determining the levels of lead normally found in a variety of plastic containers.

Experimental

Reagents and Apparatus

Lead nitrate stock standard solution. This is a 1.00 mg ml^{-1} solution of lead as lead nitrate in approximately 1 N nitric acid.

A Varian Techtron CRA-90 carbon rod atomiser was used in conjunction with a Varian Techtron, Model 1000, atomic-absorption spectrophotometer. The CRA-90 is essentially similar to the earlier Model 63 carbon rod atomiser, which has been described briefly by Culver *et al.*,[9] but it has been modified in order to permit temperature read-out. It was kept cool with water flowing at a rate of 2 l min^{-1}, and set up using standard size cup atomisers and with nitrogen as the inert gas at a pressure of 10 lb in^{-2}. Peak signals were recorded with a Rikadenki, Model B-34, or a Varian, A-25, recorder. A single-element lead hollow-cathode lamp (Varian Techtron) was used as a line source in order to determine lead at 217.0 or 283.3 nm. A lamp current of 5 mA and a spectral band width setting of 1.0 nm were used.

Systems were examined sequentially for background absorption using a hydrogen lamp (Varian Techtron) at the wavelength and band width settings used for the determination, the lamp current being adjusted so that the gain required to produce a 100% transmittance reading was the same as for the line source. They were also examined using the lead lamp at the non-lead resonance lines near 220 and 280 nm. Solid samples for the carbon rod were weighed by using a Stanton Micro-Balance (Model MC5). Liquid samples were injected into the cup of the carbon rod using a 5-μl Autopette injection syringe (Excalibur Laboratories Ltd.) fitted with disposable polypropylene tips. These tips were cleaned individually by drawing a solution of dilute nitric acid (20%) into them several times, followed by distilled water. The precautions necessary for trace analysis were taken at all times in order to prevent contamination.

Procedure

Solid-sample preparation

Wash the container thoroughly with distilled water, allow it to dry in air at room temperature, protected from aerial contamination, and then cut it into small pieces of approximately the required mass using stainless-steel scissors, handling the plastic with stainless-steel forceps. Weigh a cut sample accurately to the nearest microgram and rinse it well by swirling in distilled water in a small beaker. Without drying, transfer the weighed sample to the atomiser cup in order to determine the lead.

Selection of carbon rod atomiser control unit settings

Adjust the CRA-90 control unit settings initially to the following: dry, 130 °C for 90 s; ash, 800 °C for 60 s; and atomise, 1 600 °C for a hold time of 2 s and a ramp rate of 400 °C s^{-1}. Select a sample of the type of plastic material being examined that shows not more than a negligible or small signal for lead at the × 1 sensitivity setting of the instrument and ensure, by using the hydrogen lamp, that this signal is not the result of background absorption. Inject dilute standard lead solution containing 0.25 μg ml^{-1} of lead into the atomiser cup and determine the lead absorbance at 217.0 nm. The sensitivity to lead under these conditions is about 1.4×10^{-11} g to give 1% absorption.

In order to measure the recovery of the standard from the plastic, inject a further volume of the dilute standard lead solution into the cup and dry it at 130 °C for 90 s. Transfer about 1 mg, accurately weighed, of the plastic to the atomiser cup and operate the complete CRA-90 cycle (dry - ash - atomise) for the lead standard plus the plastic. Determine the recovery of the lead standard, correcting if necessary for any signal normally given by the plastic under the conditions applied. Atomise aqueous lead standards alone between solid sample additions to the cup to ensure that the normal lead response is being maintained. If the lead absorbance is found to be low in the presence of plastic, reduce the temperature of ashing and ash at the reduced temperature until the ash peak returns to zero on the recorder chart. Then complete the ashing by increasing the temperature to 800 °C and maintain this temperature for at least 30 s, or as long as is necessary to ensure that, if a second ash peak is produced, it returns to zero and remains there for at least 15–20 s before commencement of the atomisation stage. Continue in this way, reducing the initial ash temperature suitably, until further reduction does not result in an increase in the lead absorbance; extend the duration of ashing as necessary.

Inadequate ashing can itself cause an apparent increase in the recovery of lead because of interference from molecular absorption, and for this reason it is always advisable to carry out a final ashing at 800 °C. If the recovery of lead is still not complete, as was found with poly(vinyl chloride) and polypropylene, select the most suitable ashing conditions and increase the atomisation temperature to 1800 °C in order to overcome the deficit. Standards and standard recovery tests in the presence of plastic should still give the same response at the higher atomisation temperature. Having established suitable conditions using approximately 1-mg samples of plastic, determine the recovery of added standard from larger amounts of the plastic so as to establish the maximum amount of plastic that can be ashed effectively without loss of lead. Finally, ensure that the background absorption is zero when measured using the hydrogen lamp and with the larger amount of plastic in the atomiser cup. The CRA-90 control unit settings and the maximum plastic sample masses that were found to give complete recovery of lead, without background interference, from different types of plastics are shown in Table I. It is doubtful whether the recommended settings would reproduce the required conditions exactly from one instrument to another, and it would be advisable, before commencing an assay, always to establish the correct conditions in the manner described.

TABLE I

ASSAY CONDITIONS FOR DIFFERENT PLASTICS IN THE CRA-90 CARBON ROD ATOMISER

All samples were dried at 130 °C for 90 s before ashing.

		Control unit settings	
Plastic	Maximum sample mass/mg	Ash	Atomisation temperature with hold time 2 s and ramp rate 400 °C s^{-1}/°C
Polyethylene	3.0	650 °C for 30 s 800 °C for 30 s	1600
Polypropylene	1.3	600 °C for 120 s 800 °C for 60 s	1800
Poly(vinyl chloride)	2.0	380 °C for 60 s 620 °C for 60 s 800 °C for 60 s	1800
Polystyrene	4.0	800 °C for 60 s	1600

Solid-sample analysis

Transfer a weighed sample of plastic to the atomiser cup and determine the lead (usually at 217.0 nm) with the sensitivity (scale expansion) suitably adjusted such that the meter reading lies within the range 0.2–0.8 absorbance unit. Inject 5-µl volumes of a dilute standard lead solution, containing approximately the same amount of lead as the plastic sample, into the atomiser cup before and after each sample measurement in order to ensure that the standard response, obtained under the same conditions as the sample response, still shows conformity with the calibration graph. Determine the mean response for at least five sample measurements. For calculation of the lead content, refer to a calibration graph that has been prepared at the same sensitivity setting as that used for the sample measurements by using four or five standard aqueous dilutions in order to cover the range of measurement. In this work, calibration graphs were obtained for the concentration range 0.1–0.7 µg ml^{-1} of lead at 217.0 nm with a scale expansion of ×1 and at 283.3 nm with a scale expansion of approximately ×3, and for the concentration range 0.005–0.030 µg ml^{-1} of lead at 217.0 nm using maximum scale expansion (approximately ×17).

Results and Discussion

The amount of sample that can be placed in the atomiser cup for solid-sample analysis is necessarily limited by the density of the material and the size of the cup, but with the plastics examined the main limiting factor was the need to decompose and oxidise organic material efficiently without loss of lead before atomisation. The CRA-90 atomiser has a maximum ashing temperature of 1700 °C, which is normally maintained for up to 60 s, although the duration of ashing can be extended by switching off the atomiser and re-operating the cycle. Trial runs with standard amounts of lead (3.75 ng) showed that no loss of metal occurred from the CRA-90 with ashing temperatures of up to 1000 °C, but that at higher settings lower absorbance readings were obtained during atomisation, and small signals indicating loss of lead were observed during the ashing stage. An ashing temperature of 800 °C for 60 s was therefore selected as being suitable, as it sufficed to ash completely up to about 4 mg of plastic for all of the samples examined.

For atomisation, any temperature setting in the range 1 500–1 900 °C was satisfactory, and 1 600 °C was selected so as to prolong the life of the atomiser cup. Findlay *et al.*[10] have observed that the loss rate in charring samples for lead determinations can differ between different matrices. In this work, when standard recovery tests for lead were carried out as described in the procedure, losses of lead were initially found to reach 70% in the presence of polypropylene and were also high in the presence of poly(vinyl chloride). The poor recoveries of lead were possibly caused by mechanical loss during ashing, or else by the low atomisation efficiency resulting when polypropylene and poly(vinyl chloride) are incompletely ashed. As is shown in Table I, it was found necessary with both of these plastics to commence ashing at temperatures below 800 °C, and to operate the ashing stage three times. Polyethylene and polystyrene, however, could be ashed at 800 °C for 60 s with good recoveries of lead, although with amounts of sample greater than 2 mg it was preferable to ash polyethylene at a lower temperature for a brief initial period. In all instances, it was found to be advisable to carry out the final ashing at 800 °C in order to avoid the appearance of a background signal in the atomisation stage. Low recoveries of lead also resulted from the lead becoming more difficult to atomise after being present with the plastic during ashing. Thus, with polypropylene and poly(vinyl chloride), it was found necessary to increase the atomisation temperature from 1 600 °C to 1 800 °C in order to obtain complete recovery of the lead.

TABLE II

LEAD FOUND IN VARIOUS PLASTICS BY DIRECT SOLID-SAMPLE ANALYSIS IN THE CRA-90

Plastic	Scale expansion	Wavelength/ nm	Lead found, p.p.m.		Standard deviation (9 degrees of freedom), p.p.m.
			Mean	Range	
Brown polyethylene bottles (sample 1)	×1	217.0	0.74	0.65–0.84	0.07
	×3	283.3	0.92	0.73–1.05	0.11
Brown polyethylene bottles (sample 2)	×1	217.0	0.46	0.41–0.51	0.03
	×3	283.3	0.51	0.45–0.54	0.04
White polyethylene bottles	×17	217.0	0.032	0.017–0.051	0.012
White polypropylene bottles	×17	217.0	0.089	0.067–0.107	0.015
Poly(vinyl chloride) tubing	×17	217.0	0.082	0.067–0.092	0.008
Amber polystyrene vials	×17	217.0	0.040	0.026–0.052	0.009

The results obtained by the direct solid-sample analysis procedure with samples taken from different types of plastic container are shown in Table II. No correction was necessary for background absorption in any instance. The assay results were confirmed approximately by the standard additions method. The atomisation peaks were sharp in all instances, and were the same for both solid-sample and solution atomisation. The plastic samples containing less than 0.1 p.p.m. of lead were determined at 217.0 nm with maximum scale expansion (approximately ×17). Careful sample preparation and handling were essential when the very high sensitivity setting was used. Thus, it was found that when samples were rinsed after being weighed, instead of being placed directly into the atomiser cup, the improvement in precision was more than two-fold. As both types of brown polyethylene bottle, which had been obtained from the same supplier, had relatively high contents of lead, it was found possible to analyse them at 217.0 nm and at the less sensitive 283.3-nm line, because at the latter wavelength ashing peaks are negligible and there is less likelihood of background interference. Results could not be compared at the two wavelengths using the same sensitivity setting because of the limitation on sample size, and for comparable amounts of sample it was necessary to work with a scale expansion of about ×3 at 283.3 nm while the ×1 setting was used at 217.0 nm. The level of noise was negligible at both settings. The agreement between results obtained at the two wavelengths was good with one sample, but less so with the second sample, which showed a higher standard deviation of results at both wavelengths.

In order to establish the accuracy of results obtained by direct solid-sample analysis, the lead content of the two brown polyethylene samples was also determined by a different method, which involved wet ashing weighed samples of the plastic with sulphuric acid and hydrogen peroxide solution,[2] and extracting lead from the acidic solution into 5 ml of a solution of diethylammonium diethyldithiocarbamate in xylene, as described by Roschnik.[4] Reaction blanks were carried out at the same time under the same conditions, but omitting the plastic. The lead atomic absorption was measured at 217.0 nm by use of the CRA-90 atomiser, and the content calculated by reference to a calibration graph that had been prepared by subjecting solutions containing 0–3.0 μg of lead to the extraction procedure.

In many of the brown polyethylene bottles the pigmentation was not even, and in order to obtain corroborative results it was found necessary to select samples in which the brown pigment was, as far as possible, uniformly distributed. The direct solid-sample analysis procedure was then carried out, using portions taken at random from different parts of the bottles in order to establish the uniformity of lead distribution, so that these results could be compared with those obtained by the wet-oxidation procedure. A small sample of uniform appearance was then selected from each of the larger samples and suitable amounts were analysed alternately by the direct solid-sample procedure and by a standard additions method. The latter was carried out by injecting dilute standard lead solution containing 0.2 μg ml^{-1} of lead into the atomiser cup and evaporating it to dryness before adding the plastic sample, and was carried out by using two different mass ranges of plastic. The lead content of the plastic was calculated by deducting the amount of lead added in the standard solution from the total amount of lead found. The results obtained are shown in Table III. Results obtained by the standard additions method were 90 and 96%, respectively, of those obtained by the direct solid-sample analysis procedure using small selected samples. Results obtained by direct solid-sample analysis using random samples were 100 and 90%, respectively, of those obtained by the wet-oxidation method. The wet-oxidation method could not be applied to plastics with a low lead content (less than 0.1 p.p.m.) because blank readings were too high.

TABLE III

LEAD FOUND IN PLASTIC SAMPLES BY VARIOUS METHODS

Sample	Method of analysis	Amounts of sample/mg	Lead content, p.p.m.		Degrees of freedom	Standard deviation, p.p.m.
			Mean	Range		
Brown polyethylene bottles (sample 3)	Direct solid sample using random samples	0.715–2.278	1.18	0.90–1.47	16	0.18
	Direct solid sample using selected sample	0.982–1.901	1.16	0.87–1.32	9	0.16
	Standard addition to solid sample using selected sample	0.657–1.346	1.04	0.85–1.28	9	0.13
	Wet oxidation and chelate - xylene extraction	1.385 0–2.679 6 g	1.18	0.93–1.41	4	0.19
Brown polyethylene bottles (sample 4)	Direct solid sample using random samples	1.085–2.825	0.82	0.54–1.15	37	0.17
	Direct solid sample using selected sample	1.230–1.945	0.84	0.60–1.11	9	0.19
	Standard addition to solid sample using selected sample	0.688–1.591	0.81	0.67–0.98	9	0.12
	Wet oxidation and chelate - xylene extraction	1.277 0–2.558 6 g	0.91	0.80–1.02	4	0.08

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Infrared Determination of Quartz, Kaolin, Corundum, Silicon Carbide and Orthoclase in Respirable Dust from Grinding Wheels

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A method is proposed for the solid-state, quantitative, infrared determination of the common components found in respirable dust from grinding wheels. The entire spectral region, 1300–300 cm^{-1}, is used and the masses of components are computed by the least-squares method. The practical detection limit is 20 μg and the working range extends up to 600 μg, which is sufficient for this type of sample. Known synthetic mixtures yielded mean recoveries of 92–108%, depending on the component under consideration, the relative standard deviations being of the order of 5–18%.

Keywords: *Multi-component quantitative determination; infrared spectroscopy; respirable grinding wheel dust*

The infrared spectroscopic technique has been little used for the quantitative multi-component analysis of solid substances.[1–3] Among the reasons[4,5] for this are scattering, inhomogeneity of the components in the potassium bromide pellet, pick-up of moisture and changes in the crystalline structure with pressure. Another reason is the change in the band contours of the components as a result of different particle size distribution, which requires controlled grinding procedures for the samples if it is to be avoided. With respirable dust samples this last problem does not arise.

However, the most restrictive limitation for its use is that it is necessary to know which components can be present in the dust. Granite dust is a typical example, and some work[6] has been carried out with this type of dust, using non-overlapping bands in order to obtain the concentrations of each component.

Dust from grinding wheels is of importance in industrial hygiene. In Spain, the grinding wheels are composed of binders (kaolin, feldspar and organic substances) and abrasives (quartz, carborundum and corundum). The determination of quartz by use of infrared spectroscopy in a sample of that type of dust is not possible if the classical base-line technique at 795 cm^{-1} is used. The presence of carborundum and corundum seriously affects both the absorbance of the base line and the 795 cm^{-1} peak, so that no measurements can be taken. Nevertheless, if the over-all contour of the spectrum is used, it is possible to determine the concentrations of the components simultaneously.

The aim of the present work was the simultaneous determination of five components (quartz, kaolin, corundum, carborundum and orthoclase) in samples of respirable dust arising from grinding wheels by collection of the dust on filters.

Experimental

Calibration Mixtures

The components were mechanically ground for 4 h in a tungsten carbide ball mill. The finer fraction was then separated by means of sedimentation in ethanol. The particle size distribution was measured by direct counting, using scanning electron microscopy, and is shown in Fig. 1. This distribution was confirmed in an X-ray dispersion particle size analyser.

Stock mixtures (0.5%) were prepared for the five components mentioned above by dilution in potassium bromide, followed by mechanical mixing and then manual grinding in an agate mortar. The mixtures were dried in a furnace at 200 °C.

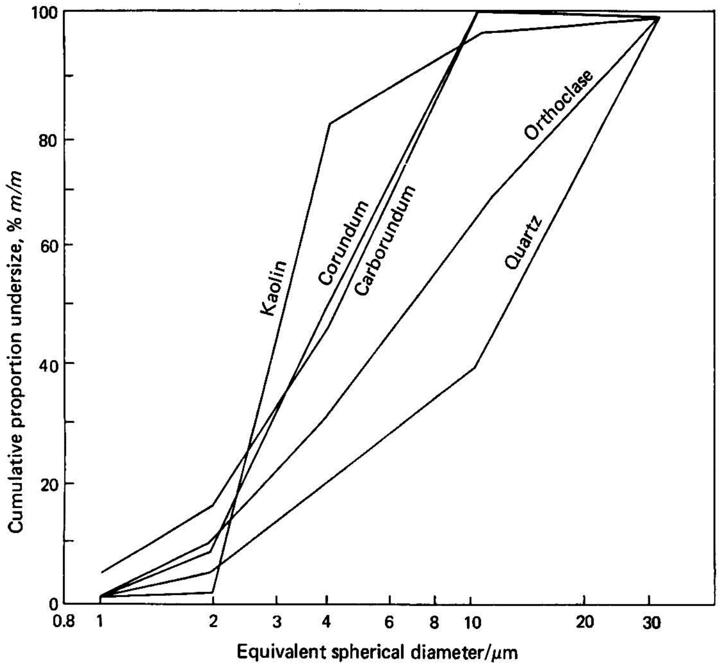

Fig. 1. Particle size distribution of the components used as standards.

A total of 65 duplicate calibration mixtures of the same mass (300 mg), containing known amounts of the components, were prepared by taking aliquots of the stock mixtures. The mass of each component was in the range 0–500 µg. Pellets were made in the usual form, weighed and scanned in the spectrophotometer without attenuation in the reference beam.

Apparatus, Materials and Reagents

Double-beam infrared spectrophotometer, Perkin-Elmer, Model 325.
Computer facilities, CII Model IRIS-50.
Muffle furnace, Heraeus Model KR-170.
Laboratory press, 30-ton.
Evacuable die, 13 mm.
Porcelain crucibles.
Agate mortar and pestle.
Mixer, Lab Line Instruments.
Ball mill, Fritsch Model Pulverisette-6.
Membrane filters, PVC, 37 mm *diameter*, 5.0 µm *pore size, Mine Safety Appliances Type FWS-B.*
Potassium bromide, Merck Uvasol grade.
Quartz, Merck reagent grade.
Aluminium silicate, Riedel de Haën reagent grade.
Aluminium oxide, Carlo Erba reagent grade.
Carborundum, Prolabo reagent grade.
Potash feldspar (orthoclase), mineral specimen, Natural Science Museum, Spain.

Method

The entire 1300–300 cm^{-1} region of the infrared spectrum is used. The amounts of each component can be obtained from the spectrum contour. These amounts give rise to a computed spectrum that fits the experimental one as near as possible in a least-squares sense. Particle size effects in several bands are minimised when the entire spectral region is used.

The mathematical treatment necessary for the spectrophotometric analysis of a multi-component mixture is well known.[7–11] A Fortran program, which performs the calculations, has been written.

Transmittances were measured at 10-cm^{-1} intervals, resulting in a total of 100 points per spectrum. The transmittance at 1 500 cm^{-1}, where an absorbance minimum exists for every component, was taken as the reference transmittance for computing absorbances. The alternative of using an internal standard that supplies a reference transmittance was discarded on the basis of not including another component in the mixture. Pellet opacity due to moisture causes light scattering and therefore causes changes in the base-line straightness. This factor is not significant, provided that special care is taken in drying the potassium bromide and the components. Care should also be taken to avoid eventual displacement of the over-all spectrum as a result of incorrect wavelength setting.

Fig. 2 shows the infrared spectrum for the components isolated. The overlapping bands at 795 cm^{-1} can be clearly observed. This overlap is the reason for the inapplicability of the classical base line and maximum absorption method[12] for the determination of quartz in a multi-component type of sample.

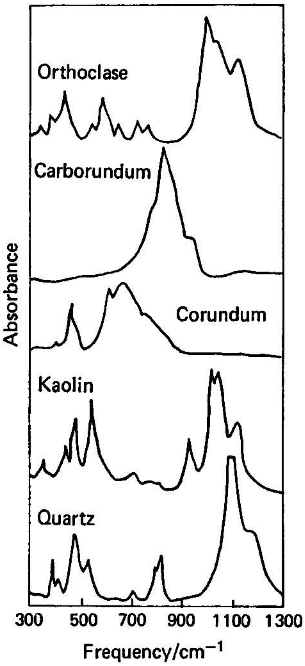

Fig. 2. Infrared spectra of the individual components of grinding wheels.

Dust samples

Respirable dust samples can be collected on PVC filters by using a particle size selector (cyclone) and an aspirating device (personal pump sampler). Low mass (less than 1 mg) and fine particle size (less than 10 µm) are the most important features of these dust samples. After sampling, the filter is weighed on an analytical balance and the mass of the dust obtained by difference. Then, it is transferred to a porcelain crucible and ashed at 380 °C for several hours in a muffle furnace in order to eliminate both the filter itself and the organic matter. At that temperature no appreciable change is observed in either the kaolin infrared spectrum or in that of the other components; the filter ash shows no infrared background absorption.

Losses are minimised if the crucible is partially covered and if the muffle temperature is raised gradually in order to avoid instantaneous ignition of the filter. Next, 300 mg of potassium bromide are added to the crucible and mechanically mixed with the ash; the whole is then transferred to the agate mortar and a pellet is made in the usual manner. Finally, the pellet is scanned in the infrared instrument.

Results

The matrix of the absorptivity of each component at each frequency was compiled, but is not included here because of its size. The relative standard deviation of each absorptivity was also computed, resulting in values of the order of 5% for the frequencies at which absorption bands exist.

An accuracy test was prepared by use of ten synthetic mixtures of known composition. The results obtained in the simultaneous determination of the components of the mixture are shown in Table I. The recoveries are expressed as percentages of the nominal value; also included is the mean recovery for the ten mixtures and for each component. The best results were obtained for corundum, with a mean recovery of 98% and a small standard deviation of ±5%. The worst was for orthoclase, with a mean recovery of 92% and a standard deviation of ±18%. For the components the nominal masses of which in the mixtures were zero, a small computed mass was obtained, less than 0.02 mg in every instance. The typical good agreement between observed and computed spectra for the test mixtures is shown in Fig. 3. Correlation coefficients obtained for the mixtures ranged from 0.985 to 0.997.

Table I

Recoveries obtained in the analysis of known synthetic mixtures

	Quartz		Kaolin		Corundum		Carborundum		Orthoclase	
Mixture number	Present/ μg	Recovery, %	Present/ μg	Recovery, %	Present/ μg	Recovery, %	Present/ μg	Recovery, %	Present/ μg	Recovery, %
1	500	96	—	—	—	—	—	—	—	—
2	330	103	—	—	—	—	—	—	170	59
3	—	—	—	—	170	101	332	109	—	—
4	173	76	167	82	—	—	173	91	—	—
5	—	—	167	107	167	99	—	—	167	95
6	150	120	150	98	103	91	101	100	—	—
7	150	108	150	81	101	104	—	—	100	104
8	150	99	150	105	—	—	100	121	100	103
9	150	89	—	—	150	99	100	103	100	108
10	—	—	150	101	175	93	100	114	100	83
Mean*		99±14		96±11		98±5		106±11		92±18

* Mean recovery ± standard deviation for the ten mixtures.

Lower accuracy is to be expected with dust samples than with synthetic mixtures, owing to the presence of some unexpected compounds in low concentration, whose effect will be to give a worse fit. Particle size distribution differences between the standards and the respirable dust samples can affect the results, but only slightly, because both distributions are rather similar and, although some bands are affected by the particle size, all of them are included in the calculation. As an example, Fig. 4 shows the agreement between observed and computed spectra for a respirable dust sample collected from a place in which grinding wheels are used. In certain regions of the spectrum the fit is not as good as above. The computed masses for this sample are shown in Table II.

Accuracy and reproducibility could not be tested with filter samples because of the lack of suitable standard filters with guaranteed masses of the five components deposited on them.

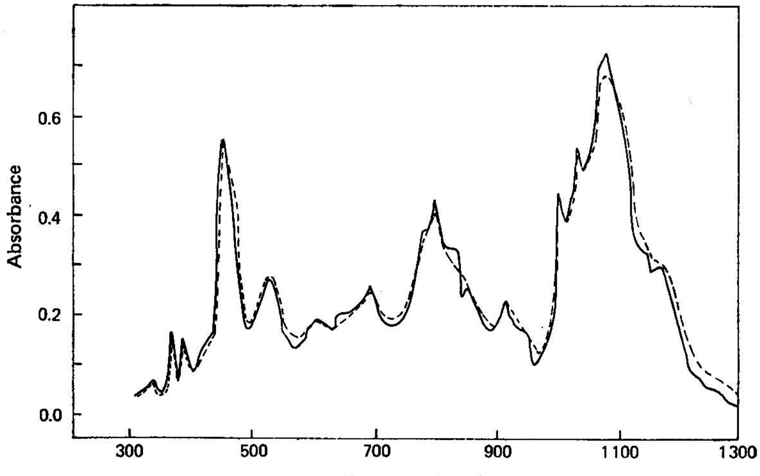

Fig. 3. Calculated and observed spectra of a typical unknown synthetic mixture. The full line shows the observed spectrum and the broken line the calculated spectrum.

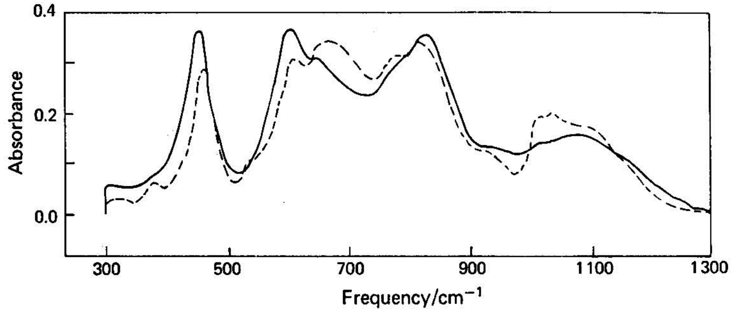

Fig. 4. Calculated and observed spectra of an actual dust sample. The full line shows the observed spectrum and the broken line the calculated spectrum.

Discussion

It is necessary to note that all mineral compounds other than the five mentioned, if present in appreciable amounts, will interfere in this type of analysis, when the over-all infrared spectrum is being used. This is not a very restrictive condition when grinding wheel dust is to be analysed. It is not important if some of the five components are missing from the dust, because the calculated masses for them will be nearly zero; the masses for the remainder of the components will be obtained simultaneously.

TABLE II

COMPUTED MASSES FOR THE RESPIRABLE DUST SAMPLE, THE SPECTRUM OF WHICH IS SHOWN IN FIG. 4

Component	Mass/mg
Quartz	<0.02
Kaolin	<0.02
Corundum	0.20
Carborundum	0.10
Orthoclase	<0.02

If a good fit is obtained, it is not a complete guarantee that exact values have been obtained for the masses of the components.[13] Nevertheless, when the overlapping among the intense bands of the components is not high, good results can be obtained. In the present work quartz, kaolin and orthoclase have an intense band at 1100 cm^{-1}, while corundum and carborundum do not. It is significant that the last two give rise to minor dispersions in the results (see Table I). Another factor that also influences the results is the minimisation of the squares of the absolute differences in absorbance between observed and computed spectra, rather than relative differences. This gives rise to higher statistical weight for the intense bands. A minimisation of the relative differences at each frequency could give better results, but in any case, from the point of view of industrial hygiene samples, this is not the main problem.[14]

I thank Miss A. Moreno for her invaluable help in the experimental work, and Mrs. C. Serrano for her co-operation with programming.

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Determination of Nickel, Cobalt and Copper by Direct Photometric Titration with Cyanide

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Nickel(II), cobalt(II) and copper(II) at the 0.1 M level are titrated photometrically with cyanide in ammoniacal solution. The nickel - cyanide reaction shows reproducible 1:4 stoicheiometry and can be used for titration. The reaction with cobalt shows firm 1:5 stoicheiometry but is complicated by formation of oxygen-containing species. The reaction with copper shows uncertain stoicheiometry of about 1:4. In the nickel titration zinc does not interfere but cobalt and copper add on, both showing 1:4 metal - cyanide stoicheiometry.

Keywords: *Nickel determination*; *cobalt determination*; *copper determination*; *photometric determination*; *cyanide*

Nickel(II) and cobalt(II), in the presence of excess of cyanide, stoicheiometrically form the complex ions $[Ni(CN)_4]^{2-}$ and $[Co(CN)_5(H_2O)]^{3-}$. Before the introduction of EDTA, nickel and cobalt were determined by reaction with a known excess amount of cyanide in mildly ammoniacal solution followed by back-titration of the remaining cyanide with standard silver nitrate solution. Visual turbidimetric or potentiometric equivalence point indication was used.

When ammoniacal solutions of nickel, copper and cobalt are titrated with cyanide, marked colour changes occur and it was decided to see if such reactions could form the basis of useful photometric titrations of these metals. The use of cyanide as titrant would introduce selectivity towards "B type" and "right-hand side transition" metal ions, an advantage in comparison with the broad-spectrum titrant EDTA. Use of dilute ammonia solution as solvent would introduce further selectivity.

Experimental

Reagents

Potassium cyanide solution, 0.4 M. Prepared from fresh solid reagent and standardised by potentiometric titration against standard silver nitrate using silver and mercury(I) sulphate electrodes.

Nickel sulphate, copper(II) sulphate and cobalt(II) nitrate solutions, 0.1 M. The solutions were standardised against standard EDTA solution.

Instrumentation

Solution absorption spectra were produced on a Pye-Unicam SP8000 spectrophotometer. Titrations were performed on an EEL photometric titrator using Ilford standard spectrum filters, a 40-ml cell and a 10-ml microburette.

Results

Titration of Nickel

The hexaamminenickel(II) complex $[Ni(NH_3)_6]^{2+}$ is coloured blue with $\lambda_{max.}$ 582 nm. Upon addition of cyanide a smooth transition to the yellow tetracyano complex occurs as shown by the regular change in absorption spectrum (Fig. 1). Fig. 2 shows nickel - cyanide titrations at 575 nm and using various over-all concentrations of ammonia. A C_{NH_3} of at least 1 M is required in order to avoid precipitation of insoluble nickel complexes.

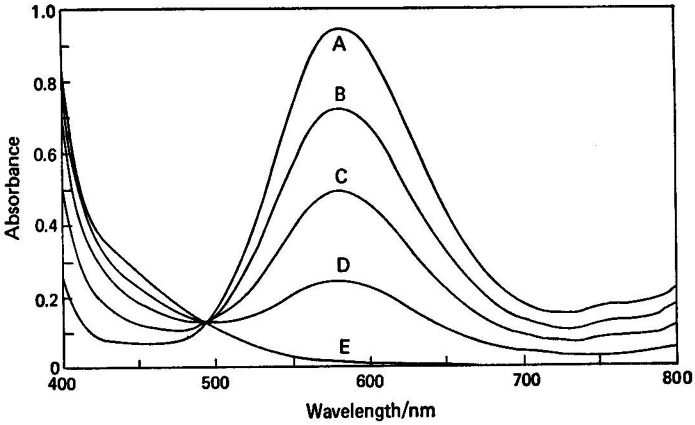

Fig. 1. Change in the absorption spectrum of $[Ni(NH_3)_6]^{2+}$ upon the addition of cyanide. $C_{Ni} = 0.0402$ M; $C_{NH_3} = 1.0$ M; cell path length = 40 mm. Molar ratios of Ni to CN: curve A, 1:0; B, 1:1; C, 1:2; D, 1:3; and E, 1:4.

A small, but distinct and reproducible, break occurs at the 1:2 nickel to cyanide molar ratio and the final end-point break seems always to occur about 0.7% low, based on 1:4 stoicheiometry.

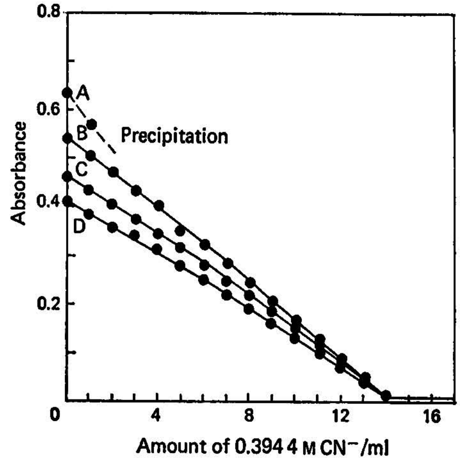

Fig. 2. Photometric titration of nickel with cyanide in ammoniacal solution. Filter 606 ($\lambda_{max.T}$ = 575 nm). Taken, 14.0 ml of 0.1004 M $NiSO_4$ solution plus *n* ml of concentrated NH_3 solution. Starting volume, 26 ml. Curve A, *n* = 1 ml; B, *n* = 2 ml; C, *n* = 4 ml; and D, *n* = 8 ml. Theoretical end-point for Ni to CN ratio 1:4 = 14.25 ml.

It is unexpected that the initial absorbance decreases with increase in ammonia concentration but the final end-point is independent of this variable.

For

$$Ni^{2+} + 4\,CN^- \rightleftharpoons [Ni(CN)_4]^{2-}$$

$\log \beta_4 = 31.3$ and for

$$Ni^{2+} + 6\,NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$$

log $\beta_6 = 8.49$,[1] where β is the over-all formation constant. This difference illustrates the readiness with which cyanide can displace ammonia in nickel complexes.

Titration of Cobalt

The reaction of hexaamminecobalt(II) with oxygen:

$$2[Co(NH_3)_6]^{2+} + O_2 \rightarrow [(NH_3)_5Co(O_2)Co(NH_3)_5]^{4+} + 2NH_3$$

causes complications. The colour change is from pink to dark brown. A similar reaction occurs with the cyanocobaltate(II) complex in the presence of oxygen:

$$2[Co(CN)_5(H_2O)]^{3-} + O_2 \rightarrow [(CN)_5Co(O_2)Co(CN)_5]^{6-}$$

the colour change being from yellow-green to brown. Because of these reactions all cobalt titrations were carried out under nitrogen. The absorption spectra of $[Co(NH_3)_6]^{2+}$ and $[Co(CN)_5H_2O]^{3-}$ are shown in Fig. 3. The high absorbance of $[Co(CN)_5(H_2O)]^{3-}$ at 800 nm is rapidly and completely destroyed by oxygen.

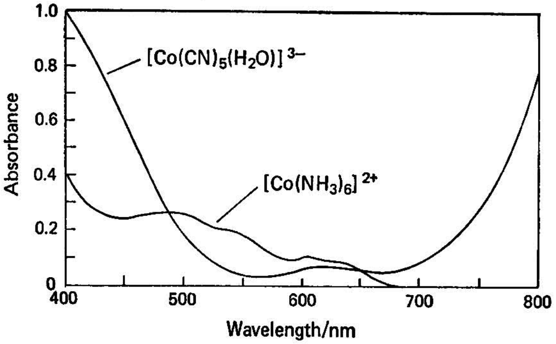

Fig. 3. Absorption spectra of $[Co(CN)_5(H_2O)]^{3-}$ and $[Co(NH_3)_6]^{2+}$. For the cyanide complex $C_{Co} = 0.008$ M; $C_{NH_3} = 1.4$ M; and $C_{CN} = 0.048$ M. For the ammine, $C_{Co} = 0.008$ M; and $C_{NH_3} = 3.7$ M. Cell path length = 20 mm. Both solutions kept under nitrogen.

Fig. 4 shows the titration of hexaamminecobalt(II) with cyanide at 435 nm; a set of curves increasing in absorbance is evident, as would be expected from the absorption spectra. An over-all ammonia concentration greater than 2 M is required in order to avoid precipitation. For a range of ammonia concentrations distinct breaks occur at 1:5 stoicheiometry; the reaction is

$$[Co(NH_3)_6]^{2+} + 5CN^- \rightleftharpoons [Co(CN)_5(H_2O)]^{3-} + 6NH_3$$

or

$$[Co_2(CN)_{10}]^{6-}$$

Precipitation is presumably due to the formation of uncharged species such as $[Co(NH_3)_4(CN)_2]^0$ or mixed hydroxy complexes. Such precipitates readily dissolve in excess of cyanide.

Titration of cobalt at 550 nm, as would be anticipated from the spectra, gives a slowly decreasing absorbance but this fall is terminated by an upward step at 1 : 5 stoicheiometry. At wavelengths above 640 nm (filter 608) a titration curve similar to that obtained at 435 nm is found. Again an acceleration of absorbance increase is evident as 1 : 5 stoicheiometry is approached.

Titration of Copper

The absorption spectra of tetraamminecopper(II)-cyanide complexes illustrating the blue to colourless transition are shown in Fig. 5. The absorbance decrease at $\lambda_{max.}$ 605 nm is not regular with cyanide addition. Precipitation tends to occur at the 1:2 copper to cyanide molar ratio, caused presumably by the insolubility of $[Cu(NH_3)_2(CN)_2]^0$.

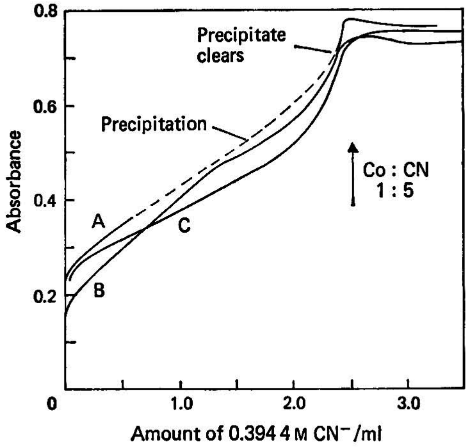

Fig. 4. Photometric titration of cobalt with cyanide in ammoniacal solution under nitrogen. Filter 601 ($\lambda_{max.T}$ = 435 nm). Taken, 2.0 ml of 0.100 2 M $Co(NO_3)_2$ solution plus *n* ml of concentrated NH_3 solution. Starting volume, 30 ml. Curve A, *n* = 4 ml; B, *n* = 6 ml; and C, *n* = 10 ml. Theoretical end-point for Co to CN ratio 1:5 = 2.54 ml.

Copper - cyanide titration curves are shown in Fig. 6. The end-points, as determined by extrapolation of the linear portions, vary somewhat with over-all ammonia concentration but the general stoicheiometry is 1:4, *i.e.*, the reaction is basically

$$[Cu(NH_3)_4]^{2+} + 4CN^- + e \rightleftharpoons [Cu(CN)_4]^{3-} + 4NH_3$$

For

$$Cu^+ + 4CN^- \rightleftharpoons Cu(CN)_4^{3-}$$

$\log \beta_4 = 30.3$ and for

$$Cu^{2+} + 4NH_3 \rightleftharpoons Cu(NH_3)_4^{2+}$$

$\log \beta_4 = 12.6$. These values show the ability of cyanide to displace ammonia but it will be seen from Fig. 6 that end-point curvature increases with increasing ammonia concentration, thus illustrating the decrease in the conditional formation constants of copper - cyanide species with increase in ammonia concentration.

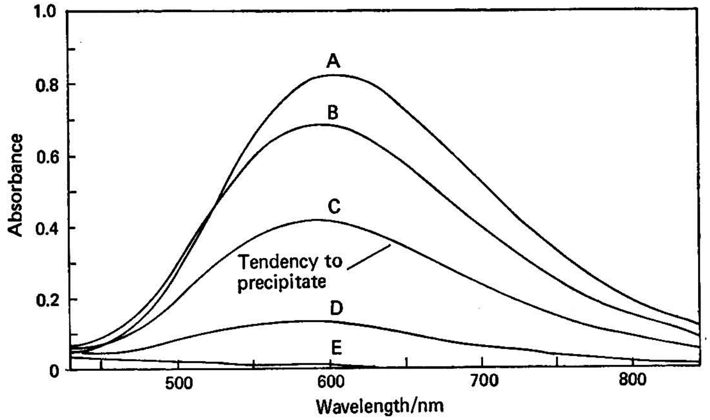

Fig. 5. Changes in the absorption spectrum of $[Cu(NH_3)_4]^{2+}$ upon the addition of cyanide. C_{Cu} = 0.004 M; C_{NH_3} = 0.30 M; cell path length = 40 mm. Molar ratios of Cu to CN: curve A, 1:0; B, 1:1; C, 1:2; D, 1:3; and E, 1:4.

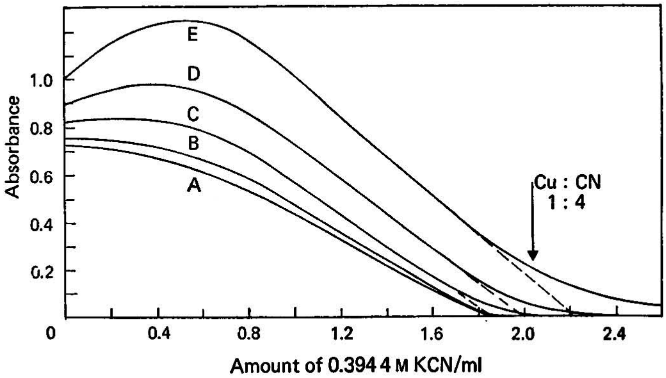

Fig. 6. Photometric titration of copper with cyanide in ammoniacal solution. Filter 607 ($\lambda_{max.T}$ = 600 nm). Taken, 2.0 ml of 0.1001 M $CuSO_4$ plus *n* ml of concentrated NH_3 solution. Starting volume, 35 ml. Curve A, *n* = 1 ml; B, *n* = 2 ml; C, *n* = 4 ml; D, *n* = 8 ml; and E, *n* = 16 ml. Theoretical end-point for Cu to CN ratio 1:4 = 2.03 ml.

Titration of Mixtures

The only really feasible determination in this system is that of nickel, and we therefore examined the effect of interferences only on the nickel titration. The interfering ions chosen were the soluble ammine formers zinc, cobalt and copper.

Titration of Nickel and Zinc

Zinc in a 1 : 1 molar ratio with nickel causes no interference. The titration curve appears as in Fig. 2, although with a less obvious break at 1:2 Ni:CN stoicheiometry.

For

$$Zn^{2+} + 4CN^- \rightleftharpoons Zn(CN)_4^{2-}$$

log β_4 = 16.7 and for

$$Zn^{2+} + 4NH_3 \rightleftharpoons Zn(NH_3)_4^{2+}$$

log β_4 = 9.1. This result is reasonable given the low log β_4 difference and high ammonia concentration existing in the titration.

Titration of Nickel and Cobalt

Under the conditions shown in Fig. 7(*a*), cobalt appears to react with 1:4 stoicheiometry and adds on to the nickel titre exactly. Small but distinct breaks occur at nickel to cyanide molar ratios of 1:2 and 1:4. The nickel is titrated first.

Titration of Nickel and Copper

Fig. 7(*b*) shows that the end-point is equivalent to the sum of nickel plus copper. The titration curve is an interesting shape and shows that nickel is titrated before copper; there is some indication of completion of nickel complexation.

$$\log \beta_4\ [Ni(CN)_4^{2-}] - \log \beta_6\ [Ni(NH_3)_6^{2+}] = 22.8$$
$$\log \beta_4\ [Cu(CN)_4^{3-}] - \log \beta_4\ [Cu(NH_3)_4^{2+}] = 17.7$$

These relationships explain why nickel is titrated first.

Discussion

The titration system described could be useful for the determination of nickel in the presence of ions that do not complex strongly with cyanide or that precipitate in dilute ammonia solution. Also, in a different sphere of interest, photometric titrations of this type are really

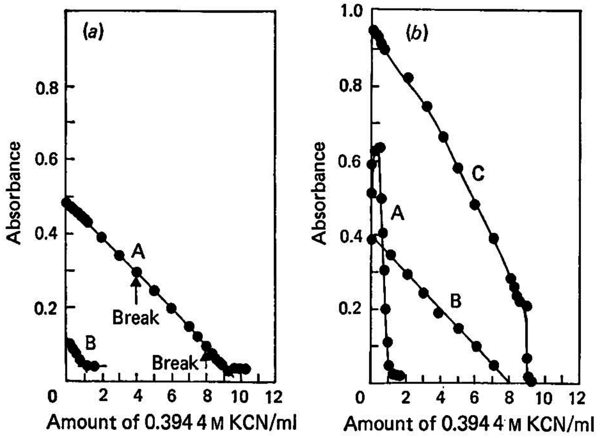

Fig. 7. (*a*), Photometric titration of a mixture of nickel and cobalt with cyanide in ammoniacal solution under nitrogen. Filter 606. Curve A: taken, 8.0 ml of 0.1004 M $NiSO_4$ solution, 1.0 ml of 0.1002 M $Co(NO_3)_2$ solution and 4 ml of concentrated NH_3 solution. Starting volume, 26 ml. Curve B, titration of 1.0 ml of 0.1002 M cobalt only under the same conditions. Theoretical end-point for Ni to CN ratio 1:4 and Co to CN ratio 1:4 = 9.17 ml; for Ni to CN ratio 1:4 and Co to CN ratio 1:5 = 9.42 ml. (*b*), Photometric titration of a mixture of nickel and copper with cyanide in ammoniacal solution. Filter 606. Curve A, 1.0 ml of 0.1001 M $CuSO_4$ solution and 4 ml of concentrated NH_3 solution. Curve B, 8.0 ml of 0.1004 M $NiSO_4$ solution and 4 ml of concentrated NH_3 solution. Curve C, 1.0 ml of 0.1001 M $CuSO_4$ solution, 8.0 ml of 0.1004 M $NiSO_4$ solution and 4 ml of concentrated NH_3 solution. All starting volumes 26 ml. Theoretical end-point for nickel only = 8.15 ml; for Ni to CN ratio 1:4 plus Cu to CN ratio 1:4 = 9.16 ml.

continuous Yoe - Jones molar ratio plots and can be valuable aids to the understanding of complexation reactions.

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Biacetyl Bis(4-phenyl-3-thiosemicarbazone) as a Reagent for the Spectrophotometric Determination of Copper

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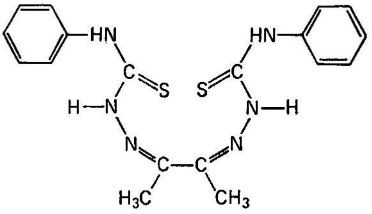
The synthesis, characteristics and analytical applications of biacetyl bis-(4-phenyl-3-thiosemicarbazone) (BBPT) are described. The reaction between copper(II) and BBPT has been studied by spectrophotometry. The reddish orange 1:1 copper - BBPT complex (ϵ = 12.7 × 10^3 l mol^{-1} cm^{-1} at 485 nm and 8.2 × 10^3 l mol^{-1} cm^{-1} at 530 nm) is formed at pH 1.8–11.9, in a solution containing 60% *V/V* of dimethylformamide. The effect of interferences was studied. A rapid and simple method for the spectrophotometric determination of copper in a white metal, in blende and in a waste water has been devised. The method is compared with others proposed for the spectrophotometric determination of copper with thiosemicarbazone reagents.

Keywords: *Biacetyl bis(4-phenyl-3-thiosemicarbazone) reagent; copper determination; spectrophotometry*

Thiosemicarbazones have been widely used for the spectrophotometric determination of metal ions and several papers have dealt with the use of dithiosemicarbazones as analytical reagents. The most studied have been derived from glyoxal,[1] bipyridylglyoxal,[2,3] cyclohexane-1,2-dione[4–6] and cyclohexane-1,3-dione.[7]

The introduction of the phenyl radical at the end of the thiosemicarbazide molecule is an excellent example of how group action in organic compounds can be modified to provide increased sensitivity; the molar absorptivities of metal - thiosemicarbazone complexes are favourably influenced by this substitution, which also causes a shift of absorption peaks towards longer wavelengths. Some phenylthiosemicarbazones have been studied as reagents[8–11]; nevertheless, compounds with the bis(phenylthiosemicarbazone) grouping have received very little attention. A search of the literature revealed that Niederschulte and Ballschmiter[12] and Ballschmiter[13] have studied some bis(phenylthiosemicarbazones) derived from biacetyl and glyoxal, varying the phenyl substituent. However, the principal application reported by these workers for this type of reagent has been the separation of complex chelate mixtures by thin-layer chromatography on aluminium oxide or by liquid chromatography.

The use of biacetyl bis(4-phenyl-3-thiosemicarbazone) (BBPT) for the selective determination of copper has been investigated, and this paper, which forms part of an investigation into the use of diphenylthiosemicarbazones as analytical reagents, describes the development of a simple procedure that has high sensitivity and selectivity. The determination of small amounts of copper in different materials is described.



BBPT

Experimental

Synthesis of BBPT

Phenylthiosemicarbazide (3.63 g) was dissolved in 100 ml of ethanol - water (1 + 1) and the solution boiled under reflux. One millilitre of biacetyl dissolved in 20 ml of ethanol and two drops of glacial acetic acid were added and the mixture was refluxed for 1 h. The solution was allowed to cool to room temperature and the product was separated by filtration. The yellow powder obtained was washed with boiling ethanol and dried in a vacuum desiccator (yield 30%). The product had a melting-point above 300 °C and elemental analysis gave the following results: C 56.2, H 5.3, N 21.9 and S 16.8%; $C_{18}H_{20}N_6S_2$ requires C 56.25, H 5.20, N 21.87 and S 16.67%.

Apparatus

A Unicam SP800 spectrophotometer was used for recording spectra in the ultraviolet and visible regions of the spectrum and a Coleman 55 (digital) instrument was used for measurements at fixed wavelengths. Quartz cells (1-cm path length) were used throughout the work.

A Philips PW 9408 pH meter, with a glass and calomel electrode pair, was used for pH measurements. Throughout this paper pH is used to denote pH-meter reading and not the actual concentration of hydrogen ions in solution.

A Metrohm E.1009 photometric titrator with a 4.0-cm glass cell was used in the determination of the p*K* of the reagent.

Reagents

All solutions were prepared with analytical-reagent grade chemicals using distilled water.

Biacetyl bis(4-phenyl-3-thiosemicarbazone) stock solution. A 0.5% *m*/*V* solution was prepared in dimethylformamide. This solution was stored in an amber-glass bottle in a refrigerator. It was diluted to 0.033% for use in the spectrophotometric procedure. The stock solution was stable for several weeks when kept under these conditions.

Copper(II) solution, 1.0003 *mg ml*$^{-1}$. This solution was prepared by dissolving copper(II) sulphate pentahydrate in water and was standardised by using a complexometric method with 1-(2-pyridylazo)-2-naphthol as a metallochromic indicator.[14]

Buffer solution, pH 4.3. Sodium acetate trihydrate (105 g) and glacial acetic acid (100 ml) were diluted to 1 l with distilled water.

Dowex 50-X8 *resin, sodium form, and Dowex* 1-X8 *resin, chloride form.*

Procedure

Determination of copper in acetate medium

To the copper solution (10–150 µg of copper) in a 25-ml calibrated flask, add 15 ml of 0.033% *m*/*V* BBPT solution in dimethylformamide, 1 ml of pH 4.3 acetate buffer and dilute to volume with water. Measure the absorbance at 485 or 530 nm against distilled water. A reagent blank has negligible absorbance at these wavelengths.

Determination of copper in moderately acidic medium

To the copper solution (10–150 µg of copper) in a 25-ml calibrated flask, add 15 ml of 0.033% *m*/*V* BBPT solution in dimethylformamide. Adjust the pH to 2.0 ± 0.05 with dilute hydrochloric acid and dilute to volume with water. Measure the absorbance at 485 or 530 nm against a reagent blank prepared simultaneously with the sample.

Determination of copper in waste water, white metal and zinc blende

Add 1 ml of 0.1 M EDTA to solutions of the first two materials and 2.5 ml of 0.1 M EDTA to solutions of zinc blende before adding the BBPT reagent solution, in order to prevent interferences by foreign ions.

Calibration graphs were prepared by using standard solutions of copper(II), treated in the same way as in the recommended procedures.

Results and Discussion

Biacetyl BBPT Reagent

BBPT has solubilities in chloroform, methanol, ethanol, nitrobenzene and dimethylformamide of 1.1, 0.2, 0.1, 1.2 and 31.3 g l^{-1}, respectively. The solubility in water is less than 0.001 g l^{-1}.

Dilute solutions in dimethylformamide (3.2×10^{-5} M) stored in darkness at low temperatures were stable for at least 1 week. A water - dimethylformamide medium (7 + 3 *V*/*V*) was used in the study of the reagent in order to prevent the precipitation of BBPT. In this medium a BBPT solution of 1.6×10^{-5} M concentration shows maximum absorption at 343 nm, with a molar absorptivity of 4.24×10^4 l mol^{-1} cm^{-1}.

Slow hydrolysis of the reagent to phenylthiosemicarbazide and biacetyl occurred in dilute solutions (1.6×10^{-5} M) at pH values of 6.0 and 10. The rate of hydrolysis of the ligand increased at pH values below 4 and above 10, but decreased when the dimethylformamide to water ratio was increased. A bathochromic shift was produced at first in alkaline medium before the reagent underwent hydrolysis.

A simultaneous potentiometric - photometric method[15] was used in the determination of the ionisation constant when the average p*K* value was found to be 10.95. This behaviour may be caused by deprotonation of thiol groups.

BBPT appears to be a tetradentate ligand with a convenient steric arrangement of its donor groups and contains a conjugated system of π-electrons connected with the donor system. The chelates of BBPT are uncharged.

A medium containing 60% of dimethylformamide and 40% of water was chosen for further experimental work. The main advantage of such a medium is that the chelates as well as the reagent were soluble in it at the concentration used in the photometric procedure. The characteristics of the most important BBPT complexes are shown in Table I.

TABLE I

CHARACTERISTICS OF BBPT COMPLEXES IN SOLUTION

Metal ion	Optimum pH	$\lambda_{max.}$/nm	Molar absorptivity/ 10^4 l mol^{-1} cm^{-1}	Colour of complex
Zn(II)	5.5–9.5	440	21.5	Yellow
Cd(II)	6.2–10.7	430	22.4	Yellow
Hg(II)	4.2–9.7	420	14.5	Yellow
Cu(II)	1.8–11.9	485	12.7	Reddish orange
		530	8.2	
Pb(II)	6.5–10.5	440	16.5	Yellow
Bi(III)	5.9–7.2	405–420	25.0	Orange
Ni(II)	2.0–10.9	450	25.5	Yellow
Fe(III)	4.8–7.5	400	31.5	Yellow
Fe(II)	4.5–7.1	400	23.5	Green
		600	3.4	
Co(II)	6.5–8.5	400	30.4	Brown
Pd(II)	1.5–10.0	428	25.3	Green
		582	2.8	

Study of Copper - BBPT System

Addition of a solution of BBPT to a solution of copper(II) ions produced a red - purple complex when the copper was in large excess; the colour changed progressively through red - purple to reddish orange as diphenylthiosemicarbazone was added in excess (Fig. 1). The absorption spectra of solutions having constant contents of the reagent but increasing contents of the metal ion show an isosbestic point at 505 nm, but as the copper content of the solution exceeds the content of BBPT, the absorptivity curves no longer pass through this point. This shift indicates that a new species is being formed in the solution and also shows that the complex formation takes place stepwise.

Stoicheiometry of the complexes

Job's curves were plotted at different pH values and wavelengths (Fig. 2). At pH 10, 6.7 and 4.1 the curves intersected at 0.5 and 0.67 molar fraction of copper. This effect indicated the existence of two complexes in which the ratios of copper to BBPT were 1:1 and 2:1, respectively. In acidic media, at pH 4.1 and 2.0, the ratio of metal to ligand differed from 1 : 1. This effect was attributed to competition of hydrogen ions for the reagent, which prevented the deprotonation of thiol groups.

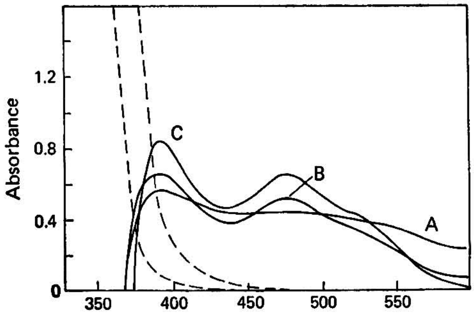


Fig. 1. Absorption spectra of copper - BBPT complexes formed from various metal to ligand ratios (pH = 6.7; acetate buffer). Copper to ligand ratios: A, 10:1 (33 μg ml^{-1} of copper); B, 1:1 (3.3 μg ml^{-1} of copper); and C, 1:10 (3.3 μg ml^{-1} of copper).

Oxidation state of copper and structure

From experimental evidence it was concluded that the reagent forms the reddish orange complex previously mentioned with copper(II). The presence of ascorbic acid in the

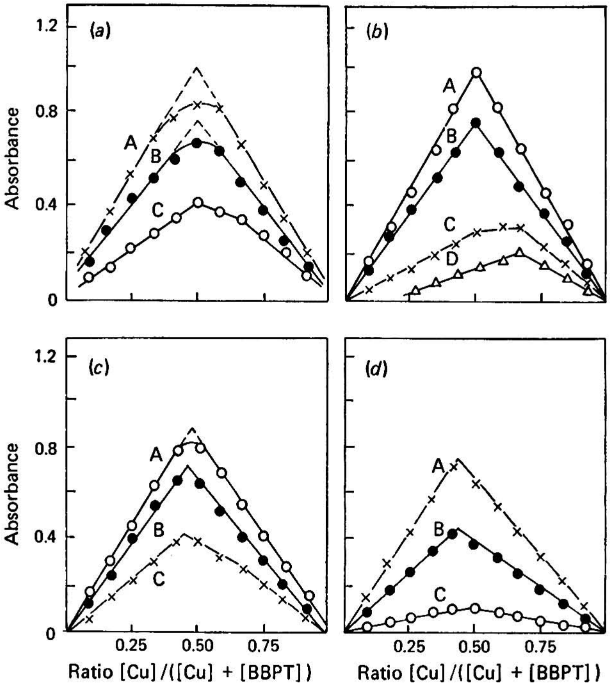


Fig. 2. Composition of copper - BBPT complexes by the continuous variation method. (*a*) pH = 10: absorbance at A, 405 nm; B, 485 nm; and C, 545 nm. (*b*) pH = 6.7: absorbance at A, 395 nm; B, 485 nm; C, 560 nm; and D, 600 nm. (*c*) pH = 4.1: absorbance at A, 410 nm; B, 485 nm; and C, 540 nm. (*d*) pH = 2.0: absorbance at A, 485 nm; B, 540 nm; and C, 580 nm.

solution before adding the BBPT reagent did not alter the absorption spectra of the complex formed at high ligand to copper ratios. Hydrogen peroxide altered the absorption peak situated at 395 nm, because oxidising agents destroy the reagent (Fig. 3). The reddish orange complex was not retained on either a cationic or an anionic ion-exchange resin, indicating that it was uncharged.

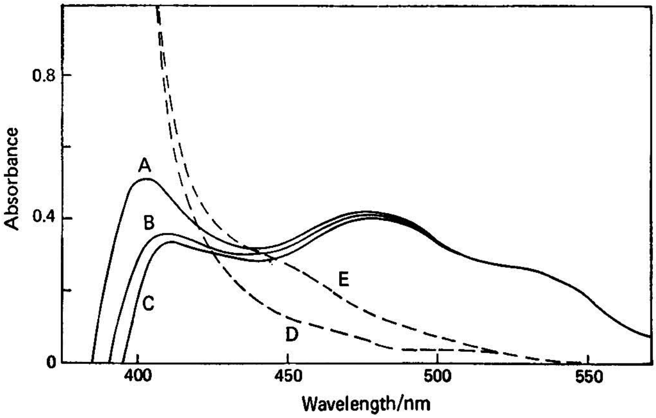


Fig. 3. Influence of hydrogen peroxide (1 ml of 30% *m*/*V*) with time on the absorption spectra of copper - BBPT complex (2 μg ml^{-1} of copper; 15 ml of BBPT, 0.033% solution): A, immediately; B, after 10 min; C, after 1 h; D, blank; and E, blank after 1 h. pH = 6.7, acetate buffer.

The exact configuration of a complex of this type, α-diketone bis(thiosemicarbazone) - copper(II), has been established.[16,17] It is apparent that BBPT acts as a tetradentate ligand; the co-ordination occurs by bonding from the first two nitrogen atoms of each phenylthiosemicarbazide residue and from the two sulphur atoms of the thiol groups so that three five-membered chelate rings are produced. This fact explains the greater stability of the reddish orange complex. This formula has been previously suggested by Bähr.[18]

When the ratio of copper to ligand was 10:1, a new yellow complex appeared in the solution in the presence of ascorbic acid. The study of the copper - BBPT system when amounts of copper exceed the amounts of the reagent will be the subject of a future report.

Influence of pH

When the pH was varied by addition of sodium hydroxide or hydrochloric acid, the absorbance remained constant over the pH range 1.8–11.9 (Fig. 4). The copper - BBPT chelate differed from cuproine analogues,[19] in that the former was formed in moderately acidic as well as basic media.

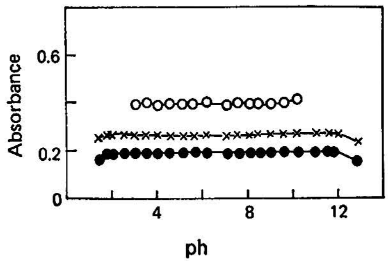


Fig. 4. Influence of pH on the formation of reddish orange copper complex. Absorbance measured at (○) 395 nm, (×) 485 nm and (●) 530 nm.

Temperature and colour development time

When the temperature varied between 15 and 60 °C the absorbances remained constant within the limits of experimental error. The complex was stable for at least 24 h over the pH range 3.6–10 and it remained stable for at least 2 h at pH 1.9 (Table II). The complex was formed immediately on addition of the reagent.

TABLE II

STABILITY OF COPPER - BBPT COMPLEX

Absorbance of solution containing 2 $\mu g\ ml^{-1}$ of copper at pH 1.9 measured against distilled water.

	Time/min					
	10	20	30	60	90	120
Absorbance at 485 nm	0.436	0.442	0.447	0.454	0.452	0.452
Absorbance of blank	0.035	0.043	0.046	0.055	0.055	0.054
Absorbance difference	0.401	0.399	0.401	0.399	0.397	0.398
Absorbance at 530 nm	0.287	0.288	0.294	0.300	0.298	0.295
Absorbance of blank	0.029	0.029	0.033	0.040	0.042	0.040
Absorbance difference	0.258	0.259	0.261	0.260	0.256	0.255

Solvent extraction

The complex can be extracted into chloroform, toluene, ethyl acetate, tributyl phosphate and benzene. The other metal - thiosemicarbazone complexes were also extracted by these solvents.

Spectrophotometric Determination of Copper with BBPT

Based on the experimental work two methods are proposed for the determination of trace amounts of copper. The photometric characteristics are similar in both instances. Beer's law is obeyed between 0.2 and 4 $\mu g\ ml^{-1}$ at 485 nm and 0.5 and 6 $\mu g\ ml^{-1}$ at 530 nm. The optimum concentration range, evaluated by Ringbom's method, is 1–3 $\mu g\ ml^{-1}$ of copper at 485 nm and 1.2–4 $\mu g\ ml^{-1}$ at 530 nm.

The reddish orange complex gave values for the molar absorptivity of $\epsilon = 12.710 \times 10^3$ $l\ mol^{-1}\ cm^{-1}$ at 485 nm and 8.260×10^3 $l\ mol^{-1}\ cm^{-1}$ at 530 nm. The sensitivities of the method according to Sandell are 0.005 and 0.0077 $\mu g\ cm^{-2}$ at 485 and 530 nm, respectively. The relative error of the method is ±0.19 and ±0.27% at 485 and 530 nm, respectively, when the pH is 6.2. At pH 2.0 ± 0.05, the method gave a relative error ($P = 0.05$) of 0.27 and 0.38%.

TABLE III

EFFECT OF FOREIGN IONS ON THE DETERMINATION OF 50 μg OF COPPER AT pH 6.2

Foreign ion	Amount tolerated/ $\mu g\ ml^{-1}$
SCN^-, Br^-, I^-, $B_4O_7^{2-}$, PO_4^{3-}, citrate, tartrate, $S_2O_3^{2-}$	2 000
Cr(III), Mo(VI), W(VI), Tl(I), As(V), Se(IV), Mn(II), Al(III), Ce(IV), Th(IV), UO_2(II), La(III), alkali and alkaline earth metals, CrO_4^{2-}, F^-	200
$C_2O_4^{2-}$	120
Pb(II), Zn(II), Cd(II), Hg(II), Pt(IV), Rh(III), Sn(II)	20
V(V)	10
Au(III)	6
Ag(I), Bi(III), Pd(II)	0.4
Ag(I), Pb(II), Hg(II), Au(III); ($S_2O_3^{2-}$, 2 ml of 0.25 N solution)	200
Sb(V); (tartrate, 50 mg)	200
Fe(III); (F^-, 180 $\mu g\ ml^{-1}$)	20

TABLE IV

EFFECT OF FOREIGN IONS ON THE DETERMINATION OF 50 μg OF COPPER AT pH 2.0

Absorbance measured at 530 nm.

Ion added	Amount tolerated/ μg ml^{-1}	Ion added	Amount tolerated/ μg ml^{-1}
Pd(II), Bi(III)	1	Cl$^-$, Br$^-$, I$^-$, SCN$^-$, CH$_3$COO$^-$, NO$_3^-$, phthalate, B$_4$O$_7^{2-}$, tartrate, citrate	10 000
Se(IV), Sb(V)	5	PO$_4^{3-}$	8 000
Pt(IV), Sn(II)	20	EDTA	4 000
Hg(II), Fe(II)	30	ClO$_3^-$	3 000
Os(VIII)	80	C$_2$O$_4^{2-}$	2 800
Rh(III)	180	F$^-$	2 200
Cr(III)	1 500	S$_2$O$_3^{2-}$	2 000
Mn(II)	2 500		
Pb(II)	3 500		
Zn(II), Cd(II), Al(III), Be(II)	8 000		
As(V) and As(III)	10 000		
Mo(VI)	>700		
Ti(IV), W(VI), Zr(IV)	>300		

For the determination of 50 μg of copper by these methods, foreign ions can be tolerated at the levels given in Tables III, IV and V. Silver and gold are reduced by BBPT to the elemental state and interfered at very low concentrations. The good results obtained by masking them with sodium thiosulphate were due to the fact that the amount of dimethylformamide contained in the samples prevented the decomposition of the metal - thiosulphate complexes.

TABLE V

ELIMINATION OF INTERFERENCES BY ADDITION OF MASKING AGENTS

pH of solution 2.0.

Foreign ion	Amount tolerated/μg ml^{-1} Without masking agent	With masking agent	Masking agent
Fe(III) ..	—	800	EDTA; 2.5 ml of 0.1 M solution
Fe(III) ..	—	300	F$^-$
Co(II) ..	—	35	EDTA; 2.5 ml of 0.1 M solution
Ni(II) ..	—	250	EDTA; 2.5 ml of 0.1 M solution
Bi(III) ..	1	2 000	EDTA; 2.5 ml of 0.1 M solution
Sb(V) ..	5	800	EDTA; 2.5 ml of 0.1 M solution
Sb(V) ..	5	2 000	Tartrate; 0.25 g
Pb(II) ..	3 500	2 000	EDTA; 1 ml of 0.1 M solution
Sn(II) ..	20	1 000	EDTA; 2.5 ml of 0.1 M solution
V(V) ..	20	50*	EDTA; 2.5 ml of 0.1 M solution
Ag(I) ..	—	200†‡	S$_2$O$_3^{2-}$; 4 ml of 0.1 N solution
Hg(II) ..	30	1 000‡	S$_2$O$_3^{2-}$; 4 ml of 0.1 N solution
Au(III) ..	—	>400‡	S$_2$O$_3^{2-}$; 4 ml of 0.1 N solution

* Absorbance measured directly after addition of reagent.
† pH adjusted with dilute nitric acid.
‡ At pH 3.0.

Applications

The method has been applied to the determination of copper in industrial effluents from a sulphuric acid plant (pyrites process), a white metal and a zinc mineral. The waste water solution was filtered through an asbestos mat contained in a Gooch crucible. The average composition of the waste water analysed (seven samples) at pH 1.4 ± 0.1 was chloride 300, zinc 27.8, iron 53.1, chromium 0.05, copper 15.6, manganese 0.5, lead 0.05, arsenic 11.0 and calcium carbonate 534 μg ml^{-1}. The copper content found by spectrophotometric determination was 15.6 ± 0.1 μg ml^{-1} (mean result of six determinations).

White metal was dissolved in aqua regia. Zinc blende was treated first with a mixture of concentrated nitric acid and bromine (2 + 1 V/V) and then with dilute nitric acid (1 + 1) and boiled to ensure complete dissolution of the ore and to remove the oxides of nitrogen as well as the excess of bromine. The silicic acid that was precipitated was dehydrated and removed. Triplicate results were obtained in both instances.

White metal 8e had the following certificate composition: copper 4.57, lead 3.13, antimony 9.5, zinc 0.04, cadmium 0.14 and tin 82.62%. The copper content found was 4.57 ± 0.02%.

A zinc blende III ore had the following certificate composition: zinc 52.99, lead 3.89, copper 0.12, tin 0.0018, mercury 0.039, arsenic 0.13, iron 6.59, manganese 1.45, cadmium 0.17, germanium 0.004, silver 0.005 and sulphur 30.04%. The copper content found was 0.124 ± 0.004%.

These results are in exact agreement with those quoted in the certificates of analysis. The method is superior to the existing colorimetric procedure involving the use of sodium diethyldithiocarbamate,[20] because it is less time consuming and involves fewer chemical manipulations.

Conclusion

Many methods are available for the determination of trace amounts of copper with thiosemicarbazone reagents (Table VI), but in our experience none of them is completely satisfactory. The great ability which the atoms of sulphur have for co-ordinating metal cations imposes a serious limitation on the use of these reagents, as it makes the establishment of selective methods of analysis difficult. This paper describes a study of the optimum conditions for a selective and sensitive spectrophotometric method for the determination of copper.

TABLE VI

CHARACTERISTICS OF COPPER - THIOSEMICARBAZONE COMPLEXES

Compound	Optimum pH	$\lambda_{max.}$/nm	Molar absorptivity/ l mol^{-1} cm^{-1}	Reference
Picolinaldehyde thiosemicarbazone	8.9–10.7	410	6 300	21
Picolinaldehyde phenylthiosemicarbazone	8.5–10	400	23 500	22
Biacetylmonoxime thiosemicarbazone	8.5–9.5	345	10 600	23
Biacetylmonoxime phenylthiosemicarbazone	8.5–9.7	360	12 700	8
Thiophenaldehyde thiosemicarbazone	4.5–8.2	372	39 000	24
Bipyridylglyoxal dithiosemicarbazone	7–9	390	9 550	25
Cyclohexane-1,2-dione dithiosemicarbazone	4–10	467	5 700	6
Biacetyl diphenylthiosemicarbazone	1.8–11.9	485 530	12 700 8 260	—

We are grateful to Professor F. Pino for his interest and encouragement.

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Potentiometric Determination of Copper in Palm Oil with a Copper(II) Ion-selective Electrode

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The applicability of a copper(II) ion-selective electrode for the determination of the copper content of crude and hydrogenated palm oils was investigated. Dry ashing was used for destroying the organic matrix and a porcelain crucible was used as container. The recovery of copper in dry ashing and the leaching of copper from the internal glazing of a porcelain crucible were investigated. A complexing antioxidant buffer was used in order to minimise the interfering effect of iron(III) on the determination of copper(II). A direct potentiometric method can be applied to determine the copper content of palm oil at a concentration higher than 10 μg kg^{-1} in the presence of 30 mg kg^{-1} of iron.

Keywords: *Copper determination*; *palm oil*; *direct potentiometry*; *copper(II) ion-selective electrode*

The deteriorating effect on the quality of oils and fats caused by the presence of trace amounts of some heavy metals is well known.[1–3] They act as pro-oxidants to catalyse the oxidation of oils and fats by the oxygen in air. The end-products of the oxidation are ketones, aldehydes and other compounds that contribute the off-flavour to oils and fats.[3–7] Copper is a strong pro-oxidant and its deteriorating effect on soybean oil even at very low levels (approximately 30 μg kg^{-1}) has been reported.[2] The effect of copper on the stability and bleachability of palm oil has been investigated[8]; the rate of oxidation during storage is strongly accelerated by the presence of trace amounts of copper. The determination of copper in palm oil is part of the routine quality control procedure.

The low levels of copper present in good quality palm oils are beyond the range of conventional flame atomic-absorption spectrophotometry or visible spectrophotometry with detection limits of about 0.1 mg l^{-1} in solution.[9,10] Large samples must therefore be used for the quantitative determination of copper by these methods and preparing the sample for chemical analysis requires a considerable time. Although the levels are above the detection limit obtainable with carbon furnace atomic-absorption spectrophotometry, and this method can be applied without prior pre-treatment,[11,12] it suffers from drawbacks such as poor reproducibility, non-atomic absorption, higher running costs and the need for higher operator skill and expensive instrumentation. The recently developed solid-state copper(II) ion-selective electrode is selective and has a limit of detection of about 10^{-8} M.[13] Thus, direct potentiometric measurement is a promising method for the quantitative determination of copper in palm oil. In this paper we describe a method of analysis in detail.

The levels of copper and iron in palm oil were found to vary between 10 μg kg^{-1} and 5 mg kg^{-1} and 0.7 and 30 mg kg^{-1}, respectively.[4] The interfering effect of iron(III) on the determination of copper(II) with a copper(II) ion-selective electrode is well known.[15–17] Hence the methods must be capable of measuring the concentration of copper(II) at the 10 μg kg^{-1} level even in the presence of 30 mg kg^{-1} of iron(III). A complexing antioxidant buffer (CAB) has been used by Smith and Manahan[16] to minimise the interfering effect of iron(III) on the determination of copper(II) with a copper(II) ion-selective electrode. However, its capacity to reduce the interference of iron(III) is not known and the solution contains a high concentration of acetate so that it is not suitable for direct potentiometric measurement. A modified buffer solution is described.

Dry ashing was employed for the destruction of the organic matrix in the palm oil in this study because wet ashing is not recommended in view of safety hazards and contamination of the solution.[18–21] Acid extraction is not desirable in a direct potentiometric method because of possible contamination and its effect on the control of the pH of the resulting solution. Controversial results for the amount of metal recovered have been reported by different groups[22–24] using porcelain crucibles for dry ashing prior to the determination of metals. We studied the recovery of copper in palm oil as well as the leaching of copper from the crucible.

The applicability of the proposed method for the determination of copper in palm oil was checked by performing atomic-absorption spectrophotometric determinations in parallel. The standard additions procedure was used for checking the matrix effect of the resulting solution on the copper determination with a copper(II) ion-selective electrode.

Experimental

Apparatus

An Orion, Model 94-29A, copper(II) ion-selective electrode and a Model 90-02 double-junction reference electrode were used with an Orion, Model 701A, digital meter for the potential measurement. A Thomas, Model 80, digital printer was used for recording the readings at 15-s or 1-min intervals, depending on the response time of the electrode. A Radiometer 26 pH meter with its associated glass microelectrode (type G2222C) and saturated calomel electrode were used for the pH measurements.

A Varian Techtron, Model 1200, atomic-absorption spectrophotometer with an air - acetylene atomiser or a Model 63 carbon rod atomiser were used for atomic-absorption spectrophotometric analysis. A 5-μl Excalibur Autopipette was used to introduce the sample solution into the carbon tube furnace and the signal was recorded with an Esterline Angus, Model 575, recorder.

An electric furnace was used for ashing the palm oil in a porcelain crucible that had been immersed in a mixture of nitric and sulphuric acids overnight before use.

Reagents

The nitric and hydrochloric acids were triply distilled in glass from analytical-reagent grade reagents. All other chemicals used in this study were analytical-reagent grade and were used without further purification. All solutions were made up with water that had been doubly distilled in glass. The stock solutions of copper(II) and iron(III) were prepared by dissolving freshly cleaned copper foil (99.9% pure) and iron wire in dilute nitric acid. The pH of the stock solution of iron(III) was adjusted to below 2 in order to keep the iron(III) in solution. Fresh standard solutions of copper(II) were prepared daily. The standard bis(1-phenylbutane-1,3-dione) - copper(II) complex was obtained from the National Bureau of Standards, USA.

The buffer solution (CAB) used for complexing iron(III) and adjusting the pH of the final solution was made up with the following composition: 1×10^{-1} M sodium perchlorate, 1×10^{-1} M potassium hydroxide, 1×10^{-2} M acetic acid, 1×10^{-2} M sodium acetate, 1×10^{-1} M sodium fluoride and 1×10^{-1} M formaldehyde.

Distilled diethyl ether and light petroleum (boiling range 60–80 °C) were used in the column-chromatographic separation.

Procedure

The palm oil samples were melted in a water-bath at 60 °C and 10 ml of the sample (approximately 9 g) were transferred into a weighed 25-ml porcelain crucible, which was re-weighed to obtain the mass of sample taken. The covered crucible was heated in a furnace for 2 h at 350 °C and then for 2–3 h at 480 °C to burn off all the carbon. The crucible was then removed from the furnace and 10 ml of the glass-distilled nitric acid were added in order to dissolve the ash. The acid was boiled off on a water-bath and 4.5 ml of perchlorate solution (containing 1×10^{-2} M perchloric acid and 1×10^{-2} M sodium perchlorate) were then added to dissolve the residue. When solution was complete 0.5 ml of CAB was added to adjust the pH of the solution to 4–5 and to complex the iron(III). The resulting solution was analysed by potentiometric and atomic-absorption spectrophotometric (flame or electrothermal atomisation) methods. Potentiometric measurements were made in the crucible at 25 °C in darkness in order to prevent errors caused by the photovoltaic effect. Before each measurement the electrodes were rinsed thoroughly with doubly glass distilled water and then dried.

The timing of the experiment was started as soon as the electrodes were immersed in the solution and readings were taken at 15-s or 1-min intervals until the reading was constant.

The blank oil was prepared by repeated extraction of palm oil with constant-boiling hydrochloric acid and 0.01% EDTA solution. The oil was then washed with doubly distilled water several times and the water was removed by heating under vacuum.

A column-chromatographic method was also employed for preparing a blank oil. The oil was dissolved in a mixture of light petroleum (boiling range 60–80 °C) and diethyl ether in the ratio of 1 : 9 and passed through a silica-gel column. The adsorbed layers in the column were then eluted with diethyl ether - light petroleum (1 + 9). The solvent was removed by vacuum distillation.

The recovery of copper was studied by adding known amounts of NBS copper standard to the melted palm oil with a known copper content in order to make up the concentration of copper to approximately 100 mg kg^{-1} and determining the copper content as described above.

Results and Discussion

Porcelain crucibles are not recommended for the quantitative determination of trace amounts of copper in organic matter[9,23] because of the leaching of copper from the internal glazing. Porcelain crucibles are inexpensive containers for dry ashing and have often been used for this purpose in different laboratories and so it was useful to find out whether or not the problem of leaching was serious in the determination of copper in palm oil. Blank crude palm oil was analysed for copper, using the same method of pre-treatment as for the sample, by carbon furnace atomic-absorption spectrophotometry and the results are given in Table I. The contamination of copper from the reagents was investigated by following the same procedure as in the sample pre-treatment in the absence of palm oil and using a platinum crucible. The copper content in the resulting solution was found to be 3.5 μg l^{-1}, which was about the same as that in the blank palm oil. Thus, leaching out of copper from the internal glazing of a porcelain crucible is not a problem in the quantitative determination of copper in palm oil. The copper content in the blank hydrogenated palm oil prepared by repeated acid extraction of a hydrogenated oil is slightly higher, which may be attributed to the incomplete extraction of copper owing to the higher viscosity and melting-point of the hydrogenated palm oil.

TABLE I

CONCENTRATION OF COPPER IN BLANK PALM OIL

Determinations carried out on a Model 1200 atomic-absorption spectrophotometer and Model 63 carbon rod atomiser operating under the following conditions: drying, 50 s at 100 °C; ashing, 20 s at 800 °C; atomisation, 3 s at 2000 °C; wavelength, 324.7 nm; spectral band width, 0.2 nm; and lamp current, 3 mA.

Sample	Pre-treatment	Number of samples tested	Mean/ μg kg^{-1}	Standard deviation/ μg kg^{-1}
Crude palm oil	Acid extraction	8	5.5	1.6
	Column chromatography	1	3.3	—
Hydrogenated palm oil	Acid extraction	7	8.1	4.8

The recovery of trace metals from the residue obtained by dry ashing without the addition of an ashing aid is a controversial problem. Loss due to volatilisation and retention on the crucible has been reported.[24] Volatilisation of copper is not a problem if the ashing temperature is kept below 550 °C[23] but retention of copper on the wall of the crucible has been reported.[24] In order to check whether or not the loss of copper in the proposed method was significant, standard samples containing a known amount of copper were pre-treated and analysed by both potentiometry and flame atomic-absorption spectrophotometry. Table II shows that close to 100% recovery was obtained. Retention of copper is not significant in the proposed sample preparation procedure.

A complexing antioxidant buffer (CAB), which consists of sodium acetate, acetic acid, sodium fluoride and formaldehyde, was used by Smith and Manahan[16] for adjusting the pH, complexing copper(II) and interfering iron(III), regulating ionic strength and providing a moderately reducing medium in the determination of trace amounts of copper in water by potentiometry. Such a solution was modified to suit our purpose. A high concentration of

TABLE II

RECOVERY OF NBS COPPER STANDARD IN PALM OIL

Sample	Number of samples tested	Amount of copper added/μg	Recovery, %	
			POT*	AAS†
Crude palm oil	2	3.2	103	93
	4	83.8	103	103
	3	90.6	103	102
	4	258.8	103	102
Hydrogenated palm oil	1	16.51	109	103
	2	68.6	93	95
	2	86.3	100	99

* POT = determination by direct potentiometry.

† AAS = determination by flame atomic-absorption spectrophotometry.

acetate ion depresses the response of the electrode by forming a complex with copper(II) and is not desirable for direct potentiometric measurement of concentrations just above the limit of detection. A low buffer capacity is adequate for adjusting the pH of the final solution under a controlled sample pre-treatment process and the matrix effect is less significant after dry ashing. Thus, 1×10^{-3} M sodium acetate and 1×10^{-3} M acetic acid were used for adjusting the pH of the final solution to 4–5. At such a low concentration, the acetate ion does not affect the response of the electrode, as shown in Table III. The selectivity ratio was estimated by the mixed solution method.[25] Sodium fluoride (1×10^{-2} M) was used for complexing iron(III) to prevent the loss of copper(II) by co-precipitation[16] and 1×10^{-2} M formaldehyde was used to provide a moderately reducing medium for stabilising the response of the electrode in very dilute copper(II) solutions. Sodium perchlorate (1×10^{-2} M) was used for adjusting the ionic strength of the resulting solution and 1×10^{-2} M potassium hydroxide was used for neutralising the acidic perchlorate solution that was used for dissolving the residue. None of these ions in these concentration ranges in CAB affects the response of the copper(II) ion-selective electrode as shown in Table III. In the presence of the modified CAB, the selectivity ratio of copper(II) to iron(III) is approximately 8×10^{-4} (as shown in Fig. 1), while the selectivity ratio required for the determination of 10 μg kg^{-1} of copper(II) in the presence of 30 mg kg^{-1} of iron(III) is approximately 3×10^{-4}. Thus, the modified CAB is capable of handling the worst combination of copper(II) and iron(III) in palm oil. Nitric acid was used in order to ensure complete oxidation of the organic matrix and the copper to copper(II), as well as to dissolve the retained copper on the wall of the crucible.

TABLE III

SELECTIVITY RATIOS OF THE COMPONENTS IN THE COMPLEXING ANTIOXIDANT BUFFER

Interfering species	Selectivity ratio*
Acetate†	4×10^{-4}
Iron(III)‡	8×10^{-4}
Formaldehyde†	$<10^{-6}$
Fluoride†	$<10^{-5}$
Perchlorate	$<10^{-5}$

* The selectivity ratio ($k^{pot}_{Cu,In}$) is defined as the ratio [Cu(II)]/[In], where In = interfering species. Concentration of copper(II) is 50 μg l^{-1}.

† In 0.1 M sodium perchlorate solution.

‡ In CAB solution.

The calibration graph, which was constructed with known amounts of copper(II) in the solution with the same matrix as the sample solution, is shown in Fig. 2. The slope of the straight line is about 30 mV per decade increase in concentration and the detection limit (when the slope is reduced to 30%) is about 10 μg l^{-1}. The deviation from Nernstian slope at low concentrations may be attributed to trace amounts of copper in the reagents, as discussed previously. The reproducibility of the electrode at various concentrations is about ±0.2 mV. The response time (which is taken as the time for the potential of the electrode to reach

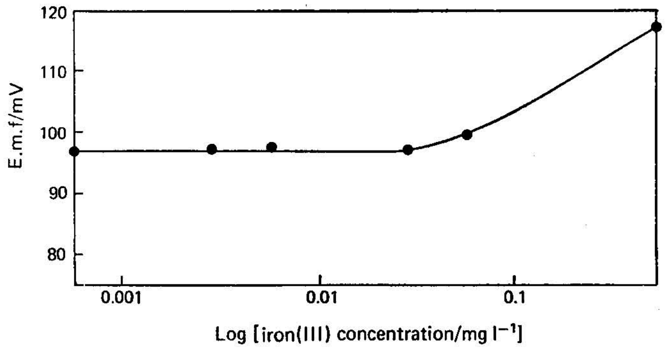

Fig. 1. Interference of iron(III) on determination of 50 μg l^{-1} of copper in the complexing antioxidant buffer.

±0.2 mV of the equilibrium value) of the electrode depends on the history of the electrode and the direction of the change of concentration. It will take only 10 min to reach the equilibrium potential if the concentration of the solution changes from 10 to 20 μg l^{-1}. However, it will take 1 h to reach the equilibrium potential if the concentration of the solution changes from 0.3 mg l^{-1} to 10 μg l^{-1}. The response time is usually fast (less than 10 min) when the concentration of copper(II) is higher than 0.1 mg l^{-1}. Only the presence of mercury(II), silver(I), sulphur(II) and strong oxidising agents will interfere in the determination[15,25] and it is unlikely that such species would be present in the sample solution.

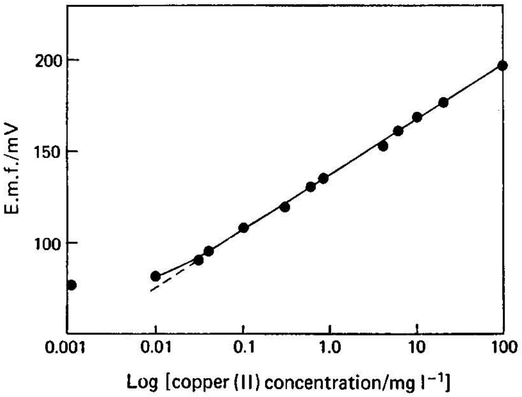

Fig. 2. Calibration graph for copper(II) in the complexing antioxidant buffer.

One of the problems in direct potentiometric measurements is the matching of the composition of the matrix of the standard solution to that of the sample solution. The presence of some foreign ions can affect the activity of copper(II). Trace amounts of phosphate (a few milligrams per kilogram) were found in some sample solutions; phosphorus is known to be present in natural impurities in palm oil as phosphatides and phosphoric acid is added to the oil during the refining process for the extraction of metals.[6,7] In order to investigate the matrix effect on the proposed method, the standard additions technique was also employed to determine the concentration of copper(II) in the sample solution. The results obtained by the two techniques are similar, as shown in Table IV, with no statistically significant difference. Thus, matrix effects are not significant in this instance.

The applicability of the method was checked with the recommended flame atomic-absorption spectrophotometric method. The sample solution was analysed in parallel by the two

TABLE IV

COMPARISON OF METHODS FOR DETERMINATION OF COPPER IN PALM OIL

Statistical test for the differences between matched pairs of copper concentrations in crude palm oils determined by atomic-absorption spectrophotometry and direct potentiometry.

Sample	Concentration of copper/mg kg^{-1}			Difference AAS−POT/ mg kg^{-1}	Difference POT−STD/ mg kg^{-1}
	AAS*	POT†	STD‡		
1	0.47	0.49	0.49	−0.02	0.00
2	0.59	0.56	0.53	0.03	0.03
3	0.24	0.20	0.22	0.04	−0.02
4	0.58	0.56	0.52	0.02	0.04
5	0.31	0.36	0.37	−0.05	−0.01
6	0.41	0.43	0.41	−0.02	0.02
7	0.22	0.21	0.20	0.01	0.01
8	0.40	0.48	0.44	−0.08	0.04
9	0.35	0.32		0.03	
10	0.31	0.34		−0.03	
11	0.35	0.30		0.05	
12	0.50	0.53		−0.03	

Methods compared	Number of samples	Mean value/mg kg^{-1}	Standard deviation /mg kg^{-1}	$t_{\text{calc.}}$§	$t_{\text{theo.}}$‖
AAS−POT ..	12	−0.042	0.040	−0.36	±2.201
POT−STD ..	8	0.014	0.023	1.72	±2.365

* AAS = determination by atomic-absorption spectrophotometry.

† POT = determination by direct potentiometry with calibration graph.

‡ STD = determination by direct potentiometry with standard additions technique.

§ The statistical test for matched pairs, $t_{\text{calc.}}$, is calculated[26] by

$$t_{n-1} = \frac{\bar{x} - \mu_0}{s/\sqrt{n}}$$

where $\mu_0 = 0$ for $H_0 : \mu_x = 0$
$H_a : \mu_x \neq 0$
s is sample variance
$\bar{x}$ is sample mean
n is number of samples.

‖ All of the theoretical t-values, $t_{\text{theo.}}$, are found at 5% significance level from Ref. 27.

methods and the results obtained were similar, as shown in Table IV, with no statistically significant difference.

The reproducibility of the method was studied by repeated analysis of a hydrogenated palm oil sample. The results are given in Table V. The relative percentage error is larger than that caused by the reproducibility of the electrode potential (0.2 mV; approximately 2%). This difference may be attributed to the inhomogeneity of the copper content in the palm oil sample and to errors introduced during the procedure. However, the reproducibility of the direct potentiometric method is better than that of the flame atomic-absorption spectrophotometric method at such low levels of copper.

TABLE V

DETERMINATION OF COPPER IN HYDROGENATED PALM OIL BY DIRECT POTENTIOMETRY AND FLAME ATOMIC-ABSORPTION SPECTROPHOTOMETRY

No. of determinations = 7.

Method	Mean copper content/ mg kg^{-1}	Standard deviation/ mg kg^{-1}	95% confidence limits/ mg kg^{-1}	Relative standard deviation, %
POT	0.14_7	0.01_5	$\pm 0.01_4$	10
AAS	0.13_7	0.02_8	$\pm 0.01_6$	20

Conclusions

Dry ashing in a porcelain crucible and a direct potentiometric method with a copper(II) ion-selective electrode can be used for determining trace amounts of copper in palm oil. The use of expensive platinum crucibles for dry ashing is not necessary. The detection limit is about 10 μg kg^{-1}, which is lower than that of the recommended flame atomic-absorption method. The method does not suffer from matrix effects and the reproducibility is reasonable. The apparatus assembly is simple, the running cost is low and the capital cost is less for the proposed method. The method can also be applied to the determination of copper in other oils and fats.

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Determination of Ethinyloestradiol in Single Tablets and Its Separation from Other Steroids by High-performance Liquid Chromatography

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A reversed-phase chromatographic system is used to separate 17α-ethinyloestradiol-1,3,5(10)-triene-3,17β-diol (ethinyloestradiol) from structurally related steroidal compounds. A direct and highly sensitive method of assay is given for uncoated tablets containing ethinyloestradiol, as used for contraception. The method is modified for sugar-coated tablets used for relief of menopause symptoms and is sufficiently sensitive to detect ethinyloestradiol if it is present with other steroids as a contaminant.

Keywords: *Ethinyloestradiol determination; tablets; high-performance liquid chromatography*

The combination contraceptive tablet contains a mixture of synthetic oestrogen and progestogen. Some sequential alternatives are commercially available. The progestogen component is formulated in milligram-scale dose, and is normally assayed by means of ultraviolet spectrophotometry,[1] or more specifically by gas - liquid chromatography. A suitable gas - liquid chromatographic column would be glass, 2 m × 6 mm i.d., filled with 3% OV-17 coating on Diatomite CLQ, 80–100 mesh, operating at 240 °C, a flame-ionisation detector being used.[2] The best results are obtained after silylating all hydroxy groups but, even so, the complete separation of the low-dose oestrogen from its combination with progestogen is seldom achieved, and there is some risk of it undergoing partial decomposition to the corresponding oestrone, as was described for mestranol by Shroff and Grodsky.[3]

Fluorimetry is a sufficiently sensitive technique to be used in order to measure a low-dose oestrogen, and a method of assay for single-component tablets of ethinyloestradiol was given by James.[4] A comprehensive account of the fluorimetric analysis of oestrogens, giving ways of overcoming the induced fluorescence and quenching effects of progestogens, was published by Miller and Duguid.[5] High-performance liquid chromatography (HPLC) has been increasingly applied to meet the demand for the rapid separation and quantitation of steroids generally, and specific separations using reversed-phase chromatography have been described by Butterfield *et al.*,[6] Bailey and Brittain[7] and King *et al.*[8]

In this paper, an HPLC technique involving the use of microfined silica-gel particles chemically bonded with octadecylsilane is described. Ethinyloestradiol in very low dose is determined in the individual tablets (uncoated) of three commercial brands, A, B, and C, as shown in Table I. The tablets are extracted into aqueous methanol solution and the extract, after clarification, is injected on to the column. The problem of the large, sugar-coated tablet, brand E, which is prescribed for the relief of menopause symptoms, is overcome by pre-extracting the ethinyloestradiol into diethyl ether. The reversed-phase chromatography requires a polar solvent to elute the non-polar phase. For ethinyloestradiol, a suitable mobile phase is found by gradually increasing the polarity of the methanol until the elution volume ($V_E - V_0$, where V_E is the total volume of eluate and V_0 the void volume) is obtained between 4 and 8 min. Alternatively, a suitable mobile phase can be obtained by plotting methanol - water concentrations against the inverse of the elution volume [$1/(V_E - V_0)$]. The preferred mixtures for separating ethinyloestradiol from other steroids vary from 65 to 80% of methanol. While emphasising that the main purpose of this work is to show that ethinyloestradiol, when formulated in very low doses, can be assayed to acceptable accuracy, it is of current interest that the same chromatographic procedure is sufficiently sensitive to detect this compound in the presence of other steroids, *e.g.*, as a possible cross-contaminant in manufactured pharmaceutical products. A wider analytical application is apparent from the separation factors given in Table II.

Experimental

Materials

Diethyl ether, analytical-reagent grade.

Methanol - de-ionised water, pH 6. Mix the components 7 + 3 *V*/*V* (or other suitable proportions) for the mobile phase and de-gas before use. Mix them 65 + 35 *V*/*V* for the extraction solvent. The methanol should be of analytical-reagent grade.

Internal standard. Prepare a solution containing 25 μg ml^{-1} of 11β,17α,21-trihydroxypregna-1,4-diene-3,20-dione (prednisolone) in the extraction solvent. Prepare a standard solution containing 500 μg ml^{-1} of prednisolone and 100 μg ml^{-1} of ethinyloestradiol in the extraction solvent, and dilute with more extraction solvent to the same concentration of ethinyloestradiol as is present in the final extract of the sample. Suggested alternatives to prednisolone are 17β-hydroxy-17α-methylandrost-4-en-3-one (methyltestosterone) and 13-ethyl-17-hydroxy-18,19-dinor-17α-pregn-4-en-20-yn-3-one (norgestrel).

The chemicals used (Tables I and II) are the British Pharmacopoeia reference standards or house standards of purity checked by use of thin-layer chromatography. Prepare 1.0 mg ml^{-1} solutions in the mobile phase. Dilute these solutions to the optimum requirement of each assay, including an internal standard where necessary.

Apparatus

The HPLC apparatus consisted of a constant-flow pump (Waters Associates Ltd., M-6000A), maintaining a delivery rate of 1 ml min^{-1} (or as required), a single-beam, variable-wavelength detector (Cecil Instruments Ltd., Model 212) fitted with an 8-μl flow-cell, and a chromatographic column, 150 × 6.3 mm o.d. (4.6 mm i.d.), made of seamless steel, packed from a slurry of 60% dry volume Spherisorb S5 ODS, average particle size of silica 5 μm (mean diameter) (Phase Separations Ltd., Queensferry, Clwyd), in methanol, introduced through a pre-column and pressurised to 5 000 lb in^{-2} by using the procedure described by Cox *et al.*[9] The ultraviolet monitor was set at wavelengths varying from 210 to 215 nm. Injections were made from a 10-μl syringe by using a stop-flow technique. The chromatograms were obtained on a recorder, using a chart speed of 5 mm min^{-1}. Work was carried out at ambient temperature. Other apparatus included a steam-bath (or rotary evaporator) and an ultrasonic bath (Dawe Sonicleaner, Model 6441A).

Assay for Uncoated Tablets

Place the single tablet in a 10-ml stoppered test-tube, introduce 2 ml of the internal standard solution by pipette and stopper the tube. Disintegrate and dissolve the bulk of the tablet by placing the tube in an ultrasonic bath for 20 min at room temperature. Complete the dissolution of the active components of the tablet by shaking the tube for a further 10 min. Next, clarify the extract by centrifuging it for 5 min at 2 000 rev min^{-1} and inject 4 μl of clear solution into the chromatograph. Elute the active components in the mobile phase, then record the chromatogram with the ultraviolet detector set at about 212 nm. Measure the ethinyloestradiol content of the tablet by comparing the peak height with that obtained by injecting 4 μl of diluted prednisolone standard solution, containing the dose level of ethinyloestradiol in 2 ml, using the more precisely measured peak height of the prednisolone in order to correct for any variation between injections.

Assay for Sugar-coated Tablets

Place the tablet in a 25-ml beaker, add 10 ml of methanol - water (1 + 1), and warm for 15 min on a steam-bath with occasional swirling, using a flattened glass rod (if necessary) to disintegrate the tablet. Cool the beaker to room temperature and transfer the contents quantitatively into a 100-ml separating funnel, rinsing the glassware three times with 3–5-ml portions of diethyl ether. Add 30 ml of diethyl ether, shake the funnel for 1 min, then allow the contents to settle. Decant the ethereal extract into a 150-ml calibrated flask and repeat the operation with two further portions of 30 ml of diethyl ether. Draw off any remaining ethereal extract by using a Pasteur pipette and add this to the bulk. Evaporate the solvent extract on a steam-bath, using a current of nitrogen. Next reduce the volume to about 5 ml, then evaporate the residual solvent at room temperature. Dissolve the residue in 2 ml of the mobile phase. Finally, inject 4 μl of this solution into the chromatograph and measure the content of ethinyloestradiol by following the procedure under Assay for Uncoated Tablets, but with a suitable alternative standard to prednisolone.

Results and Discussion

Calibration Graph

A calibration graph of peak height against concentration was plotted over the range 0–100 μg ml^{-1} of ethinyloestradiol in the mobile phase, and a linear graph was obtained down to the limit of detection of 0.5 μg ml^{-1}.

Assay of Ethinyloestradiol in Commercial Tablets

The ethinyloestradiol content of individually assayed tablets from each of five proprietary brands, A–E, and the results for the spiked powders, B′, D′, E′ and F, are given in Table I. The standard deviation for six injections of the internal standard (prednisolone) was 2.37%. Brand C, containing norgestrel, was measured without the internal standard, as in the chromatogram shown in Fig. 1. The assay figures for D(1) and D(2) were obtained independently by two analysts.

TABLE I

ANALYSIS OF FORMULATIONS CONTAINING ETHINYLOESTRADIOL (EOD)

		Amount of ethinyloestradiol/μg	
Sample*	Mass/mg	Claim	Found
A	62	10	11.5, 10.7, 10.7, 10.7, 10.5
B	142	10	8.7, 8.3, 8.3, 7.8, 7.8
B′	142	10	9.9 (mean of 20 determinations), $s = 4.4\%$
C	130	30	29.9, 29.3, 29.3, 29.3, 28.7
		150 NGT†	161, 161, 157, 157, 154
D	159	100	(1) 98.5, 95.0, 95.0; (2) 97.5, 97.5, 95.8, 95.8
D′	158	100	100.8
E	420	10	10.0, 9.8, 9.8, 9.8, 9.6
E′	420	10 + 20	28.7, 28.2
F	100	10	(1) 10.0, 10.0; (2) 9.4, 9.3

* A, Uncoated tablets, EOD, 10 μg; B, uncoated tablets, EOD, 10 μg + ethisterone, 10 mg; B′, placebo powder + EOD, 10 μg + ethisterone, 10 mg; C, uncoated tablets, EOD, 30 μg + norgestrel, 150 μg; D, sugar-coated tablets, EOD, 100 μg; D′, sugar-coated placebo tablets + EOD, 100 μg; E, sugar-coated tablets, bromvaletone, 30 mg + carbromal, 90 mg + EOD, 10 μg; E′, E + EOD, 20 μg; F, placebo powder + EOD, 10 μg.

† Norgestrel.

Recovery of Ethinyloestradiol

It is apparent from Table II that where ethinyloestradiol is well separated from another steroid, for example norgestrel in Fig. 1, a comparison of peak height with that of ethinyloestradiol from a standard solution is sufficient. Where components such as ethinyloestradiol and 17β-hydroxy-17α-pregn-4-en-20-yn-3-one (ethisterone) are less efficiently separated, as seen in Fig. 2, a comparison with a standard solution similar in composition to the sample is preferred. This procedure was used to calculate the recovery and the standard deviation for B′. The placebo powder used in all recovery experiments except D′ (mainly sugar-coat of lactose) had the following composition: lactose, 90%; starch, 5%; carboxymethylcellulose, 2%; magnesium stearate, 2%; and talc, 1%. The recoveries of 100% for F(1) and 93.5% for F(2) were obtained by (1), dry mixing 2.00 mg of ethinyloestradiol with 20 g of the placebo powder, then taking two separate 100-mg aliquots, and (2), by mixing 2 ml of a 100 μg ml^{-1} solution of ethinyloestradiol in methanol with 2 g of the powder, drying in vacuum for 2 h, restoring the mixture to ambient temperature, then taking two 100-mg portions of the spiked mixture through the procedure under Assay for Uncoated Tablets. Although the results indicate satisfactory recoveries, the difficulty of pre-mixing a micro-amount of an oestrogen with large amounts of tablet excipients has been discussed by Brunner,[10] who gives the impression that no method is ideal. In accordance with this view, our results obtained by using different techniques for recovering ethinyloestradiol, even at the 10-μg level, when added to both sugar-coated and uncoated tablets, appear to be sufficiently reliable for the purpose of quality control.

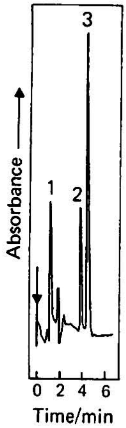

Fig. 1. Separation of ethinyloestradiol from norgestrel in tablet extract C. 1, Solvent front; 2, EOD; 3, norgestrel. Column, Spherisorb S5 ODS. Mobile phase, methanol - water (4 + 1). Flow-rate, 1 ml min^{-1}. Detector, ultraviolet at 212 nm. Sensitivity, 0.02 a.u.f.s.

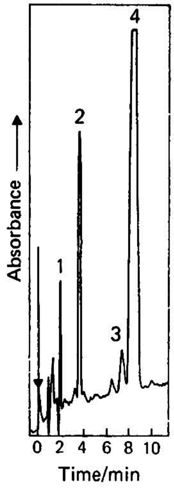

Fig. 2. Separation of ethinyloestradiol (EOD) from ethisterone in tablet extract B. 1, Solvent front; 2, prednisolone internal standard; 3, EOD; 4, ethisterone. Column, Spherisorb S5 ODS. Mobile phase, methanol-water (65+35). Flow-rate, 1 ml min^{-1}. Detector, ultraviolet at 212 nm. Sensitivity, 0.02 a.u.f.s.

Feasibility and Specificity

The need for a suitable fluorescence detector for the analysis of oestrogens in contraceptive tablets was declared by Miller and Duguid,[5] on the reasonable basis that the ultraviolet detector is insufficiently sensitive at the absorbance maximum of 280 nm. However, an eight-fold improvement in the sensitivity is obtained by reading at 212 nm, making the assay of 10 μg of ethinyloestradiol just possible. For compounds with retention times similar to those illustrated in Fig. 2, a further advantage comes from the fact that ethisterone has an absorbance minimum at about 210 nm. The methanol used must be optically acceptable, *i.e.*, a 1-cm layer, when compared with water, should have a transmittance of not less than 20%, a standard normally met by analytical-reagent grade material, but guaranteed only for spectroscopic grades. An important compensation for using a non-specific wavelength is that it permits the simultaneous determination of steroids, as in tablet C of ethinyloestradiol and norgestrel shown in Table I and in Fig. 1, and this principle can be applied to the detection of cross-contaminants.

Cross-contamination by Ethinyloestradiol and Other Steroids

The potential risk involved in ingesting 6 μg of ethinyloestradiol four times a day from contaminated paracetamol tablets was expressed by Edmond.[11] A specific example of using HPLC was to search for a cross-contaminant was given by Phillips.[12] This useful technique, combining adequate separating power with high sensitivity, enables a significant level of ethinyloestradiol to be detected. As other steroids are equally suspect, these too could be monitored in the same exercise, although preferably by setting the detector to their appropriate wavelength, a guide to which is given by Bailey.[13] Obtained from a current exercise carried out on Ascorbic Acid Tablets BP (500 mg), of average mass 848 mg, the chromatograms in Fig. 3 show the methanolic extracts of the powdered tablets before and after spiking with the equivalent, per tablet, of 2 µg of ethinyloestradiol and 25 µg of each of four other steroids. The result absolves the sample of any consequential contamination by ethinyloestradiol, or by any of the three steroids eluted after it.

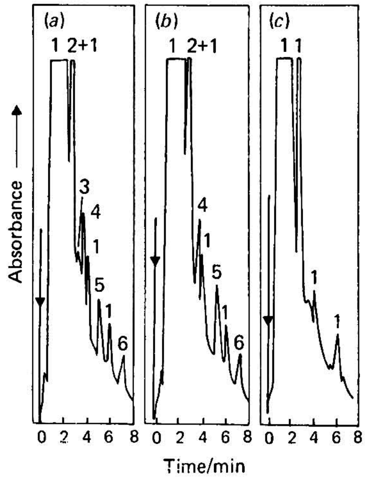

Fig. 3. A, Detection of ethinyloestradiol, 2 µg, with four other steroids, added to an ascorbic acid tablet, 500-mg dose. 1, Dried ethereal extractives from the tablet; 2, prednisolone (25 µg); 3, EOD (2 µg); 4, ethisterone (25 µg); 5, methyltestosterone (25 µg); 6, progesterone (25 µg) dissolved in 1 ml of methanol. B, Chromatogram of A without the EOD spike. C, Chromatogram of the tablet extractives only (1 = major peaks). Column, Spherisorb S5 ODS. Solvent, methanol - water (7+3). Flow-rate, 1.5 ml min^{-1}. Detector, ultraviolet at 210 nm. Sensitivity, 0.02 a.u.f.s.

Reversed-phase Chromatographic Separation of Steroids

The separation factors (ratios) given for the steroids classified in Table II have been calculated by dividing their k' values (capacity factors as discussed by Shroff[14]) by the k' value of

TABLE II

SEPARATION FACTORS RELATIVE TO 1.0 FOR ETHINYLOESTRADIOL

Androgen	Factor	Corticoid	Factor	Oestrogen	Factor	Progestogen	Factor
Fluoxymesterone	0.84	Dexamethasone	0.49	Equilin	0.82	Ethisterone	1.12
Methyltestosterone	1.76	Hydrocortisone	0.45	Mestranol	3.15	17α-Hydroxyprogesterone	1.10
Stanolone	1.86	Hydrocortisone 21-acetate	0.60	α-Oestradiol	1.12	DL-Norgestrel	1.24
Testosterone	1.36	Prednisolone	0.42	17β-Oestriol	0.44	Norethisterone	1.00
Testosterone propionate	4.60	Prednisolone 21-stearoylglycolate	—	Oestrone	0.94	Norethisterone acetate	1.84

ethinyloestradiol. The steroids listed were chromatographed from 1 mg ml^{-1} solutions in methanol - water (7 + 3) at a flow-rate of 1 ml min^{-1}; stanolone, with the lowest ultraviolet absorbance, was the least readily detected.

The ratios for most of the compounds in Table II follow the polarity of their functional groups and the number of such groups contained in their molecular structure. The polarity of the functional groups typically associated with steroids increases in the order $-OCH_3$, $-COOR$, $-C{=}O$ and $-OH$, and it is seen that prednisolone and all other trihydroxysteroids in Table II elute before while most of the androgens and the progestogens elute after ethinyloestradiol. The retention of the steroid on the column is shown to increase after esterification, and prednisolone 21-stearoylglycolate is unsuccessfully eluted by using the conditions given, requiring instead a mobile phase of methanol - water (9 + 1) at a flow-rate of 2 ml min^{-1}.

Conclusions

It has been shown that by using reversed-phase chromatography, steroids of similar structure can be separated. By using an ultraviolet detector capable of reading down to 210 nm, it has been possible to determine individually the content of ethinyloestradiol down to a limit of 10 μg. The method of assay for the uncoated tablets is rapid, although the results should be checked for their reproducibility. The alternative procedure for the sugar-coated tablets, which has been shown to give satisfactory recoveries, provides the basis of a general method of assay. A fluorescence detector could prove to be still more sensitive for ethinyloestradiol, but acceptable reproducibility of readings would be an essential requirement. The importance of checking pharmaceutical products for trace amounts of ethinyloestradiol and other steroids manufactured on the same premises is emphasised. The column described in this paper is particularly suited to routine steroid analysis in a quality-control laboratory; several hundred injections have been made without appreciable loss in sensitivity or separating power, and its application to very low doses of ethinyloestradiol in tablets has been a useful specialised study.

We thank Janice Avery for assisting in the recovery experiments and for checking the thin-layer chromatographic purity of the reference chemicals used. We also thank the Government Chemist for permission to publish this paper.

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Differential Electrolytic Potentiometry with Periodic Polarisation

Part XXIV.* An Appraisal of the Amplitude-biassed Mode

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A simple device for amplitude biassing a periodic waveform without distortion has been developed to overcome the difficulty with earlier instrumentation of obtaining more than a 2% bias. Amplitude-biassed differential electrolytic potentiometry has been compared with zero-current potentiometry, classical d.c., symmetrical periodic and time-biassed periodic differential electrolytic potentiometry in oxidation - reduction titrimetry for electrode reactions of various rates, and in acid - base titrimetry. The behaviour of individual electrodes with reference to zero-current and standard electrodes has been examined. The behaviour observed is in accord with theoretical prediction, and is analogous to the application of a d.c. offset to symmetrical periodic polarisation. The advantages of rapid potential equilibration and extended electrode life between activations accrue, but with appreciable bias the end-point periodic signal deviates from the equivalence point.

Keywords: *Differential electrolytic potentiometry; periodic polarisation; amplitude-biassed mode*

In previous studies of biassed periodic differential electrolytic potentiometry[1] the available instrumentation[2] did not permit more than a small amount of bias to be applied in shaping the waveform, although d.c. offset could be examined.[1] Devices have been developed to overcome this limitation, and the time-bias method will be the subject of a further paper. Time-biassing[1] preserved the advantages of both symmetrical periodic[3] and classical d.c. differential electrolytic potentiometry. It will be shown that amplitude biassing, while retaining the advantages of symmetrical periodic polarisation, retains the disadvantages of classical d.c. differential electrolytic potentiometry for certain reactions and for the reasons expounded,[1] and also the deviations incurred by a d.c. offset.[1] It has been shown[1,3] that with a pure d.c. input to the electrodes there is no periodic output, and with perfectly symmetrical input waveforms free from offset and distortion there is no d.c. component in the output. Any distortion, bias or offset in the input periodic waveform results in both d.c. and periodic outputs, and the presence of 2% or more distortion, bias or offset causes progressive deterioration of the periodic differential electrolytic potentiometric end-point. Offset, moreover, shifts the single or double electrode end-point away from the equivalence point, eventually splitting the peak type of curve into two peaks for twin electrodes.

Experimental

Apparatus

Most of the apparatus has been described before.[2] The amplitude-biassing circuit is shown in Fig. 1. The input is a perfectly shaped symmetrical periodic waveform produced by the Feedback TWG 300 generator, and the wipers on the two potentiometers RV_1 and RV_2 control independently the amplitude of each half-cycle without disturbing the precise equality in the time duration of the two half-cycles, and without introducing harmonics or other distortion over the range 0–96% bias. Distortion in the half-cycle of smaller amplitude is evident at 98% bias. A 33% biassed triangular wave is shown in Fig. 2. The theoretical relationship between the d.c. component and the percentage bias for amplitude bias, when the peak-to-peak current, I_{p-p}, is as follows:

Triangular wave— $$I_{d.c.} = I_{p-p} \times \frac{\%\ \text{bias}}{400}$$

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* For details of Part XXIII of this series, see reference list, p. 175.

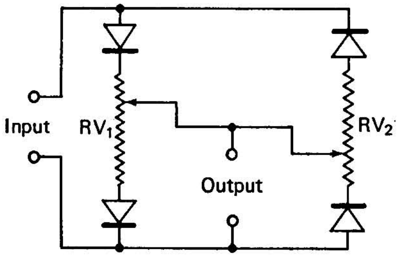


Fig. 1. Amplitude-shaping circuit. Diodes 1N4004. $RV_1 = RV_2 = 5\ k\Omega$, carbon. Input from TWG 300 waveform generator.

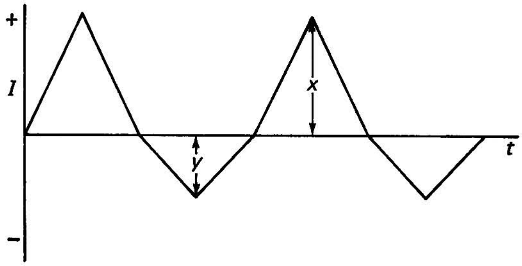


Fig. 2. Triangular wave with 33% positive amplitude bias. Percentage bias = $100\ (x - y)/(x + y)$.

Sine wave—

$$I_{d.c.} = I_{p-p} \times \frac{\%\ \text{bias}}{100\pi}$$

Experimental measurements using a standard resistor in place of the cell gave straight-line relationships between $I_{d.c.}$ and percentage bias at all frequencies, but the higher the frequency the more closely did the experimental line, *e.g.*, 300 Hz triangular wave, slope 0.970, standard deviation 0.248 mV, approach the theoretical line, slope unity. At low frequency, $I_{d.c.}$ measured was less than $I_{d.c.}$ calculated, being about 10% down at 3 Hz, slope 0.896, standard deviation 0.4 mV. The titration cell was a 250-ml beaker with the top sawn off and with a machined Perspex lid drilled to accommodate the diverse electrodes,[2] a nitrogen bubbler and an overhead stirrer. Differential electrolytic potentiometric electrodes were twinned, two platinum wires sealed into the same soda-glass sheath and the connections immobilised by filling the tube with paraffin wax. Other electrodes, single for zero-current and twinned for differential measurement, were fabricated as described elsewhere.[4] In order to compare results precisely with those of established methods, in any titration twinned indicator electrodes were provided for amplitude-biassed periodic differential electrolytic potentiometry, classical d.c. differential electrolytic potentiometry and mark-to-space (time) biassed differential electrolytic potentiometry, and two single zero-current indicator electrodes, both for zero-current potentiometric reference, and as zero-current electrodes against which the overpotential of individual polarised electrodes could be measured. A high-capacity saturated calomel electrode was connected by a double-junction salt bridge to the titration solution and served as the reference electrode. The multiplicity of electrodes and the polarisation circuitry necessitated careful coaxial screening to prevent current-field interactions, and the calomel cell and salt bridge were wrapped with aluminium foil and the whole screening earthed at the optimum point. Carefully designed switching units avoiding the danger of ground loops were used to provide simultaneous, sequential or alternating monitoring of the various electrode systems. A block diagram of the general assembly is shown in Fig. 3, and detail of individual switch boxes in Fig. 4. The periodic component of the electrode output was displayed on a double-channel high-precision measuring oscilloscope, whilst the d.c. signals were monitored via a high-input impedance pH meter (EIL 39A) with a time constant that was long compared with the lowest periodic frequency involved.

Reagents

Aristar or AnalaR reagents were used without further purification. Solutions were prepared by methods previously described.[2,5] Carbon dioxide free solvents and reagents were used for acid - base titrations.

Procedure

Titrations were conducted under a continuous stream of oxygen- and carbon dioxide-free nitrogen. The pipette-dilution method[2,6] was employed because only the equivalence point region is of interest, and simultaneous zero-current potentiometric and differential electrolytic potentiometric methods of proven accuracy provided precise information on the exact

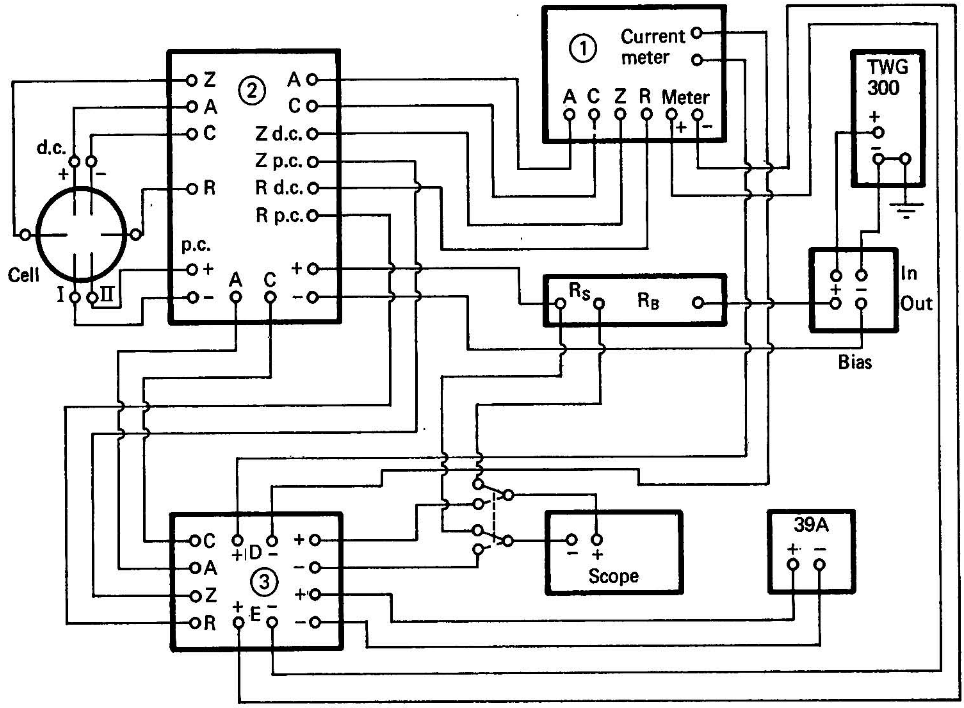


Fig. 3. Block diagram of experimental assembly. All wiring is co-axial, and the single earthing point is on the signal generator. TWG 300, precise waveform generator, output 80 V p.–p. Bias, amplitude-biassing unit of Fig. 1. R_B, decadic ballast resistor. R_s, standard resistor, the voltage drop across which gives the periodic current monitored by the oscilloscope.

Box 1, d.c. differential electrolytic potentiometry box. This contains the high-precision constant-current source,[8] and a standard resistor to which the "current-meter" terminals are connected so that the d.c. differentiating current can be measured. The "meter" terminals present the potential to be measured. Switching is included in this box for polarity and for selecting the potential to be measured: d.c. anode, A, *versus* S.C.E., R; d.c. cathode, C, *versus* S.C.E.; $E_{\Delta \text{d.c.}}$ (A *versus* C); and zero-current indicator electrode, Z, *versus* S.C.E.

Box 2, the electrode-selection switching, is shown in detail in Fig. 4 (*a*). Electrodes I and II are the periodic differential electrolytic potentiometric electrodes.

Box 3, the potential and measuring instrument selection switching is shown in detail in Fig. 4 (*b*).

Cell, shown with one pair of d.c. differential electrolytic potentiometric electrodes, one pair of p.c. differential electrolytic potentiometric electrodes, one zero-current electrode and one reference (S.C.E.) electrode. Scope, a Hewlett-Packard double-channel precision measuring oscilloscope, Model 1200A. 39A, a high-input impedance EIL pH meter used in the mV mode.

equivalence point. An aliquot of 25 ml of the titrand was pipetted into the titration vessel which was already charged with any necessary reagents and solvents to give a constant end-point volume. This operation was followed by pipetting a 25-ml aliquot of titrant of concentration 0.4% less than that equivalent to the titrand. The region ±0.1 ml around equivalence was then traversed with the titrant delivered from a micro-burette, or with 10- or 100-fold diluted titrant. After addition of each increment of titrant, the following measurements were made:

(1) potential of zero-current electrodes with respect to the saturated calomel electrode;

(2) potentials of anode and cathode of d.c. polarised differential electrolytic potentiometric electrodes with respect to the saturated calomel electrode;

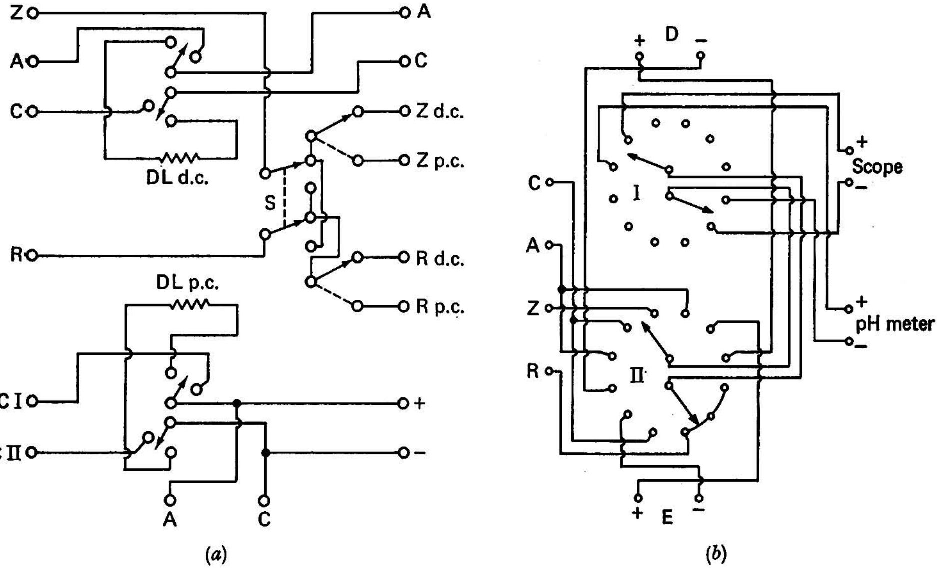
(3) the differential d.c. potential between anode and cathode of the d.c. polarised electrodes;

(4) when used, the d.c. component from time-biassed periodic current (p.c.) polarised electrodes[1];

(5) labelling the two amplitude-biassed electrodes I and II, the d.c. component of the potentials of:
  (*a*) electrode I with respect to the saturated calomel electrode;
  (*b*) electrode II with respect to the saturated calomel electrode, these measurements yielding the total potential deviation from the formal potential;
  (*c*) electrode I with respect to a zero-current indicator electrode;
  (*d*) electrode II with respect to a zero-current electrode, these measurements giving the sum of the mass and charge-transfer overpotentials for each electrode;
  (*e*) electrode II with respect to electrode I, giving the differential d.c. potential;

(6) the p.c. component of the potentials of:
  (*a*) electrode I with respect to the saturated calomel electrode;
  (*b*) electrode II with respect to the saturated calomel electrode;
  (*c*) electrode I with respect to a zero-current indicator electrode;
  (*d*) electrode II with respect to a zero-current indicator electrode;
  (*e*) electrode II with respect to electrode I.

Thus, 15 measurements were made at each point, and in the instances of zero-current and d.c. polarised electrodes time was allowed for the drift rate to drop below 1.0 mV min^{-1}



(*a*) (*b*)

Fig. 4. (*a*) Switch box 2: A, d.c. anode; C, d.c. cathode; Z, zero-current indicator electrode; $Z_{d.c.}$ and $Z_{p.c.}$, for use in obtaining the current-generated overpotential; R, reference (S.C.E.) electrode; $R_{d.c.}$ and $R_{p.c.}$, for use in observing single-electrode potentials; PCI and PCII, the two p.c. polarised electrodes; and $DL_{d.c.}$ and $DL_{p.c.}$, dummy load resistors to maintain a constant drain on the current sources when the electrodes are switched out of circuit. Switch S (DPDT) allows choice of reference to S.C.E. or a zero-current electrode. (*b*) Switch box 3, two two-pole six-way switches: I selects the measuring instrument, oscilloscope or pH meter; II selects the electrodes and the p.c. or d.c. components of the output signals from the p.c. electrodes (selection of d.c. electrodes is made in Box 1), "anode" *versus* reference (A *versus* R), "cathode" *versus* reference (C *versus* R), zero-current indicator *versus* reference (Z *versus* R), and electrode I — electrode II and selects the d.c. or p.c. components by choosing the measuring instrument. Input D accepts the output from Box 1 current-meter terminals so that the d.c. polarisation current can be measured and set by the controls on Box 1. Input E accepts the d.c. output signals.

Results and Discussion

Rehearsal of the multiple examination of the entire spectrum of titration reactions and electrode kinetic parameters would be too tedious, so examples of oxidation - reduction reactions involving combinations of the various groups of electrode reaction speeds[7] are offered, together with an example of an ion-combination reaction involving moderate to fast electrode processes.

Fast electrode processes can be illustrated by the copper(II) - copper(I) titrand and bromine - bromide titrant reactions, the latter being the reactive species in titration in acidic bromide media with potassium bromate. Molecular oxygen must be carefully excluded in these titrations. Platinum electrodes are kept clean in this system, the electrode processes before and after the equivalence point are so fast as to be virtually diffusion-controlled, and the normal d.c. and symmetrical p.c. curves are peaks.

For twin electrodes the effect of amplitude bias on the periodic differential electrolytic potentiometric output component is the same as the effect of adding a d.c. offset to a symmetrical periodic input. As the bias is increased the p.c. differential potential curve deteriorates: the peak height decreases, the peak broadens and eventually splits into two peaks at high bias. In this type of curve the equivalence point is at the minimum of the trough until the bias becomes very high, when deviation occurs. Before splitting, the p.c. peak deviates from equivalence to give negative errors with a positively biassed input and to give positive errors with a negatively biassed input.

The d.c. component of the output from twin electrodes appears when any bias is applied, and two effects are displayed, depending on the amount of bias. For low biasses, as predicted, a second derivative curve is produced by the periodic differentiation of the d.c. differentiation. At large biasses the titration curve lapses into the normal first derivative peak as the d.c. differentiation swamps the p.c. differentiation, which is a function of the power factor of the electrode double-layer capacitors, and now there is no error in the d.c. component end-point. The effect of increasing bias on the p.c. component and the d.c. component of the twin indicator electrode output is illustrated in Fig. 5.

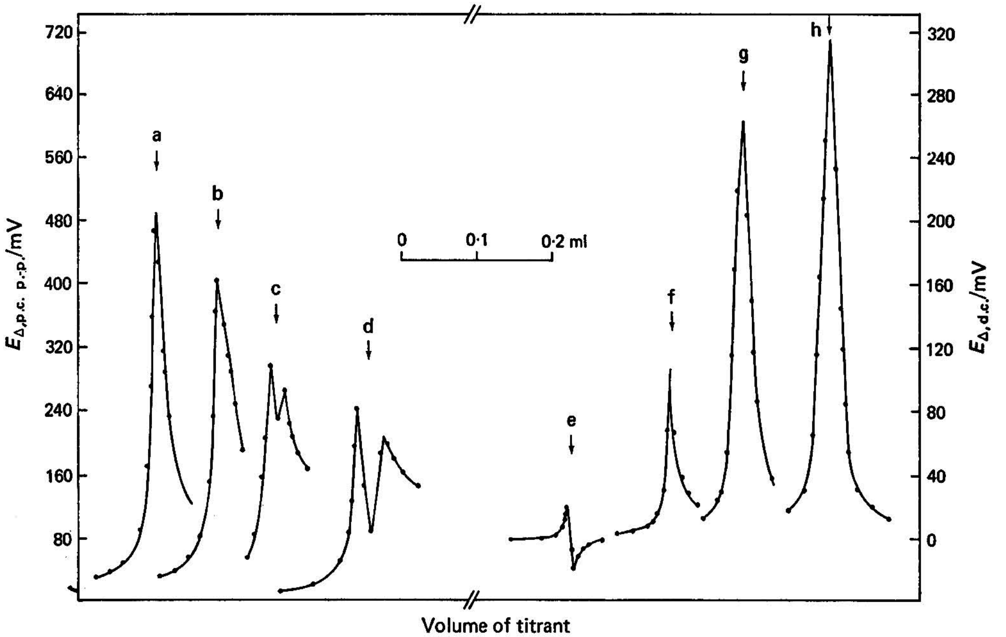


Fig. 5. Differential curves for fast electrode processes. Titration of copper(I) in acidic bromide medium with bromate. Triangular wave, frequency 3 Hz, p.c. current density 90 μA cm^{-2} p.–p. Periodic components: (a) 5%; (b) 25%; (c) 50%; and (d) 75% amplitude bias. Direct components (e) to (h) corresponding to (a) to (d). The arrows indicate the true equivalence points.

The d.c. and p.c. components of individual electrodes can be referenced to a constant potential, a standard electrode such as a saturated calomel electrode, and can effectively monitor both the changes in bulk concentrations of the active species and the changes in contact-layer concentrations at the electrode surface occasioned by electrolysis, $\Delta E = \eta_{c_B} + \eta_{c_S} + \eta_a$. Or they can be referenced to a zero-current indicator electrode, in which case only the true overpotential caused by electrolysis is observed, $\eta_{c_s} + \eta_a$. These measurements emphasised the difference between a small amplitude bias and a large bias, and for the bromate - copper(I) titration the observed potential with respect to a zero-current indicator electrode is essentially η_{c_s}, the charge-transfer overpotential being small or negligible. With the amplitude-biassed input, electrodes can be identified as plus and minus, or anodic and cathodic.

Taking the periodic components first, referenced to a saturated calomel electrode, for small biasses each electrode gave a sharp first-derivative peak, that of the anode being higher, because of the two-electron reaction, than that of the cathode, with a barely detectable deviation from the true equivalence point. Increasing the bias caused three effects: the peak height diminished for both electrodes, the peaks moved farther apart with the expected displacement along the volume axis, positive for the cathode and negative for the anode, and the peaks broadened. Referenced to a zero-current indicator electrode, the true current-generated overpotential shows the same form of behaviour, but now the potentials are lower because the effect of changes in the bulk concentrations has been subtracted. The curves are shown in Fig. 6.

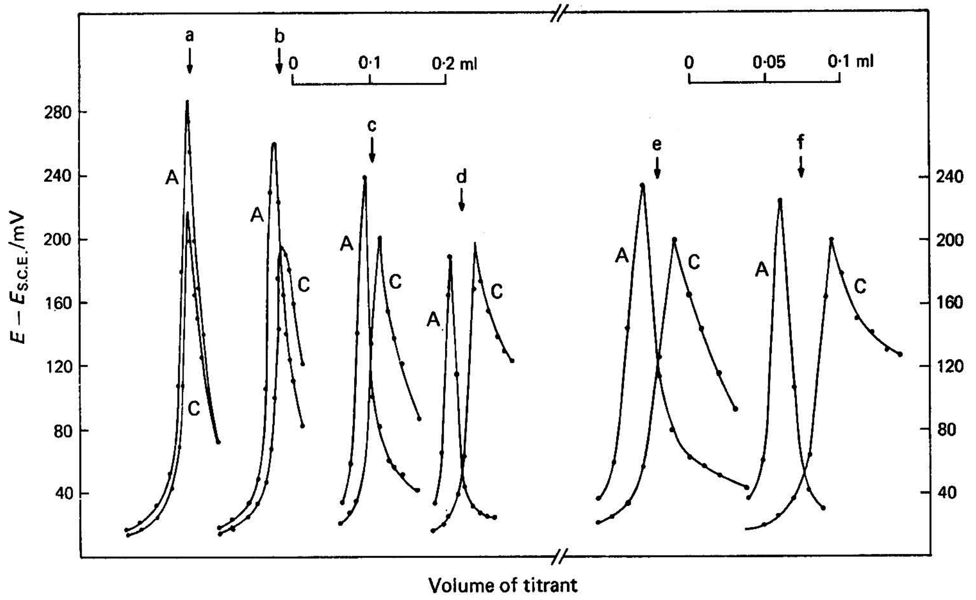


Fig. 6. Periodic potential components of the anodic, A, and cathodic, C, p.c. polarised electrodes, for fast electrode processes as in Fig. 5: (a), (b), (c) and (d) with reference to S.C.E. at 5, 25, 50 and 75% amplitude bias, respectively; (e) and (f) with reference to a zero-current indicator electrode, at 50 and 75% amplitude bias, respectively. The arrows indicate the true equivalence points.

The d.c. component of the output appears only when bias is applied, and because the d.c. differentiation at a given current density is 20–50 times more effective than p.c. differentiation, the effect is marked at low biasses. Referenced against a saturated calomel electrode and including change in bulk concentrations, at low biasses sigmoid curves appear, and because of the different number of electrons involved in the reactions the cathode curve shows a higher wave height and crosses the anode curve. Increasing the bias increases the wave height and causes anode and cathode curves to separate on both axes. Referenced to a zero-current electrode, at a small bias d.c. and p.c. differentiation occur simultaneously, and both anode and cathode give second differential titration curves, with a slight negative shift along the volume axis for the anode and a positive shift for the cathode. At higher biasses the d.c. differentiation swamps the p.c. differentiation and twin peaks appear, separating farther and increasing in height as the bias increases. Collective illustrations of the d.c. component curves are shown in Fig. 7.

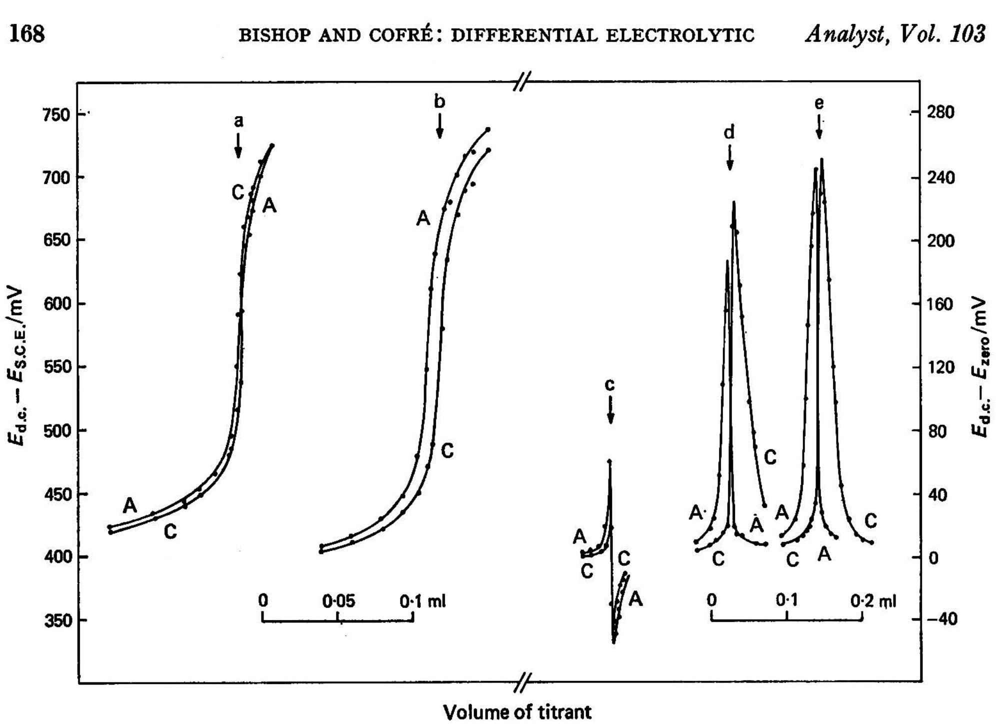


Fig. 7. Direct potential components of the anodic, A, and cathodic, C, p.c. polarised electrodes for fast electrode processes as in Fig. 5: (a) and (b), with reference to S.C.E. at 5 and 25% amplitude bias, respectively; (c), (d) and (e) with reference to zero-current indicator electrode, so showing the current-generated over-potential at 5, 50 and 75% amplitude bias, respectively. The arrows indicate the true equivalence points.

In an earlier paper[2] a "scoreboard" of predicted titration curve shapes for a 50% bias was given. This was based on an early analogue model for fast reactions, but had certain gaps where possible fine structures might occur. The complete rigorous mathematical theory of differential electrolytic potentiometry was later developed and confirmed the predictions, which also agreed with experimental results. What was not realised, because small biasses were treated with suspicion at the time and were not tested by computer, was that with amplitude bias, the behaviour differed with small and large biasses, or, as is now known, with comparable d.c. and p.c. differentiation and with swamping d.c. differentiation. The scoreboard can now be completed with an extra line in Table I for fast reactions.

The mathematical theory predicts that the d.c. peak height should be proportional to the logarithm of the d.c. current density. The d.c. component of the amplitude-biassed p.c. has been shown to be proportional to the percentage bias up to 96%. The d.c. component potential of twinned electrodes in a copper(I) - bromate - bromide titration solution adjusted precisely to equivalence was measured as a function of the log (percentage bias), for a triangular wave, and was found to obey the following relationships:

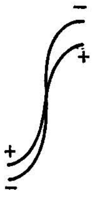
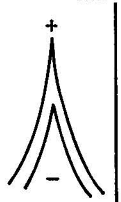
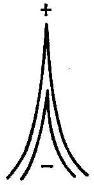
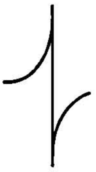
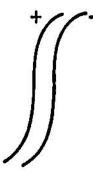
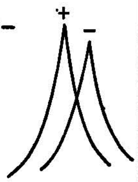
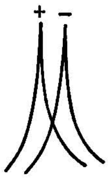
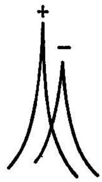
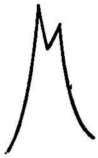
30 Hz $E_{\Delta\text{peak d.c.}} = [171.3 \log_{10}(\text{percentage bias}) - 90.3]$ mV; standard deviation, 1.8 mV

300 Hz $E_{\Delta\text{peak d.c.}} = [177.1 \log_{10}(\text{percentage bias}) - 97.7]$ mV; standard deviation, 1.8 mV

Slowing down the electrode processes introduces charge-transfer overpotential, η_a, in increasing degree. In a moderate extent this is useful in increasing the peak height and in producing pointed instead of rounded tops at higher current densities. There is a limit to this benefit when the base of the peak lifts off the zero or near-zero line and the peak is pushed up the potential axis without becoming sharper or higher with respect to its base line. The iron(III) - (II) system with an α value of about 0.45 and a charge-transfer rate constant around 10^{-6} l cm^{-2} s^{-1} is an example of the slower end of the moderate region,[6] bordering on the pattern region. Essentially, the cerium(IV) - (III) system has similar kinetics but offers

TABLE I

TITRATION CURVE FORMS FOR TWINNED AND SINGLE POLARISED ELECTRODES FOR FAST ELECTRODE PROCESSES [COPPER(I)/(II) - BROMIDE/BROMINE]

Applied signal	Single electrode				Twin electrodes	
	versus S.C.E.		*versus* zero-current			
	d.c.	p.c.	d.c.	p.c.	d.c.	p.c.
Amplitude biassed (positive)	Small bias				Small bias	
						
	Large bias				Large bias	
						

the additional complication that the potential at equivalence becomes high enough to oxidise the surface of a platinum electrode, with drastic effects on the charge-transfer rate parameters, particularly of the solvent reaction. Drastic reduction of charge-transfer rate causes loss of potential control, which normally passes to electrolysis of solvent ions or molecules, or reduction of dissolved molecular oxygen at a cathode. Such a system is chromium(VI) - (III), in which, as in the cerium system, an added complication, potential-dependent specific adsorption on the electrode surface with a corresponding drastic effect on charge-transfer rate parameters, is introduced. In both examples quoted, if equilibrium of the d.c. potential is awaited the differential electrolytic potentiometric end-point is late in titration of iron(II) by an amount corresponding to the completion of the change in the electrode surface of the anode by the first excess of oxidant. This is shown to apply to amplitude-biassed p.c. polarisation, for the reasons stated,[1] but if the point of reversal of drift be taken as the end-point the error is removed.[1]

Moderate electrode-process rates, complicated by oxidation of the electrode surface, will be illustrated by the titration of iron(II) with cerium(IV). The two-electrode differential curves are shown in Fig. 8. The p.c. component curves tend towards the rising Z form as the anodic electrode becomes more oxidised, and the effect of increasing bias is to cause deterioration of the p.c. component curve with the development of errors and splitting of the curve into two peaks, as usual. The d.c. component gives the normal peak, increasing in height with increasing bias and also broadening. The increasing charge-transfer overpotential after the end-point reveals the growth of oxide on the anode. Because the electrode potentials are allowed to reach equilibrium, consumption of reagent in the oxidation of the electrode causes late end-points, in agreement with the classical d.c. differential electrolytic potentiometric performance.[1]

The behaviour of the single-electrode potential is illustrated for the p.c. component referenced to a saturated calomel electrode in Fig. 9. These curves reflect the change in bulk concentration as well as in contact-layer concentrations, and show the eccentric influence of electrode filming. Essentially all are of rising Z configuration, and as the bias increases the potentials decrease, anodic peaks move to more negative volumes and cathodic peaks move to

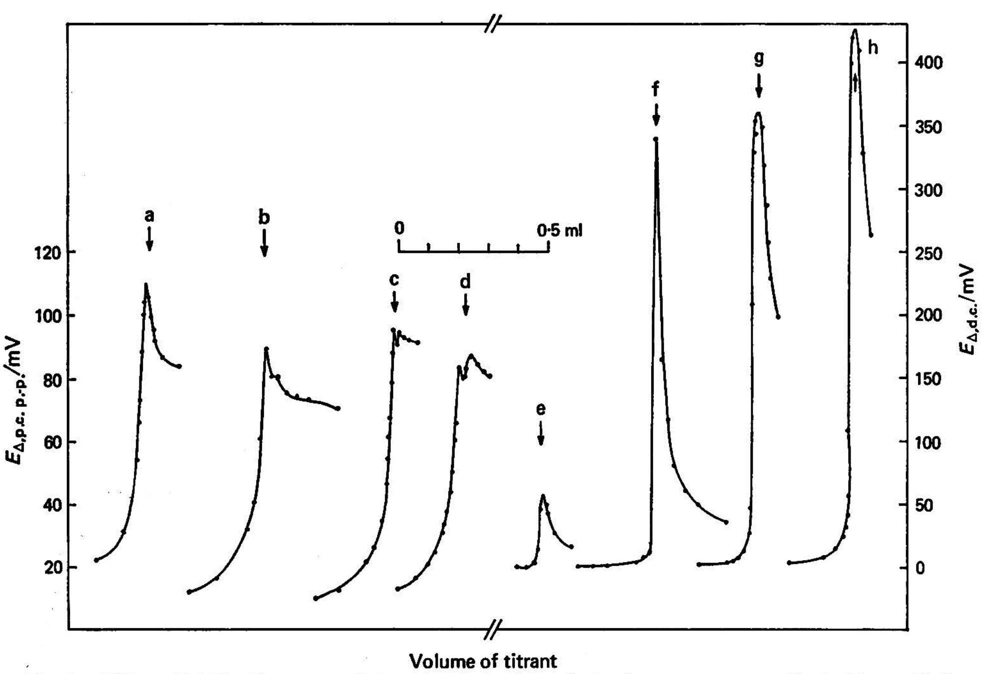


Fig. 8. Differential titration curves for moderate to slow electrode processes, complicated by oxidation of the anodic electrode. Titration of iron(II) in 1 M sulphuric acid with cerium(IV), triangular wave, frequency 3 Hz, p.c. current density 25 μA cm^{-2} p.-p. The p.c. components of the output of electrode I minus electrode II are shown at 5%, (a), 25%, (b), 50%, (c) and 75%, (d) amplitude bias: the d.c. components for the same series of biasses are shown in curves (e) to (h). The arrows indicate the true equivalence points.

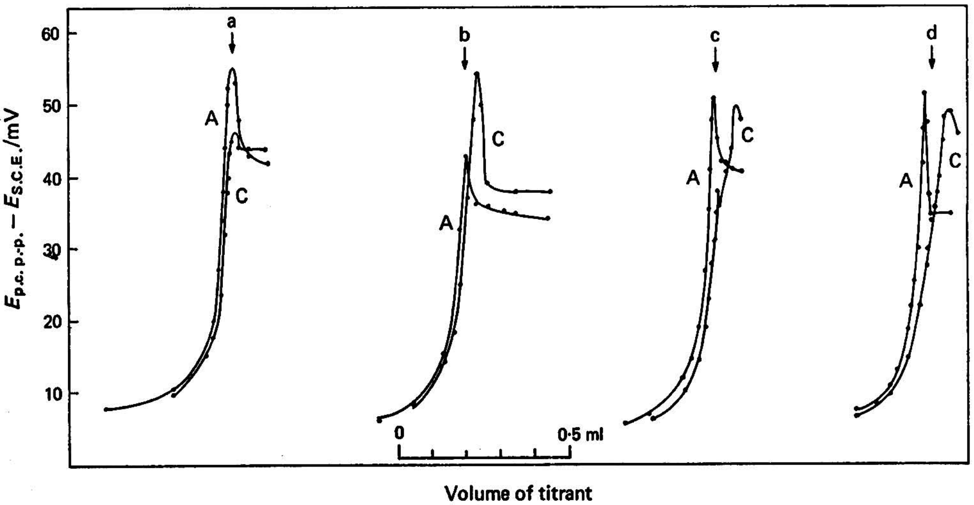


Fig. 9. The p.c. potential components of anodic, A, and cathodic, C, electrodes referenced to S.C.E. at 5%, (a), 25%, (b), 50%, (c) and 75%, (d) amplitude bias. The conditions are as in Fig. 8 and the arrows indicate the true equivalence points.

more positive volumes with respect to the equivalence-point volume, and while anodic peaks sharpen and are usually higher than the cathodic peaks, the latter broaden and become more diffuse.

The d.c. component referenced to a saturated calomel electrode (Fig. 10) shows the normal increasing separation of the sigmoid curves and increasing anodic charge-transfer overpotential. Referenced to a zero-current indicator electrode, the true current-generated mass- and charge-transfer overpotentials are revealed, and are, of course, first differentials. The anodic peak is early and the cathodic peak is late with respect to the equivalence point, and the peak heights increase, more for the filmed anode than for the cathode, and the peaks separate progressively with increasing bias. The charge-transfer control sharpens the anode peak.

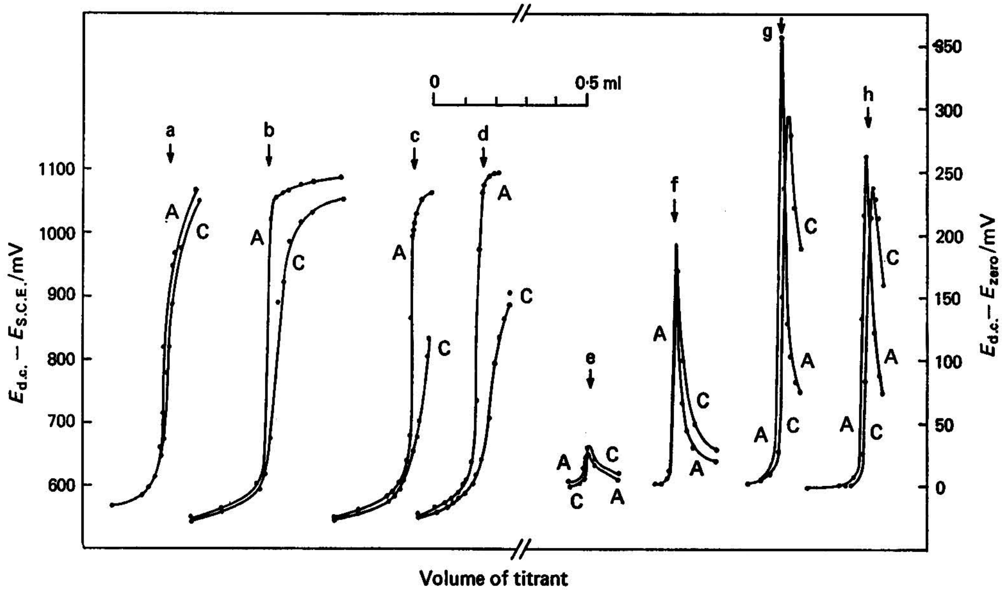


Fig. 10. The d.c. potential components of anodic, A, and cathodic, C, electrodes referenced to S.C.E. at 5%, (a), 25%, (b), 50%, (c) and 75%, (d) amplitude bias. The d.c. potential components referenced to a zero-current electrode, *i.e.*, the current-generated overpotentials, at 5%, (e), 25%, (f), 50%, (g) and 75%, (h) amplitude bias. The conditions are as in Fig. 8 and the arrows indicate the true equivalence points.

Slow combined with moderate electrode processes, complicated by a case of specific adsorption, are illustrated by the titration of iron(II) with dichromate. At least one of the reactants must have such charge-transfer kinetics that the electrode process will proceed without material contribution from electrolysis of solvent ions or molecules, otherwise no meaningful curve is obtainable: dichromate and arsenic(III) do not react chemically, neither can any polarised electrode titration curve be obtained for the reaction. The two-electrode differential titration curves are shown in Fig. 11. The p.c. component curves are rising Z in form and show a rapid deterioration with increasing bias, so that at 75% bias the points are badly scattered after equivalance. The d.c. component curves are of the same general shape, and the step height increases with increasing bias, but at 75% bias the curve gives evidence of excessive current density and there is an excessive scatter of the points. Before the end-point, both electrodes are operating on the iron(III) - iron(II) titrand, but at and after equivalence specific adsorption of chromium species[1] occurs, and if time is allowed for the drift rate of the potential to fall to 1.0 mV min^{-1} consumption of a small amount of titrant occurs and more must be added (because the adsorption is concentration-dependent) before an equilibrium state is reached. As in classical d.c. differential electrolytic potentiometry the equilibrium end-point is late, but once again if the point of reversal of drift is taken the end-point agrees closely with the equivalence point.

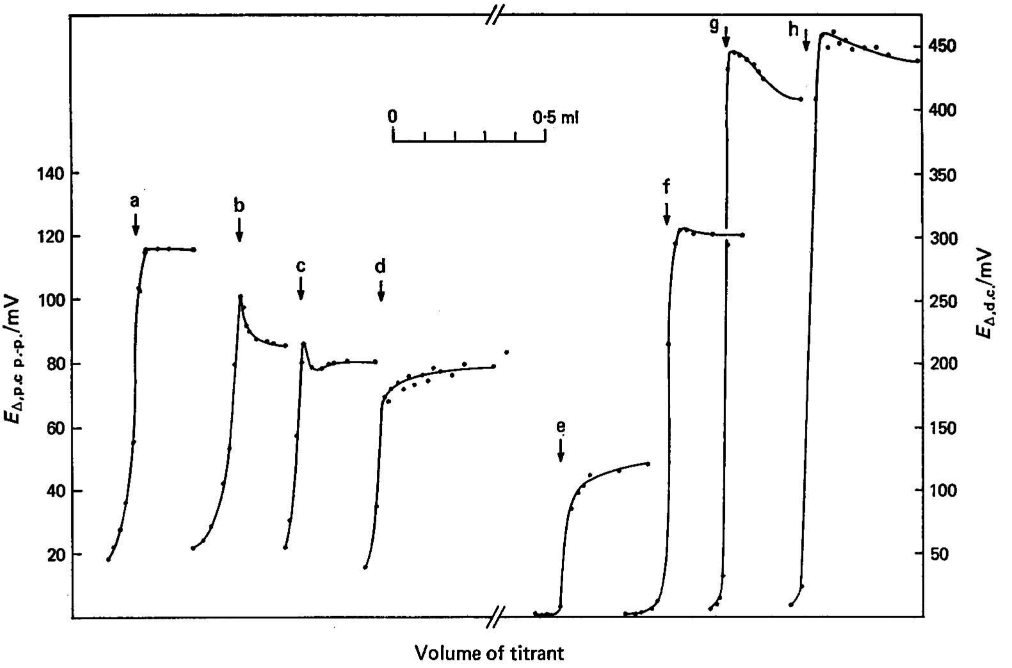


Fig. 11. Differential curves for moderate and very slow electrode processes, complicated by specific adsorption. Titration of iron(II) in 1 M sulphuric acid with dichromate(VI), triangular wave, frequency 3 Hz, current density 25 μA cm^{-2} p.-p. The p.c. components of the potential difference between electrodes I and II are shown at 5%, (a), 25% (b), 50%, (c) and 75%, (d) amplitude bias. The d.c. components of the differential potential are shown at 5%, (e), 25%, (f), 50%, (g) and 75%, (h) amplitude bias. The arrows indicate the true equivalence points.

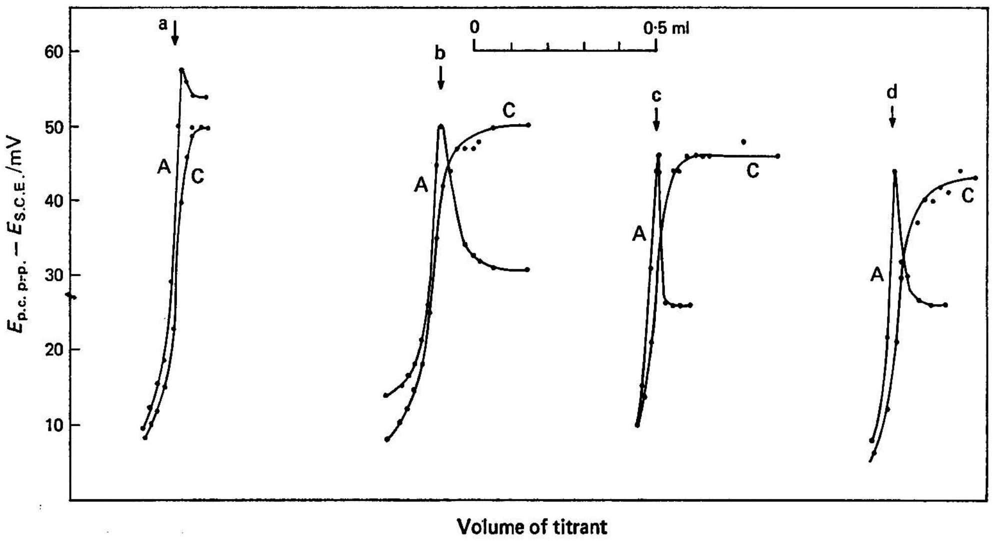


Fig. 12. The p.c. potential components of anodic, A, and cathodic, C, electrodes referenced to S.C.E. at 5%, (a), 25%, (b), 50%, (c) and 75%, (d) amplitude bias. The conditions are as for Fig. 11 and the arrows indicate true equivalence points.

The single-electrode titration curves are illustrated in Fig. 12 for the p.c. component referenced to a saturated calomel electrode, and so contain the contribution from the change in bulk concentrations. The anode curves are essentially first-differential peaks with major charge-transfer overpotential after equivalence, and these curves decrease in height and move earlier along the volume axis as the bias increases. The cathode curves, however, are sigmoid, being controlled by the iron(III) reduction, decreasing slightly in wave height and moving later along the volume axis as the bias increases. At high biasses point scatter is severe.

For the d.c. components referenced to a standard calomel electrode, the normal sigmoid shape, changing to rising **Z** for the anode at high biasses, obtains, as shown in Fig. 13. The cathode curves reflect simply the removal of iron(II) and the effect of this on reduction of iron(III). The anode curves show enormous overpotentials that are little influenced by the oxidation of chromium(III) but reflect oxidation of the solvent at an adsorption-blocked electrode. Referenced to a zero-current electrode, the cathode curves are sigmoid, increasing in step height, with increasing bias, while the anode curves change from pseudo-sigmoid to a hybrid rising **Z** peak with very large overpotentials characteristic of solvent attack. No second-differential effects are observable.

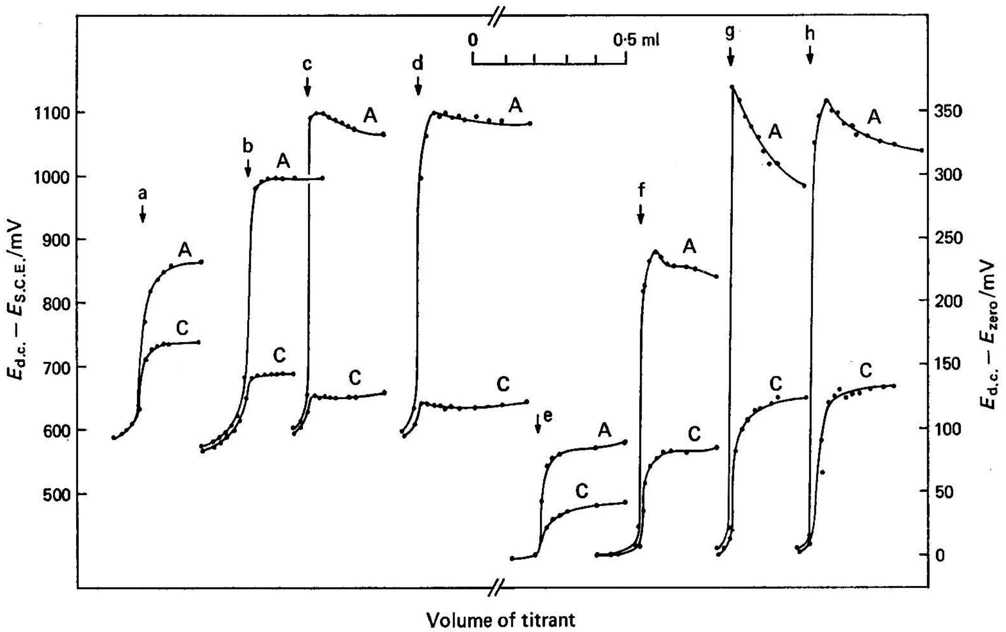


Fig. 13. The d.c. potential components of anodic, A, and cathodic, C, electrodes referenced to S.C.E. at 5%, (a), 25%, (b), 50%, (c) and 75%, (d) amplitude bias, with the current-generated overpotentials obtained by reference to a zero-current electrode at 5%, (e), 25%, (f), 50%, (g) and 75%, (h) amplitude bias. The conditions are as for Fig. 11 and the arrows indicate the true equivalence points.

Ion-combination reactions

Many titration reactions have been examined, including complexation reactions at amalgamated-gold electrodes and precipitation reactions at silver electrodes. In all instances the experimental results accorded with computer prediction and with the determined kinetic behaviour of the electrode processes, which include formation of active porous films and their deactivation by capillary sealing, and specific adsorption of certain complexes. As the procedure offers no advantage in respect of mark-to-space periodic differential electrolytic potentiometry,[1] it will suffice to offer a brief account of one example of ion-combination reactions.

Moderate to fast electrode processes occur at antimony electrodes in acid - base titrimetry. These follow the patterns detailed for the fast - fast copper(I) - bromate titration with some charge-transfer overpotential added and the experimental complication of complete removal and exclusion of carbon dioxide. In Fig. 14 are shown the differential p.c. component, the differential d.c. component, the p.c. and d.c. components of single electrodes referenced to saturated calomel electrodes, and the d.c. components referenced to a zero-current electrode, for a single, high bias. The expected split peak for the p.c. E_Δ curve, the broad, high, rounded peak for the large d.c. component E_Δ curve, the shifted first-differential separated anode and cathode p.c. component curves, and the sigmoid d.c. component anode and cathode curves well separated at this bias, are all demonstrated. These last (d) show an effect that might be ascribed at first sight to trace amounts of carbon dioxide, and it is not possible to prove a negative so that this explanation must be allowed in part. The major part of the explanation of the inflection points, however, is due to the characteristics of antimony electrodes.[8,9] These electrodes show a linear, but deficient, slope in pH response over the pH range from about 2 to 6.5 and the mechanism involves hydrogen ions. In alkaline media over the pH range from 7.5 to 12.5 there is a second-order response to hydroxyl ions, and this has a different, but still deficient, slope to that for acidic media. In unpoised solutions both responses fail in the region around pH = 7 and there is no change in potential in the pH range from 6.5 to 7.5 and comparatively little change over a further interval of 0.5 pH unit outside that range. Hence the flattened single-electrode potential curves as first the anode and then the cathode traverse this failure region. The d.c. component referenced to a zero-current electrode reveals the real overpotential situation. At this high bias, the two first-differential peaks are broad and well separated, with rounded tops. These are mass-transfer controlled curves; the charge-transfer overpotential does not exceed about 1 mV.

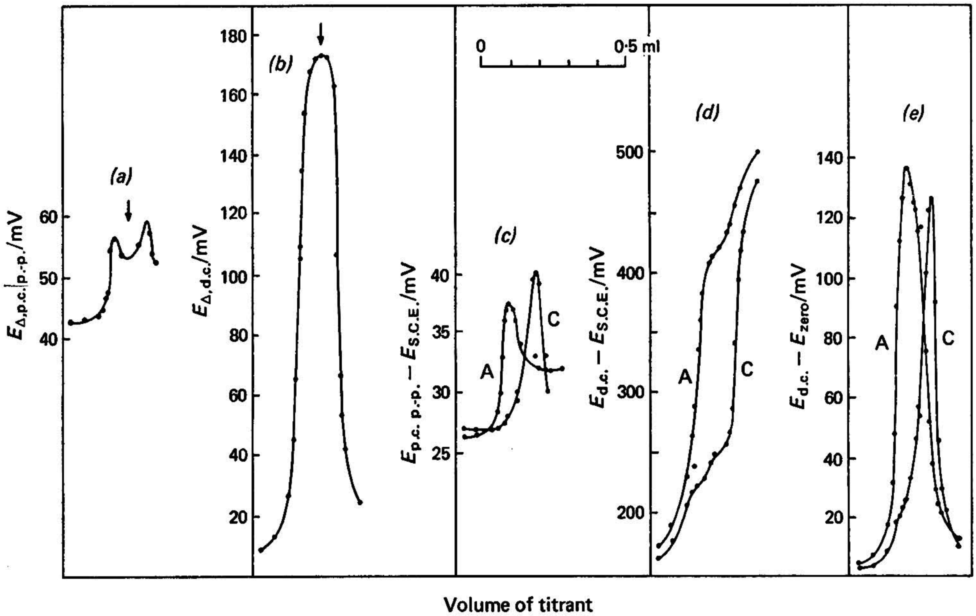


Fig. 14. An example of an ion-combination reaction with fast electrode processes. Titration of perchloric acid with barium hydroxide solution under carbon dioxide free conditions, using antimony slug electrodes. Triangular wave, frequency 3 Hz, current density 100 μA cm^{-2} p.-p. All curves are at 75% amplitude bias. The arrows indicate the true equivalence points. (a), Differential p.c. potential component, electrode I *versus* electrode II. (b), Differential d.c. potential component, electrode I *versus* electrode II. (c), The p.c. potential components of anodic, A, and cathodic, C, electrodes referenced to S.C.E. (d), The d.c. potential components of anodic, A, and cathodic, C, electrodes referenced to S.C.E. (e), The current-generated d.c. overpotentials: the d.c. components of anodic, A, and cathodic, C, electrodes referenced to a zero-current electrode.

Conclusions

The insertion of any appreciable amplitude bias into a periodic polarising wave form causes a deterioration in the p.c. component of the output of twinned electrodes in any titration curve. At the same time, a d.c. component appears in the output, which at low biasses produces an error-free second-differential titration curve for fast electrode processes. In some instances the conjunction of two differentiating effects, p.c. and d.c., produces second-differential titration curves for a single electrode referenced to a constant-potential electrode or a zero-current indicator electrode. In all instances the end-point for a single polarised electrode, however referenced, deviates from the equivalence point when a bias is applied to the input signal.

What is not, of course, revealed in the titration curves is the speed with which the electrode potentials reach an acceptable drift rate, and how steady the resultant potentials are. Nor do they show the extended service life between activations. Herein lie the real advantages of the technique, and maximum benefit can be derived from them at low biasses with measurement of the d.c. component of the output. Equilibration is much faster, and the resultant potentials are much steadier than in classical d.c. differential electrolytic potentiometry, but the same positive errors, which are eliminated in time-biassed differential electrolytic potentiometry, are given by the titrants cerium(IV) and dichromate.

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NOTE—References 1, 2, 3 and 5 are to Parts XXIII, XXI, XXII and VI of this series, respectively.

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SHORT PAPERS

Differential-pulse Polarography of Selenium(IV) in the Presence of Metal Ions

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Keywords: *Selenium(IV) determination*; *differential-pulse polarography*; *metal-ion interferents*

The importance of selenium as an essential trace element in animal nutrition[1] has stimulated the development of many sensitive analytical techniques. Neutron-activation analysis,[2] gas chromatography,[3] spectrochemical[4–6] and electrochemical methods[7–9] have been reported for the measurement of selenium at the sub-parts per million levels present in foodstuffs, biological materials and soils. Electrochemical methods are rapid and require a small volume of sample but suffer from interferences from some heavy metals. The polarographic behaviour of selenium can be summarised by the following electrode reactions[7]:

At pH≈0:

1st wave: −0.05 V *versus* S.C.E., 0.2 M HCl

$$H_2SeO_3 + 6H^+ + 6e^- \rightleftharpoons H_2Se + 3H_2O \quad .. \quad .. \quad .. \qquad (1)$$

$$Hg + H_2Se \rightleftharpoons HgSe + 2H^+ + 2e^- \quad .. \quad .. \quad .. \qquad (2)$$

net reaction: $$H_2SeO_3 + 4H^+ + 4e^- + Hg \rightarrow HgSe + 3H_2O \quad .. \qquad (3)$$

2nd wave: −0.54 V *versus* S.C.E. in 0.2 M HCl

$$HgSe + 2H^+ + 2e^- \rightleftharpoons Hg + H_2Se \quad .. \quad .. \quad .. \qquad (4)$$

At higher pH:

−1.1 V *versus* S.C.E. at pH 3, −1.6 V *versus* S.C.E. at pH 8

$$H_2SeO_3 + 6H^+ + 6e^- \rightarrow H_2Se + 3H_2O \quad .. \quad .. \quad .. \qquad (5)$$

The depolarisation step in the initial reduction [equation (2)] can be interrupted by ions of metals such as lead, copper and iron owing to deposition of insoluble selenides, *e.g.*,

$$H_2Se + 2Cu^+ \rightarrow Cu_2Se + 2H^+ \quad .. \quad .. \quad .. \quad .. \qquad (6)$$

This reaction reduces the concentration of H_2Se at the electrode surface and affects both the first and second polarographic waves.

Because copper is commonly found in digests of plant materials and in soil extracts, the effects of the copper ion on the differential-pulse polarographic analysis of selenium in both acidic and alkaline solutions were studied.

Experimental

Polarograms were obtained with a Princeton Applied Research PAR 174A Polarographic Analyzer and an Omnigraphic X - Y recorder. A dropping-mercury electrode with a reservoir height of 45 cm and a flow rate of 1.25 mg s^{-1} was used. Solutions were prepared from analytical-reagent grade chemicals and distilled, de-ionised water, with the exception of hydrochloric and nitric acids and ammonia solution, which were BDH Chemicals Aristar-grade materials. Selenium(IV) solutions were prepared by dissolving sodium selenite (Na_2SeO_3) in water. The concentrated solution (1 000 μg cm^{-3} of selenium) was standardised by gravimetric analysis of elemental selenium.[10] Other standards were prepared by serial dilution.

Samples for analysis were prepared by adding aliquots of concentrated supporting electrolyte solution to the analyte and adjusting the pH (measured with a glass electrode) to the required value. Solutions were de-oxygenated with nitrogen, which had previously been passed through a wash-bottle containing the supporting electrolyte.

Calibration graphs of peak current *versus* concentration were constructed by making sequential additions of selenium to the supporting electrolyte. Interference studies were carried out by adding the interferents to the supporting electrolyte both before and after adding the selenium, as the order of addition was found to affect the peak current in some instances.

Results and Discussion

Calibration graphs of the second polarographic wave of selenium(IV) in 0.2 M hydrochloric acid were non-linear, with a minimum detectable amount of 10 ng cm^{-3}. The addition of copper to the analyte increased or decreased the peak current obtained from selenium alone according to circumstances. The former occurred at low Cu to Se ratios, and the latter as the copper concentration was increased. The results of the interference of copper on selenium analyses are given in Tables I and II. Standard additions techniques of analysis are not applicable as the calibration graph is non-linear and, unless the metal-ion content of the analyte is known, differential-pulse polarographic determination of selenium in 0.2 M hydrochloric acid is not recommended.

TABLE I

PEAK CURRENTS (nA) OBTAINED FOR SEQUENTIAL ADDITIONS OF SELENIUM (IV) TO COPPER SOLUTIONS IN 0.2 M HYDROCHLORIC ACID

	Selenium concentration/ng cm^{-3}			
Copper concentration/ng cm^{-3}	50	150	250	350
0	20	75	148	226
1 000	24	97	179	274
5 000	18	75	140	191

Several alkaline solutions (sodium hydroxide, sodium sulphite, triethanolamine, ammonium chloride and ammonium acetate) were evaluated as supporting electrolytes for the single-step, six-electron reduction of selenium(IV). Good polarographic waves were obtained in both ammonium chloride and ammonium acetate with an optimum electrolyte concentration of 1.0 mol l^{-1}.

TABLE II

PEAK CURRENTS OBTAINED FOR SEQUENTIAL ADDITIONS OF COPPER TO SELENIUM(IV) SOLUTIONS IN 0.2 M HYDROCHLORIC ACID

Selenium(IV) concentration/ng cm^{-3}	Copper concentration/ng cm^{-3}	Peak current/nA
50	0	20
	200	16
	400	16
	600	15
	800	14
	1 000	13
160	0	85
	1 000	114
	3 000	83
	5 000	79

The peak potential of the reduction (E_p) was dependent on pH (Table III), but was independent of whether ammonium chloride or ammonium acetate was used as the supporting electrolyte. The peak was analytically useful between pH 5.4 and 9, but the best separation of the selenium current from that of the supporting electrolyte was obtained at pH 8.0, with a peak potential of −1.34 V *versus* S.C.E.

After optimisation of the control parameters of the PAR 174A instrument (modulation amplitude 100 mV, scan rate −2 mV s^{-1}, drop time 2 s), a non-linear calibration graph, with a peak current of 200 nA at a selenium concentration of 150 ng cm^{-3}, and a detection limit (signal to noise ratio = 50%) of 5 ng cm^{-3} was obtained.

TABLE III

pH DEPENDENCE OF PEAK POTENTIAL (E_p) IN AMMONIUM CHLORIDE OR AMMONIUM ACETATE SUPPORTING ELECTROLYTES

pH	6.2	6.6	7.2	7.6	8.0	9.0
E_p/V *vs.* S.C.E. ..	−1.21	−1.24	−1.28	−1.31	−1.34	−1.41

The addition of metal ions known[11,12] to affect the reduction of selenium in acidic solutions [iron(III), lead and copper] had no effect on the selenium wave when in a 1 000-fold excess under the conditions of this experiment. Interferences would, therefore, be expected only from overlapping polarographic peaks. Data on half-wave potentials[10] show that although many ions could interfere ($E_p \pm 0.1$ V) in ammonium chloride, the possible inorganic interferents in ammonium acetate and their peak potentials are cobalt(II) −1.2, vanadium(III) −1.25, tellurium(VI) −1.2, chromium(III) −1.2, molybdenum(VI) −1.2 and zinc(II) −1.38 V. With the exception of zinc, these ions do not interfere when in a 100-fold excess and, considering their probable concentrations in soil, plant and biological extracts, it can be concluded that they will not be major interferents.

The interference from zinc was completely removed by complexing it with 0.01 M EDTA. In EDTA solutions the lead reduction peak is moved to an E_p of −1.2 V, but as with cobalt(II), vanadium(III), etc., it will interfere only at high concentrations.

In the analysis of soil and plant materials, organic species may also interfere. At the potential and pH conditions used for the reduction, the most likely interferents are simple organic compounds containing carbonyl groups, and organic acids. Of the acids subject to reduction under these conditions, maleic, fumaric, laevulinic, "humic" and "fulvic" acids were investigated. Of these, only maleic acid was an interferent ($E_p = -1.3$ V) and, although it is unlikely to be present in soil solutions, it could easily be removed by mild acid hydrolysis.

Various carbonyl-containing compounds, including polysaccharides, gave no interference, and analyses of several soil extracts showed that only one overlapping polarographic peak was present. This peak was identified as the reduction of furfuraldehyde, which was present in the extracts of some air-dried soils. When present in solution, the furfuraldehyde could be removed by acid hydrolysis with nitric acid (or with hydrochloric acid in a sealed tube to prevent volatilisation of selenium) and subsequent neutralisation prior to the addition of supporting electrolyte.

Polarographic Measurement of Selenium(IV) in Water Extracts of Soils Using an Ammonium Acetate - EDTA Supporting Electrolyte

Differential-pulse polarographic analysis of selenium(IV) in alkaline solutions was evaluated by measuring the recovery of selenium from water extracts of soil (1 g of air-dried soil in 20 cm^3 of water) to which selenium had previously been added. The results of this analysis are given in Table IV.

TABLE IV

RECOVERY OF SELENIUM FROM WATER EXTRACTS OF SOILS MEASURED BY DIFFERENTIAL-PULSE POLAROGRAPHY IN AMMONIUM ACETATE - EDTA SOLUTION

Relative standard deviation at 50 ng cm^{-3} = 4.4% (10 samples).

Selenium concentration in extract/ng cm^{-3}				
Initial	Added	Found	Recovered	Recovery, %
0	200	198	198	99.0
0	400	402	402	100.5
0	600	595	595	99.2
31	50	80	49	99.0
63	100	153	90	90.0
78	200	280	202	101.0
78	400	476	398	99.5
635	200	840	205	102.5
644	200	845	201	100.5

Conclusions

Differential-pulse polarography provides a rapid and convenient method of analysis for selenium(IV). In an ammonium acetate (1.0 M) - EDTA (0.01 M) supporting electrolyte at pH 8.0, there are no serious inorganic interferences. Organic interferences can be removed by hydrolysis.

Although the detection limit of 5 ng cm^{-3} is insufficiently low for the analysis of extracts of selenium-deficient soils, the technique offers a reliable method for the determination of selenium with a sensitivity at least comparable to that of alternative methods of analysis, and is well suited to the study of the adsorption characteristics of soils. Further work on this topic is in progress.

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Determination of Small Amounts of Bismuth in Antimony(III) Oxide by Using Anodic Stripping Voltammetry

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Keywords: *Bismuth determination*; *antimony(III) oxide*; *anodic stripping voltammetry*

An antimony concentrate that is suitable for further processing contains a minimum of 50% of antimony and the content of bismuth must be less than 0.01%. The antimony concentrate obtained by hydrometallurgical processing is basically antimony(III) oxide (70–80% Sb) containing 10^{-3}–10^{-4}% of bismuth. The determination of bismuth in this material is difficult because of the similar chemical properties of the two elements.

The methods frequently employed for the separation of bismuth and antimony are extraction with diethyldithiocarbamate from cyanide solutions containing EDTA,[1] the use of cation[2] or anion exchangers[3] and column chromatography with a liquid stationary phase.[4]

For the determination of bismuth, voltammetric methods have been found to be very advantageous, particularly anodic stripping voltammetry (ASV) with mercury-film coated solid electrodes. The application of ASV permits the determination of 5×10^{-8}% of bismuth.[5]

In the work described in this paper, ASV was used for the determination of bismuth following the separation of antimony on an ion exchanger.

Experimental

Apparatus

A polarograph with built-in *iR* compensation (OH-102, Radelkis, Hungary) was used for the recording of ASV curves. The rotating disc electrode was made from a glassy carbon rod (Le Carbon Lorraine, France) fixed in a PTFE tube. The surface area of the carbon disc was 7 mm^2 and the diameter of the PTFE coating was 25 mm. Measurements were carried out by use of a three-electrode arrangement; a saturated calomel electrode (S.C.E.) and the auxiliary platinum electrode were placed in the close vicinity of the rotating disc. The rate of polarisation was 2.8 V min^{-1}, while the rate of rotation during plating and stripping was 2 300 rev min^{-1}. Pre-treatment of the electrode involved polishing of the electrode surface with metallographic papers (SIA, Switzerland) before each series of measurements.

Reagents

All solutions were prepared from analytical-reagent grade chemicals. Standard antimony solution was prepared from antimony(III) oxide and standard bismuth solution was prepared by dissolution of metallic bismuth (1.0 g) in 5 ml of nitric acid (sp. gr. 1.40). After cooling the resulting solution, 5 ml of perchloric acid (sp. gr. 1.70) were added and the solution was evaporated until white fumes appeared. The solution was then transferred into a 1 000-ml calibrated flask, 40 ml of perchloric acid (sp. gr. 1.70) were added and the solution was diluted to 1 000 ml with water. The solution prepared in this manner was diluted appropriately before use on each occasion.

Preparation of the Ion Exchanger

The fresh exchanger (Dowex 50-2X, 100–200 mesh) was left in water for 24 h, then transferred into a glass tube (diameter 1 cm, length 15 cm). Before use, the column was washed with 150 ml of 0.5 M perchloric acid.

Procedure

The sample (0.1 g) is dissolved in 100 ml of 1% tartaric acid solution, 4 ml of perchloric acid (sp. gr. 1.70) are added and the solution is transferred to the prepared column of Dowex 50. The column is washed with 150 ml of 0.5 M perchloric acid and bismuth is eluted with 25 ml of 3 M hydrochloric acid into a 100-ml calibrated flask. The column is then washed with 70 ml of water into the same flask. The solution in this flask is diluted to 100 ml with water.

The separation must be carried out twice when the sample contains more than 50% of antimony. A 5-ml volume of perchloric acid (sp. gr. 1.70) is added to the solution containing the eluted bismuth and this solution is evaporated until white fumes appear. Tartaric acid (1.5 g) is then added to the cold residue and the volume is adjusted to 100 ml with water; any insoluble matter is dissolved by gentle heating. This solution is next transferred on to the column and the elution is repeated.

A 50-ml volume of the solution containing the eluted bismuth is transferred into the 50-ml electrolysis vessel, 0.15 ml of 1×10^{-2} M mercury(II) nitrate solution is added, the electrodes are immersed and the dissolved oxygen is removed by a 5-min flow of pure nitrogen. Electrolysis is carried out at a potential of −0.8 V *versus* S.C.E. for 2–10 min with rotation of the disc electrode. The electrolysis time depends on the amount of bismuth in the sample. A scan of potential in the range −0.8 to +0.3 V starts immediately after the electrolysis time has elapsed. The peak potential of bismuth corresponds to the value −0.29 V and this peak is followed by the dissolution peak of mercury (Fig. 1, curve B).

Calibration graph

A known amount of bismuth standard solution (containing 0.2–5.0 µg) and 0.1 g of antimony(III) oxide are placed in a 150-ml beaker, then 100 ml of 1% tartaric acid solution are added and the material is dissolved by gentle heating. After dissolution and cooling 4 ml of perchloric acid (sp. gr. 1.70) are added, the solution is transferred on to the column and the procedure described above is followed.

Results and Discussion

Application of Thin Mercury-film Carbon Electrode

The hanging mercury drop electrode frequently employed in ASV[3] has some disadvantages when used in routine analysis. The application of carbon electrodes[6] and mercury-coated carbon electrodes has therefore been recommended. The deposition of bismuth on a carbon electrode is feasible; more advantageous, and likely to lead to more sensitive results, is the application of thin mercury-film electrodes prepared *in situ*.[7]

Mercury is deposited simultaneously with the metal undergoing analysis on the clean, polished electrode surface. The deposit is very thin[8] and the anodic dissolution of the amalgam formed with the analysed metal yields sharp dissolution peaks. The peaks obtained by anodic dissolution of bismuth on glassy-carbon and mercury-film glassy-carbon electrodes are presented in Fig. 1. Curve A (peak potential ∼−0.30 V) corresponds to the glassy-carbon electrode, while curve B, with a sharper and higher peak, corresponds to the mercury-film glassy-carbon electrode.

The deposited mercury is removed from the electrode surface by mechanical cleaning with wet filter-paper after the completion of the analysis. The concentration of mercury(II) ions in the analysed solution is 3×10^{-5} M.

Dissolution of the Sample and Separation of Antimony from Bismuth

Various techniques of sample dissolution and separation have been tested, for example, dissolution and removal of the substantial amount of antimony present with hydrobromic acid.[9] In this instance, the evaporation must be carried out carefully as a small amount of bismuth may volatilise together with the antimony.

Dissolution of the sample with aqua regia, followed by the extraction of bismuth with diethyldithiocarbamate, can be recommended only when the content of bismuth is higher than 10 μg. The use of sulphuric acid at a concentration identical with that of the perchloric acid was also

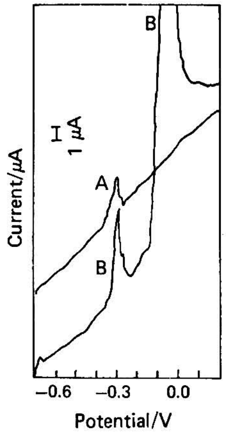

Fig. 1. Peaks of bismuth on the glassy-carbon electrode (A) and on the same electrode with thin mercury film (B). Curve A, 5 μg of bismuth in 100 ml of 0.75 M hydrochloric acid; and curve B, 5 μg of bismuth in 100 ml of 0.75 M hydrochloric acid + 3×10^{-5} M mercury(II) nitrate. Electrolysis potential, −0.8 V; time of electrolysis, 2 min; and scan rate, 2.8 V min^{-1}.

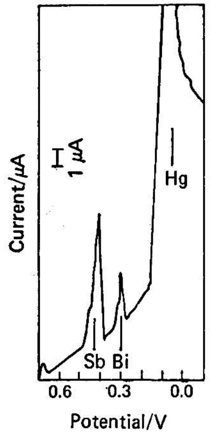

Fig. 2. Typical stripping voltammogram of antimony, bismuth and mercury on the mercury-film electrode in 0.75 M hydrochloric acid.

tested for the separation of bismuth using Dowex 50-2X. However, the stripping determination gave lower results in this instance.

Antimony concentrates may contain large amounts of antimony oxychlorides, which may influence the separation on Dowex 50. The concentration of bismuth remained unchanged in the eluate if the concentration of chloride ions was equal to or less than 0.03 M in the solution before the separation. At a chloride ion concentration of 0.06 M, a 7% decrease in the peak height corresponding to bismuth was observed; at 0.12 M this decrease was 68%.

If the sample contains a large amount of antimony, the separation of antimony from bismuth must be carried out twice, as described above. If the concentration of antimony(V) ions in the eluate is high, the dissolution peaks of antimony and bismuth coincide. If, on the other hand, the concentrations of both of these ions are of the same order of magnitude, the peaks of antimony (−0.40 V) and bismuth (−0.29 V) can easily be distinguished (see Fig. 2).

Anodic Stripping Voltammetry

No difficulties arise when ASV is applied to the final determination of bismuth. The following requirements should, however, be fulfilled: the concentration of the mercury(II) salt must be less than 5×10^{-5} M, otherwise a thick mercury deposit is formed; if the concentration of bismuth is less than 0.001%, the concentration of mercury(II) ions should be kept below the level of 1×10^{-5} M, because a lengthy electrolysis time must be employed (approximately 10 min); dissolved oxygen must be completely removed; for this purpose, passing pure nitrogen through the analysed solution for 5 min is usually sufficient. The determination is only slightly influenced by the rate of polarisation during the anodic dissolution.

Determination of Bismuth

By using ASV bismuth was determined in the concentration range 2×10^{-4}–3×10^{-2}% in various samples of antimony concentrates. A comparison of the results obtained by ASV, oscillopolarography, atomic-absorption spectrophotometry and ultraviolet - visible spectrophotometry is given in Table I.

TABLE I

COMPARISON OF ANALYSES OF ANTIMONY CONCENTRATES CONTAINING BISMUTH

	Bismuth found, %			
Sample number	Anodic stripping voltammetry	Oscillopolarography	Atomic-absorption spectrophotometry	Ultraviolet - visible spectrophotometry
1	0.008	0.007	—	—
2	0.010	0.009	—	—
3	0.012	—	0.011	0.010
4	0.020	—	0.021	0.022
5	0.026	—	0.026	0.026
6	0.0002	—	—	<0.002

The reproducibility does not exceed 15% at a bismuth concentration of 10^{-8} M.

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Titrimetric Determination of Halogens in Halo- and Dihalo-β-diketones

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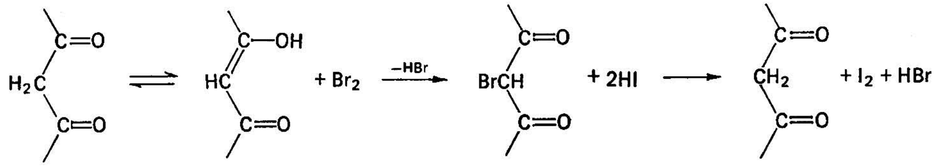
Keywords: *Halogen determination*; *halo- and dihalo-β-diketones*; *titrimetry*

The bromine in bromo-β-diketones is usually measured by Meyer's method, which is one of the oldest procedures for determining the enol content of β-diketones[1]:



A similar procedure has been reported by Macbeth[2] for the determination of chlorine in chlorobenzoylacetone by iodimetric titration. However, when attempts were made to verify the results, required in connection with another investigation, the volume of the titrant (sodium thiosulphate solution) far exceeded the theoretically required volume. Similar errors have also been stated earlier to give absurdly high enol contents of certain compounds (in excess of 100%).[3–5] These discrepancies led us to examine the determination of halogens in monochloro-, monobromo- and dibromobenzoylmethanes, mono- and dichlorobenzoylacetones and monobromo-, monochloro- and dichloroacetylacetones in 40% *V*/*V* aqueous ethanolic solutions.

Experimental

Reagents and Chemicals

Ethanol, about 80%.
Hydrochloric acid, 10 N.
Hydrobromic acid, 7.6 N.
Acetic acid, 16 N.
Potassium iodide. AnalaR grade.
Acetylacetone. Distilled before use.
Benzoylacetone.

Dibenzoylmethane. Dibenzoylmethane was prepared[6] and then used to prepare its halo derivatives. The halo derivatives of acetylacetone, benzoylacetone and dibenzoylmethane were prepared by the reported procedures.[2,3,7–9]

Procedure

Solutions of the required concentrations (see Table I) of the halo and dihalo derivatives of the three β-diketones in 80% ethanol and of potassium iodide in water were prepared separately. Equal volumes of the halide and potassium iodide solutions were placed in flasks in a thermostatically controlled water-bath and, when these solutions attained the temperature of the bath, they were mixed together and 10-ml portions were withdrawn at different intervals of time and titrated against standard sodium thiosulphate solution. Blank runs (without any halo derivatives) were also carried out when necessary. The percentage completion of the reactions of the various halo derivatives of the three β-diketones were studied in the presence and absence of hydrochloric, hydrobromic and acetic acids. When the effects of these acids were studied, different amounts of the acids (see Table I) were added to halo and dihalo derivatives of the β-diketones at the time their solutions were prepared. The remainder of the procedure was followed as described above.

Results and Discussion

The percentage completion of the reactions in the presence and absence of the three acids is shown in Table I. The results obtained indicate that the halogens in the halo derivatives (especially the monobromo and dibromo derivatives) of dibenzoylmethane were determined almost quantitatively in the presence of small amounts of hydrochloric, hydrobromic and acetic acids. Under similar conditions, these acids had no effect on the removal of halogens from monochloro- and dichlorobenzoylacetone. The halo derivatives of acetylacetones were least affected, and in fact were inert to the removal of halogen when similar concentrations were used. This necessitated the use of higher concentrations of the reactants when monobromo- and mono- and dichloroacetylacetone were used. The latter experiments (the results for which have not been incorporated in Table I) revealed that the amount of halogen determined in these compounds far exceeded the theoretical values, probably owing to a direct reaction between potassium iodide and the acids to give hydriodic acid, which ultimately is oxidised to iodine.

TABLE I

REACTION PARAMETERS FOR DETERMINATION OF HALOGENS IN HALO- AND DIHALO-β-DIKETONES AT 40 °C

Amount of halo derivatives reacted (moles per litre) = volume of 0.001 N $Na_2S_2O_3$ solution × 0.0001, except for dibromodibenzoylmethane, for which the amount reacted (moles per litre) = volume of 0.001 N $Na_2S_2O_3$ solution × 0.00005.

Halo derivative	Time/ min	Concentration of halo derivative/ mol l^{-1}	Concentration of KI solution/ mol l^{-1}	Volume of acid used/ml			Volume of 0.001 N $Na_2S_2O_3$ solution/ml	Percentage completion of reaction
				10 N HCl	16 N CH_3COOH	7.6 N HBr		
Monochlorodibenzoylmethane	120	0.004	0.004	—	—	—	0	0
	30	0.002	0.002	0.022	—	—	19.1	95
	15	0.002	0.002	0.22	—	—	20.0	100
	30	0.002	0.002	—	—	0.03	2.20	11
	30	0.002	0.002	—	0.013	—	1.61	8
Monobromodibenzoylmethane	120	0.004	0.004	—	—	—	3.61	9
	110	0.004	0.004	0.11	—	—	21.10	53
	10	0.004	0.004	2.5	—	—	28.13	70
	0	0.004	0.004	5.0	—	—	40.00	100
	10	0.004	0.004	—	—	0.15	39.98	100
Dibromodibenzoylmethane	16	0.004	0.004	—	—	—	33.95	42
	0	0.002	0.002	0.22	—	—	40.00	100
	4	0.002	0.002	0.022	—	—	40.00	100
	4	0.002	0.002	—	—	0.03	37.50	93
	4	0.002	0.002	—	0.013	—	35.50	88
Monochlorobenzoylacetone	0	0.4	4.0	1.0	—	—	>100	
	15	0.004	0.004	1.0	—	—	6.5	16
	15	0.004	0.004	—	1.0	—	6.5	16
	15	0.004	0.004	—	—	1.0	5.5	14
Dichlorobenzoylacetone	30	0.004	0.004	—	—	—	25.20	63
	30	0.004	0.004	1.0	—	—	25.21	63
	30	0.004	0.004	—	1.0	—	25.18	63
	30	0.004	0.004	—	—	1.0	24.82	62
Monochloroacetylacetone	100	0.004	0.2	—	—	—	4.35	11
	100	0.004	0.4	—	—	—	7.85	20
Dichloroacetylacetone	110	0.0032	0.2	—	—	—	3.85	12
	110	0.0032	0.4	—	—	—	7.45	23
Monobromoacetylacetone	90	0.004	0.4	—	—	—	1.00	2.5
	90	0.002	0.4	—	—	—	1.00	5
	120	0.004	0.004	1 mol l^{-1}	—	—	0	0
	60	0.004	0.4	—	0.1	—	1.45	3.6*
	60	0.004	0.072	—	0.1	—	0.45	1*

*At 35 °C.

It is obvious from these results that the various halo- and dihalo-β-diketones studied show considerable variations in their reactivities towards the removal of halogen. The reasons for these variations and the kinetics of the reactions involved are currently being studied and possible mechanisms operative in different instances will be reported later.

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Relationship Between Refractive Index and Specific Gravity of Aqueous Glycerol Solutions[*]

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Keywords: *Refractive index*; *specific gravity*; *glycerol*

The refractive indices of solutions, other than those of strong electrolytes, are known to be rectilinear functions of their concentrations on a mass-in-volume (m/V) basis.[1] The concentration by volume (m/V) is equal to the concentration by mass (m/m) multiplied by a density factor. These relationships permit the mutual comparison of refractive index and specific gravity data,[2–5] and the data available for glycerol[6,7] at 20 °C are examined here.

Over the range 0–100% of glycerol, the regression of the refractive index on concentration was found to be

$$\text{Refractive index} = 1.33303 + [0.0011356 \times \text{glycerol } (\%\ m/m) \times \text{specific gravity}] \quad (1)$$

The residual standard deviation was 0.0010 refractive index unit. The differences between the tabulated data and those predicted from equation (1) were calculated, and are shown as line A in Fig. 1; their magnitude (tabulated minus predicted values) ranges from about +0.0012 at 35% and 58% m/m of glycerol, equivalent to about 1.2% of glycerol, to −0.0025 at 100% m/m of glycerol, equivalent to about 1.5% of glycerol. It is clear from Fig. 1 that the differences are systematic, and consist of three sections, from 0 to 44%, from 45 to 79% and from 80 to 100% m/m of glycerol, corresponding to the three sectional equations of the refractive index table.

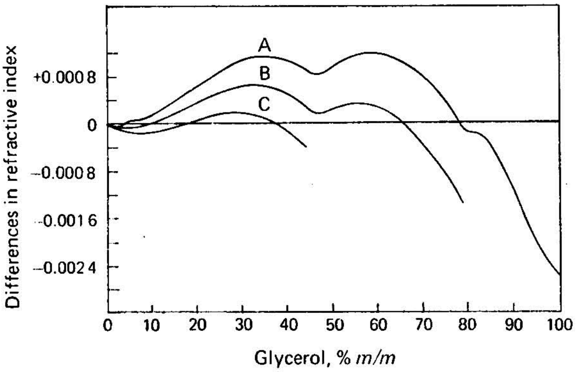

Fig. 1. Differences between tablulated and predicted values of the refractive index of glycerol solutions: A, 0–100%; B, 0–79%; and C, 0–44%.

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[*] Contribution from the Agricultural Research Organization, The Volcani Centre, Bet Dagan, Israel, 1977 Series, No. 115-E.

Over the range 0–79% *m/m* of glycerol, the regression was found to be

$$\text{Refractive index} = 1.333\,03+[0.001\,148\,9 \times \text{glycerol } (\%\ m/m) \times \text{specific gravity}] \quad (2)$$

The residual standard deviation was 0.000 5 refractive index unit. The differences between the tabulated data and those predicted from equation (2) were calculated as before, and are shown as line B in Fig. 1; their magnitude ranges from about +0.000 6 at 32% *m/m* of glycerol, equivalent to about 0.5% of glycerol, to about +0.000 3 at 55% *m/m* of glycerol, equivalent to about 0.2% of glycerol, and about −0.001 3 at 79% *m/m* of glycerol, equivalent to about 0.9% of glycerol.

Over the range 0–44% *m/m* of glycerol, the regression was found to be

$$\text{Refractive index} = 1.333\,03+[0.001\,162\,6 \times \text{glycerol } (\%\ m/m) \times \text{specific gravity}] \quad (3)$$

The residual standard deviation was 0.000 1 refractive index unit. The differences between the tabulated data and those predicted from equation (3) were calculated as before, and are shown as line C in Fig. 1. Even over this range the differences are seen to be systematic, and remain within an accuracy of about 0.1% of glycerol only up to 41% *m/m* of glycerol.

It follows that the table of refractive indices[7] is not as accurate as the claimed "at least 0.1%." Improved accuracy may be obtained by comparing the experimental data with the results of similar determinations of specific gravity, so that interpolated values of both parameters should vary by less than one unit in the last decimal place from the ideal relationship, and the differences are random in sign.

It can be argued that glycerol solutions may deviate from the ideal linear relationship because of molecular interactions[1]; however, the very high proportions of the variance explained by the above equations (0.999 412, 0.999 798 and 0.999 932, respectively) make non-linearity appear unlikely. It can also be argued that the discrepancies found by mutual comparison of refractive index and specific gravity data may result from either of these properties; however, the specific gravity data[6] represent empirical measurements while the refractive index data[7] were calculated from three sectional equations that approximate to empirical measurements with a stated deviation of 0.000 11 refractive index unit; the latter are thus considered more likely to be inaccurate than the former.

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S-Benzylthiuronium Chloride as an Acidimetric Standard in Non-Aqueous Titrimetry

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Keywords: S-*Benzylthiuronium chloride*; *non-aqueous titrimetry*; *acidimetric standard*

In non-aqueous titrimetry, perchloric acid is the most frequently used acidimetric titrant because of its high acid strength. Potassium hydrogen phthalate is often used for the standardisation of this titrant, but it has the disadvantages of forming a mucilaginous precipitate[1] during the titration and of requiring hot glacial acetic acid for its dissolution. Anhydrous sodium carbonate is also used as a standard substance, but has the disadvantages that it is hygroscopic and has a comparatively low equivalent mass. Tris(hydroxymethyl)aminomethane,[2] which is obtainable in a high state of purity, is also a favoured primary standard, but its use is restricted by its ability to be acetylated. *S*-Benzylthiuronium chloride is easily prepared, and is readily purified and thus is available in a state of high purity.[3] It was, therefore, decided to study its use as an acidimetric standard. Visual titrations of solutions of perchloric acid in acetic acid, dioxan and acetonitrile have been carried out against potassium hydrogen phthalate and *S*-benzylthiuronium chloride - mercury(II) acetate[4] in acetic acid medium using crystal violet as indicator.

Standardardisation of Perchloric Acid Solutions

Solutions of perchloric acid in anhydrous glacial acetic acid, dioxan and acetonitrile were prepared according to published procedures.[5] The required amounts of *S*-benzylthiuronium chloride (BDH, OAS grade) and potassium hydrogen phthalate (AnalaR grade) were dissolved in 10 ml of glacial acetic acid, 10 ml of mercury(II) acetate (2% *m*/*V* solution in glacial acetic acid) were added and the solution was titrated with perchloric acid solution using crystal violet as indicator. Mercury(II) acetate was not added in the titration with potassium hydrogen phthalate. The colour change when titrating with solutions of perchloric acid in glacial acetic acid and dioxan was from violet - blue to blue - green and with the acetonitrile solution it was from violet - blue to clear blue. Blank determinations were carried out and the values of the blanks deducted from the values of the actual determinations.

TABLE I

RESULTS FOR STANDARDISATION OF PERCHLORIC ACID

Sample number*	Mass of KHP†/mg	Volume of $HClO_4$ consumed/ml	Molarity of $HClO_4$	Mass of BC‡/mg	Volume of $HClO_4$ consumed/ml	Molarity of $HClO_4$
1	50.6	4.13	0.060 01	50.6	4.17	0.059 92
2	55.4	4.52	0.060 03	53.2	4.38	0.059 96
3	70.2	5.73	0.059 99	70.4	5.80	0.059 94
4	72.4	5.91	0.059 99	77.0	6.34	0.059 96
5	91.4	7.46	0.060 01	104.4	8.60	0.059 94
6	105.2	8.59	0.059 98	125.8	10.36	0.059 96
7	125.8	10.27	0.060 01	154.8	12.75	0.059 94
8	154.0	12.58	0.059 95	175.2	14.43	0.059 94
9	172.4	14.07	0.060 02	190.2	15.66	0.059 96
10	200.4	16.36	0.059 98	201.4	16.58	0.059 96
11	52.0	4.15	0.061 38	54.0	4.34	0.061 44
12	55.0	4.39	0.061 37	63.8	5.13	0.061 41
13	70.6	5.63	0.061 42	73.6	5.92	0.061 39
14	73.8	5.90	0.061 39	80.0	6.44	0.061 34
15	107.2	8.55	0.061 41	101.4	8.15	0.061 42
16	126.6	10.10	0.061 41	123.2	9.91	0.061 38
17	158.0	12.60	0.061 42	150.4	12.10	0.061 37
18	176.6	14.09	0.061 41	176.0	14.15	0.061 42
19	186.0	14.84	0.061 38	185.2	14.90	0.061 38
20	208.0	16.60	0.061 38	201.4	16.20	0.061 38
21	57.0	5.42	0.051 51	50.2	4.82	0.051 42
22	63.2	6.01	0.051 50	55.2	5.30	0.051 41
23	74.0	7.04	0.051 47	70.6	6.78	0.051 41
24	80.2	7.62	0.051 54	76.6	7.35	0.051 45
25	101.0	9.60	0.051 52	102.8	9.87	0.051 41
26	105.2	10.00	0.051 52	120.2	11.54	0.051 42
27	127.8	12.15	0.051 53	127.6	12.25	0.051 44
28	144.0	13.70	0.051 48	153.8	14.76	0.051 44
29	169.4	16.10	0.051 54	166.2	15.95	0.051 44
30	203.0	19.30	0.051 51	200.2	19.22	0.051 42

* Perchloric acid in acetic acid, dioxan and acetonitrile was used for titrations 1–10, 11–20 and 21–30, respectively.

† KHP = potassium hydrogen phthalate.

‡ BC = *S*-benzylthiuronium chloride.

Results

The results are recorded in Tables I and II. The mean molarities, standard deviations and confidence limits show that *S*-benzylthiuronium chloride compares favourably with other acidimetric standards, and therefore seems to merit recommendation.

TABLE II

STATISTICAL ANALYSIS OF RESULTS

	Perchloric acid in		
	Acetic acid	Dioxan	Acetonitrile
Mean molarity against KHP*	$6\,000 \times 10^{-5}$	$6\,140 \times 10^{-5}$	$5\,151 \times 10^{-5}$
Standard deviation	2.380×10^{-5}	1.913×10^{-5}	2.357×10^{-5}
90% confidence limit	1.380×10^{-5}	1.109×10^{-5}	1.367×10^{-5}
95% confidence limit	1.702×10^{-5}	1.369×10^{-5}	1.690×10^{-5}
99% confidence limit	2.446×10^{-5}	1.966×10^{-5}	2.423×10^{-5}
Mean molarity against BC†	$5\,995 \times 10^{-5}$	$6\,139 \times 10^{-5}$	$5\,143 \times 10^{-5}$
Standard deviation	1.415×10^{-5}	2.961×10^{-5}	1.563×10^{-5}
90% confidence limit	0.8202×10^{-5}	1.716×10^{-5}	0.9059×10^{-5}
95% confidence limit	1.012×10^{-5}	2.117×10^{-5}	1.118×10^{-5}
99% confidence limit	1.454×10^{-5}	3.043×10^{-5}	1.606×10^{-5}

* KHP = potassium hydrogen phthalate.
† BC = *S*-benzylthiuronium chloride.

The authors are grateful to CSIR (India) for the award of a Research Fellowship to N.K.

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Book Reviews

THE ANALYTICAL CHEMISTRY OF SYNTHETIC DYES. Edited by K. VENKATARAMAN. Pp. xxvi + 591. New York, London, Sydney and Toronto: John Wiley. 1977. Price £31.90; $54.

Colour chemists and colour technologists will need no introduction to the Editor of this book, who has successfully brought together many interesting aspects of chemical analysis appertaining to dyes and pigments into this book, with extensive contributions from the du Pont organisation. One can safely assume that readers will be familiar with the established volumes of "The Chemistry of Synthetic Dyes" that have resulted from the same editorial pen over the last quarter-century, and also with the "Colour Index." When actual chemical constitutions or structural formulae are not specifically set out in the text, there are appropriate cross-references to the above-mentioned sources.

In four chapters, Schweppe, Srámek and Papa explore the established procedures, applications and potentialities of chromatographic techniques that still form the basis of many rapid determinations of the purity, identity and constitution of dyes. Though ionic dyes are among the most difficult to analyse and separate, liquid - solid (absorption) techniques are still the most important, success often being achieved by using polar phases and a gradient elution technique in order to reveal dyes and their precursors. Consideration is given to problems associated with the chromatographic separation of anthraquinone intermediates and cationic dyes, also the limitations of exclusion chromatography as recognised at present. Garland deals with colour measurement, the associated fundamental calculations and terminology, quality-control parameters and variables encountered in analytical methods. Whitaker gives a succinct account of the X-ray powder diffraction technique for characterising crystalline pigment forms, particularly copper phthalocyanine and linear *trans*-quinacridone, with supporting data. Infrared and nuclear magnetic resonance spectroscopy, and mass spectrometry are dealt with by Miller, Foris and Beukelman, respectively. A valuable résumé of infrared correlations pertinent to the interpretation of dye spectra is provided.

Significant advances in the use of nuclear magnetic resonance in dye chemistry for structure determination and confirmation during the last 7 years are reviewed. Owing to the complexity of dye molecules, complete structures can seldom be deduced from mass spectra alone; the "rings plus double bonds" concept may well throw further light on their interpretation. Gasparič explains the fundamental ideas behind chemical-degradation methods, describing established experimental techniques that are applicable to different dye classes. When combined with chromatographic evaluation of the degradation products, as in pyrolysis - gas - liquid chromatography - mass spectrometry, they are invaluable. Structural problems receive especially detailed treatment in three chapters (Beukelman, Foris and Miller, Lanzarone and Schrier). Schweppe and Thomson, respectively, offer practical guides to the analysis and identification of dyes on textile fibres, and of organic pigments on substrates other than these.

The analysis of food, drug and cosmetic colours (Leatherman *et al.*) and hair dyes (Corbett) is reviewed in two chapters. Methods utilising the latest instrumentation, *viz.*, X-ray fluorescence for heavy metals and HPLC for the determination of intermediates, are described, and the importance of reference standards in spectrophotometric certification analyses is emphasised. In the analysis of hair colourants, electrophoretic and thin-layer chromatographic separation techniques facilitate characterisation. Both the assay of raw materials and the analysis of the finished product need to be considered. Kissa devotes attention to the problems of quantitative analysis, particularly spectrophotometry and reflectance colorimetry, with a critical review of the dissolution and extraction methods that are applicable to dyed fibrous substrates. Considerations arising in ecological and toxicological monitoring are put forward by Yllo, who points out that the availability of sensitive and rapid analytical methods has generated much interest in probing into ecological systems more deeply. The need for continuing research is now widely recognised.

Analysts who are in any way concerned with dyes and pigments will find this authoritative survey an excellent guide to the transformations that have taken and indeed are still taking place in identification schemes, analytical rationale, data accumulation and data analysis, not forgetting the impact of sophisticated, automatic analysis when justified in terms of the work-load, cost, urgency, and the reproducibility and accuracy attainable.

W. A. STRAW

DITHIZONE. By H. M. N. H. IRVING. *Analytical Sciences Monographs, No. 5.* Pp. iv + 106. London: The Chemical Society. 1977. Price £7.25 (CS members £5.50).

Countless organic reagents have been proposed for the separation and determination of trace metals. Most of these have received only passing interest, even from their originators, and no more has been heard of them. A comparatively small number, however, became widely applied and changed the course of chemical analysis. Among these, dithizone is pre-eminent. It combines in solution, under suitable conditions, with the ions of 20 or so metals to form intensely coloured complexes that can be extracted into a variety of immiscible solvents. Dithizone was introduced into analysis in 1925 by Hellmuth Fischer, whose early publications dealing with its applications pioneered a new range of techniques for the analyst, which have since been applied in trace analysis generally. These techniques included solvent extraction, extractive titrations and the use of pH control and masking agents to obtain selectivity. Since its introduction, several hundred papers have appeared dealing with the properties and applications of dithizone and describing fundamental studies of the physical chemistry of dithizone reactions and solvent extraction. The application of dithizone to trace analysis is the subject of an invaluable book by Iwantscheff, which deals mainly with analytical methodology.

Studies of dithizone and related compounds have been made by many eminent analytical chemists and the author of this publication has been recognised for many years as an outstanding authority in this field. In this monograph, Professor Irving has not attempted to produce another "Iwantscheff" and, indeed, the practising analyst will search in vain for details of any particular analytical method. He has provided instead a concise yet detailed account of the present state of knowledge of the behaviour of dithizone and its complexes.

It was a great pleasure to read such a well written and authoritative account of a reagent that I have always found fascinating. The author has presented his material with the usual clarity and depth that one has come to expect from him, and the fundamental topics discussed are related, where appropriate, to practical considerations. My only regret is that he did not write an earlier version 10 or 20 years ago when I was using dithizone daily in my laboratory. Nowadays, many of the analyses that were formerly made by dithizone methods have been replaced by instrumental techniques such as AAS. Nevertheless, dithizone still has important functions for analysts in many laboratories, and this monograph can be recommended to all who need to know more than simply "how to follow a method."

The main sections of this book deal with: the properties of dithizone; metal dithizone complexes and their formulae; the photochemistry of metal dithizonates; the extraction of metal dithizonates; the less familiar dithizone complexes; organometallic dithizonates; practical considerations; and additional applications of dithizone. Finally, there is a section on some unresolved problems. References to 489 publications are cited.

E. J. NEWMAN

MODERN PRACTICE OF GAS CHROMATOGRAPHY. Edited by ROBERT L. GROB. Pp. xx + 654. New York, London, Sydney and Toronto: John Wiley. 1977. Price £16; $28.

The book is a compilation of presentations from a group of authors who have worked together for a number of years. The book is divided into three parts, the first two for those unfamiliar with the theory, techniques and instrumentation of gas chromatography, and the third for readers familiar with gas chromatography but requiring information on particular applications. The reproduction is not of a very high standard, and the drawings, in particular, have suffered. The Introduction contains a list of definitions of some terms used in chromatography, which, although incomplete, is useful. The first chapter on theory introduces the reader to the various separation techniques and then to theories of gas chromatography. The role of the support and stationary phase, and the means of describing column performance, are discussed. The chapter also includes a section on preparative-scale gas chromatography and gas - solid chromatography. A separate chapter is devoted to column preparation and selection, which, despite being in the theoretical part of the book, contains a great deal of practical information and advice. The chapter on qualitative analysis gives only brief mention of the value of comparing selective and non-selective detector responses, while giving unwarranted attention to relative molecular mass chromatography. The standard methods of area measurement for quantitative analysis are given with reference to drawings of peaks exhibiting a most extraordinary profile.

Part 2 is entitled Techniques and Instrumentation, and it was good to note in the chapter on detectors a description of the microwave plasma detector. The chapter on instrumentation covers gas controllers, inlet systems, oven control and programming, detector operation and data handling. The technique of trace analysis is afforded a complete chapter and covers sampling, isolation, concentration and derivatisation where appropriate, with particular reference to the analysis of aqueous samples to determine volatile organic compounds. Chapter 8 has the rather puzzling title of "Selection of Analytical Data from a GC Laboratory." It is devoted to a discussion on the choice of integrators and computers, with advice, the types of systems available and the economics of the systems. A more appropriate title would be "Selection of a Data System for a GC Laboratory."

The final part of the book is entitled "Applications" and contains a chapter on the analysis of food to determine lipids, proteins and carbohydrates. One chapter is devoted to clinical applications, predominantly of urine and blood. Drugs are included, although there is also a complete chapter on drug analysis at the end of the book. The other application discussed is the use of gas chromatography in physiochemical measurements.

Although some of the contributions cover similar topics there is very little overlap of information. However, for the reader a more orderly presentation of facts would have been desirable. The book, in its attempt to cover so many aspects of chromatography, does fall a little short of a comprehensive coverage, and very little of the information is not available in other recent books on chromatography.

T. A. GOUGH

PROGRESS IN DRUG METABOLISM. Volume 2. Edited by J. W. BRIDGES and L. F. CHASSEAUD. Pp. x + 348. London, New York, Sydney and Toronto: John Wiley. 1977. Price £13.50; $27.

In this series one looks for selective and critical reviews sufficient to inform new drug developers and regulatory assessors, without blinding them with the minutiae of specialist papers. The first volume* consisted of five articles, by seven authors, providing a judicious blend of detection, activation, intermediates, induction and protein binding. This second volume, with 25% more text, has six articles, by 13 authors, on comparably diverse topics. All but the first article meet the Editors' aim of highly readable reviews.

For the enzyme system UDP - glucuronyltransferase there is a review of cellular properties, activation - inhibition, solubilisation and kinetics. This review is preceded by a heavily condensed account of the mechanism of glucuronide formation, and followed by a comprehensive review of factors affecting it, although assay methods are only briefly mentioned. A telegraphic supplement covers 1975. This chapter is a gold-mine of information but stylistically is about as digestible as the London telephone directory, an analogy enhanced by the Editors' preference for the Harvard citation system.

Much more readable is a review of *in vitro* cellular metabolism of foreign substances, with some extrapolation to *in vivo* situations. The choice, advantages and problems of cell suspensions and cultures are discussed and attention is then directed to biochemical parameters of xenobiotic metabolism in fresh isolates and maintained cultures; substrates include tranquillisers, pesticides and hydrocarbons. The authors suggest future trends in the use of cell suspensions and cultures and look to instrumental study of single cells using, for instance, microdensitometers and, eventually, microspectrofluorimeters.

A shorter chapter examines the topical subject of drug transfer across the placenta and foetal metabolism of xenobiotics. Particular emphasis is given to species differences at different development stages in the embryo and neonate. Of special interest is a review of drug labelling with stable, heavy isotopes (notably ^{2}H, ^{13}C, ^{15}N and ^{18}O). Brief mention is made of limited toxicity studies and the circumstances favouring use of cold tracers, with passing reference to typical syntheses and detection techniques (magnetic resonance and mass spectrometry, and microwave-generated plasma detectors for gas - liquid chromatography). Most of the chapter discusses the identification and measurement of particular drug metabolites variously labelled.

Ion-pair extraction methods are versatile and selective in separating metabolites from parent drugs. Chapter 5 provides accounts of kinetic principles, solvent selectivity, uses in partition chromatography, quantitative (including counter-current) applications and some reference to reversed-phase systems.

The seemingly impossible task of reviewing work on bioavailability and drug dissolution is tackled by restriction of the scope to the period 1970–74 and to absorption data for humans with

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* Reviewed in *Analyst*, **1977**, **102**, 71.

dissolution studies on the corresponding formulations. General concepts and methods of measurement are briefly assessed but the bulk of the chapter summarises *in vitro/in vivo* correlations for 23 drugs. Not surprisingly, digoxin is extensively reported but attention is also given to two other steroids, four analgesics, four antibiotics, seven sulfa and one nifur antibacterials, two sedatives, a diuretic and an anticoagulant. Few dissolution studies are absolutely predictive of human absorption but new approaches to interpretation of both areas should lead to better correlations.

G. F. PHILLIPS

COLORIMETRIC CHEMICAL ANALYTICAL METHODS. Eighth Edition, 1974. By L. C. THOMAS and G. H. CHAMBERLIN. Pp. xlvi + 626. Salisbury: The Tintometer Ltd., and Dortmund: Tintometer GmbH. Distributed by John Wiley, London, New York, Sydney and Toronto. 1977. Price £20. $34.40.

This Eighth Edition of Tintometer's manual of colorimetric methods now reaches the general public as a result of a distribution arrangement with the John Wiley organisation. Although this edition was prepared by Tintometer in 1974, it has not previously been published or received by *The Analyst* for review.

The methods, of course, require the use of the Lovibond Comparator and Lovibond Nessleriser. This apparatus, together with the appropriate permanent colour standards, is manufactured by The Tintometer Company, and enables a very wide range of colorimetric determinations to be made with ease, simplicity and, in most instances, accuracy.

Many readers will be familiar with the technique, so that attention is given here only to the principal features of this comprehensive collection of analytical methods. The main text is in sections dealing in turn with the determinations of pH, organic materials, inorganic materials, biochemical, pathological and pharmacological substances, and toxic substances in air, with a final section covering colour grading and quality tests.

By far the largest section (300 pages) is devoted to the determination of various elements, both metals and non-metals, in ionic form, in various types of sample. This section contains useful information on appropriate preparation of the analytical solution from a variety of sample sources, and will help the analyst to select the most suitable procedure for the particular sample he may wish to analyse.

If it is recognised that this book is not much more than a practical manual of Comparator/Nessleriser methods, then its limitations become obvious. It is *not* a manual of general colorimetric methods for use with photoelectric colorimeters, although doubtless there are many methods described that originate from photometry and many others that could easily be adapted for photometric purposes.

Were it not for the fact that the manual and the apparatus are interdependent, it would be only too easy to criticise the rather high cost of this book. As things are it is difficult to understand its promotion as a separate entity by the Wiley publishing group. The relatively low cost of the apparatus compared with the cheapest spectrophotometer surely enables the cost of the manual to be absorbed when both are purchased simultaneously.

It is difficult to visualise the type of operator who would want to use more than a few of the methods described, and presumably the details of each method are provided when the necessary colour standards are purchased.

In fairness to the authors of this latest edition, they have produced a useful and comprehensive manual, the very size (and hence cost) of which may prove to be its major disadvantage. It is not easy to suggest a particular user to whom this book might be recommended. Certainly, as a source of available methods it might encourage a wider use of the Comparator technique, which, for many purposes, gives results within acceptable analytical limits.

W. I. STEPHEN

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The Praesidium of Euroanalysis III extends a cordial invitation to participate in the Conference to be held in Dublin, Ireland, from 20–25 August 1978.

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Determination of Ethinyloestradiol in Single Tablets and Its Separation from Other Steroids by High-performance Liquid Chromatography

A reversed-phase chromatographic system is used to separate 17α-ethinyloestradiol-1,3,5(10)-triene-3,17β-diol (ethinyloestradiol) from structurally related steroidal compounds. A direct and highly sensitive method of assay is given for uncoated tablets containing ethinyloestradiol, as used for contraception. The method is modified for sugar-coated tablets used for relief of menopause symptoms and is sufficiently sensitive to detect ethinyloestradiol if it is present with other steroids as a contaminant.

Keywords: *Ethinyloestradiol determination*; *tablets*; *high-performance liquid chromatography*

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Analyst, 1978, **103**, 156–161.

Differential Electrolytic Potentiometry with Periodic Polarisation

Part XXIV. An Appraisal of the Amplitude-biassed Mode

A simple device for amplitude biassing a periodic waveform without distortion has been developed to overcome the difficulty with earlier instrumentation of obtaining more than a 2% bias. Amplitude-biassed differential electrolytic potentiometry has been compared with zero-current potentiometry, classical d.c., symmetrical periodic and time-biassed periodic differential electrolytic potentiometry in oxidation - reduction titrimetry for electrode reactions of various rates, and in acid - base titrimetry. The behaviour of individual electrodes with reference to zero-current and standard electrodes has been examined. The behaviour observed is in accord with theoretical prediction, and is analogous to the application of a d.c. offset to symmetrical periodic polarisation. The advantages of rapid potential equilibration and extended electrode life between activations accrue, but with appreciable bias the end-point periodic signal deviates from the equivalence point.

Keywords: *Differential electrolytic potentiometry*; *periodic polarisation*; *amplitude-biassed mode*

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Analyst, 1978, **103**, 162–175.

Differential-pulse Polarography of Selenium(IV) in the Presence of Metal Ions

Short Paper

Keywords: *Selenium(IV) determination*; *differential-pulse polarography*; *metal-ion interferents*

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Analyst, 1978, **103**, 176–179.

Determination of Small Amounts of Bismuth in Antimony(III) Oxide by Using Anodic Stripping Voltammetry

Short Paper

Keywords: *Bismuth determination*; *antimony*(*III*) *oxide*; *anodic stripping voltammetry*

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Analyst, 1978, **103**, 179–182.

Titrimetric Determination of Halogens in Halo- and Dihalo-β-diketones

Short Paper

Keywords: *Halogen determination*; *halo- and dihalo-β-diketones*; *titrimetry*

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Analyst, 1978, **103**, 183–185.

Relationship Between Refractive Index and Specific Gravity of Aqueous Glycerol Solutions

Short Paper

Keywords: *Refractive index*; *specific gravity*; *glycerol*

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Analyst, 1978, **103**, 185–186.

S-Benzylthiuronium Chloride as an Acidimetric Standard in Non-aqueous Titrimetry

Short Paper

Keywords: S-*Benzylthiuronium chloride*; *non-aqueous titrimetry*; *acidimetric standard*

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Analyst, 1978, **103**, 186–188.

INSTITUTE OF GEOLOGICAL SCIENCES

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Following an inter-laboratory survey of ore analysis by the Institute of Geological Sciences, a series of standard ores and concentrates is now available. The samples have been analysed by up to thirty-one laboratories in fourteen countries and after statistical elimination of questionable results, mean concentrations and 95% confidence limits have been calculated. Samples vary in weight from forty to one hundred grams and are as follcws:

Sample	Description	Main analyses	Approx. weight, grams	Price £ Sterling
IGS 20	Nickel concentrate	Ni 7.60%, Cu 5.79%, Co 0.33%, Zn 0.147%, Fe 38.07%	65	15
21	Nickel ore (norite)	Ni 1.97%, Cu 0.798%, Co 0.069%, Fe 23.40%	50	15
22	Nickel ore (serpentinite)	Ni 1.255%, Cu 0.106%, Co 0.051%, Fe 22.73%	45	15
23	Nickel ore (laterite)	Ni 1.68%, Fe 26.85%, Cu 0.013%, Co 0.081%	50	15
24	Cobalt ore	Co 0.323%, Cu 4.91%, Fe 2.94%, Ni 0.043%	40	15
25	Wolframite	W 39.50%, Sn 9.42%, Fe 19.43%	55	15
26	Tin-tungsten ore	Sn 33.36%, W 13.63%, Fe 12.20%, Cu 2.11%	45	15
27	Molybdenum-tungsten ore	Mo 0.29%, W 0.036%, Fe 1.76%	65	10
28	Lead-zinc concentrate	Pb 54.01%, Zn 4.21%, Fe 11.14%, As 4.24%, Ag 1740 ppm, Sb 0.14%, Cu 0.188%, Cd 0.029%	100	15
29	Pyrolusite	MnO_2 93.31%, Ba 0.59%	40	15
30	Chromite	Cr 23.95%, Fe 11.21%, Ti 0.14%	55	15
31	Ilmenite	Ti 32.78%, Fe 30.36%, Fe^{++} 19.11%, Fe^{+++} 11.29%	45	15
32	Rutile	Ti 57.19%	45	15
33	Columbite	Nb 47.93%, Ta 4.37%, Ti 1.04%	50	15
34	Tantalite	Ta 40.88%, Nb 18.83%, Ti 0.69%	45	15
35	Zircon	Zr 48.76%, Hf 1.16%, Ti 0.16	50	15
36	Monazite	REO + ThO_2 60.39%, Th 5.82%	45	10
37	Uranium ore	U 0.148%	40	15
38	Baryte	Ba 51.39%, SO_3 30.77%, F 2.9%	80	15
39	Fluorite	F 46.69%	55	15

Orders for samples, which will be despatched to overseas destinations by air mail, should include the appropriate payments (cheques etc. should be made payable to the Natural Environment Research Council Deposit Account) and should be addressed to the Institute of Geological Sciences, Geochemistry and Petrology Division, 64-78 Gray's Inn Road, London WC1X 8NG, United Kingdom and marked *STANDARD SAMPLES*. Requests for further information should be made to the same address.

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REPORT BY THE ANALYTICAL METHODS COMMITTEE

SHORT PAPER

COMMUNICATION

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