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Summaries of Papers in this Issue

Analytical Optoacoustic Spectrometry Part I. Instrument Assembly and Performance Characteristics

A simple single-beam spectrometer suitable for the study of optoacoustic spectra from small solid samples is described and the design of a suitable sample cell is reported. The performance characteristics of the spectrometer have been evaluated using different types of sample. A preliminary assessment of the predicted advantages of optoacoustic spectrometry over conventional techniques of ultraviolet - visible absorption and reflectance spectrometry for solid samples has been made.

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Department of Chemistry, Imperial College, London, SW7 2AY.

Analyst, 1976, **101**, 73–85.

Observations on the Limitation Imposed by Interferences in Flame Atomic-absorption Spectrometry at High Analyte Concentrations

When burner rotation or an absorption line of poorer sensitivity is used in flame atomic-absorption spectrometric analysis, care must be taken to establish the absence of fresh or increased interferences at higher concentrations of the analyte element. At high concentrations, sulphate was found to cause severe depressions in the determinations of magnesium, cobalt and nickel, although under normal conditions the interference is negligible. The risk of substantial error can be reduced either by dilution of samples and standards, or by taking measurements by using the upper part of a fuel-lean flame that is burning on a slot burner with a triangular cross-section, or by adding a suitable releasing agent.

M. S. CRESSER and D. A. MACLEOD
Soil Science Department, University of Aberdeen, Aberdeen, AB9 2UE.

Analyst, 1976, **101**, 86–90.

An Improved Digestion Method for the Extraction of Mercury from Environmental Samples

An improved digestion procedure for the extraction of mercury from environmental material is reported. The method involves the digestion of the sample at 60 °C with sulphuric acid - nitric acid (2 + 1), containing a trace amount of hydrochloric acid, and subsequent oxidation with permanganate and persulphate solutions. With this procedure mercury is successfully recovered from organic matter and resistant inorganic forms such as mercury(II) sulphide. Unlike digestion with aqua regia, this procedure is simple and safe, and is applicable to the digestion of a large number of samples simultaneously. The method can be adapted to the automated cold-vapour and flame atomic-absorption techniques and is therefore ideal for routine monitoring.

HAIG AGEMIAN and A. S. Y. CHAU
Canada Centre for Inland Waters, Water Quality Branch, P.O. Box 5050, 867 Lakeshore Road, Burlington, Ontario, L7R 4A6, Canada.

Analyst, 1976, **101**, 91–95.

The Application of a Wide-slot Nitrous Oxide - Nitrogen - Acetylene Burner for the Atomic-absorption Spectrophotometric Determination of Aluminium, Arsenic and Tin in Steels by the Single-pulse Nebulisation Technique

Single-pulse nebulisation of 10 per cent. *m/V* iron or steel solutions into a nitrogen-diluted nitrous oxide - acetylene flame maintained on a specially designed wide-slot burner is a useful technique for the determination of tin, arsenic and soluble aluminium in iron and steels. Use of this method avoids the need for prior separation of the analyte. A deuterium lamp was found to be unsatisfactory for measuring the background (non-specific) absorption when determining aluminium and tin, the explanation for which is postulated.

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Shandon Southern Instruments Limited, Frimley Road, Camberley, Surrey, GU16 5ET.

Analyst, 1976, **101**, 96–102.

The Determination of Mobile Nitrogen in Steel Using an Ammonium Ion-selective Electrode

An absorption cell containing an ammonium ion-selective electrode has been constructed and used for the determination of mobile nitrogen in steel; this nitrogen is released as ammonia when the steel is heated at 500 °C in a stream of hydrogen. The cell was used in conjunction with a digital voltmeter and a recorder in order to obtain a continuous record of the progress of the reaction between mobile nitrogen and hydrogen. Results are presented for the determination of 0·0005–0·0108 per cent. of mobile nitrogen in 10 steels using the new equipment and are compared with those obtained by using a spectrophotometric finish based on indophenol blue. The method, with relative standard deviations of 0·0001–0·0003 per cent., is more precise than that with the spectrophotometric finish, with relative standard deviations of 0·0002–0·0006 per cent.

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Analyst, 1976, **101**, 103–110.

The Determination of Substituted Phenylurea Herbicides and Their Impurities in Technical and Formulated Products by Use of Liquid Chromatography

The application of liquid chromatography to the identification and determination of the active ingredient and the impurities in phenylurea herbicides commonly employed in agriculture is described. Technical materials are dissolved in dichloromethane and chromatographed on microparticulate silica with dichloromethane or dichloromethane - methanol as eluting agent, or on microparticulate silica bonded with octadecyltrichlorosilane with methanol - water as eluting agent. An initial extraction procedure is required for dispersible powders. Detection was by means of ultraviolet absorbance.

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Analyst, 1976, **101**, 111–121.

FEBRUARY 1976 Vol. 101 No. 1199

The Analyst

Analytical Optoacoustic Spectrometry

Part I. Instrument Assembly and Performance Characteristics

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A simple single-beam spectrometer suitable for the study of optoacoustic spectra from small solid samples is described and the design of a suitable sample cell is reported. The performance characteristics of the spectrometer have been evaluated using different types of sample. A preliminary assessment of the predicted advantages of optoacoustic spectrometry over conventional techniques of ultraviolet - visible absorption and reflectance spectrometry for solid samples has been made.

In 1881, Alexander Graham Bell[1] was able to demonstrate that the illumination of different solid and liquid substances with a rapidly interrupted beam of light resulted in the emission of acoustic energy at the same frequency as that at which the incident radiation was modulated. Tyndall[2] repeated these observations and also studied gaseous samples; he was unable to observe a quantitative effect with gases, probably owing to the lack of detectors of sufficient sensitivity. With the advent of sensitive microphone detectors, a number of optoacoustic analysers were later reported for use in gas analysis using infrared sources of illumination[3,4]; for example, this type of equipment permitted the determination of carbon dioxide in air at the parts per million level. More recently, the optoacoustic effect has been used in molecular spectroscopy to measure vibrational relaxation times of gaseous molecules[5,6] and, utilising infrared sources, for the detection of trace levels of atmospheric pollutant gases.[7]

Although from the earliest work of Bell[1] it was evident that some of the strongest optoacoustic signals were observable from solid materials, it is only recently that the possibilities of developing a new analytical technique, based on optoacoustic spectrometry (OAS), for the direct examination of solid and semi-solid samples have become apparent.[8,9] This paper describes this novel technique, the development of an instrument assembly for optoacoustic spectrometry and our preliminary studies with the instrument utilising small solid samples.

Principle of Operation

The optoacoustic effect can be demonstrated with a very simple apparatus such as that shown in Fig. 1. When radiation in the visible and near infrared region of the spectrum from a 100-W quartz - iodine lamp is allowed to fall on a suitable absorbing material, *e.g.*, carbon black, contained in a closed system, the energy is absorbed by the sample and, if the material does not luminesce or degrade photochemically, is converted into heat. This conversion of absorbed energy takes place rapidly, as the energy absorbed by electronic excitation of the molecules of the sample may be degraded through the cascade process through lower electronic and vibrational energy levels within 10^{-8} s or less. If the incident radiation is interrupted periodically by use of a rotating sector, the absorption of energy is interrupted at the frequency of modulation by the sector and consequently the heat produced in the sample after energy conversion also appears at this frequency. In a closed system of constant volume, therefore, the heating produces a periodic increase in pressure which follows the modulation frequency of the incident radiation. At modulation frequencies between 30 Hz and 20 kHz, this varying pressure gives an acoustic signal whose amplitude can be measured with a simple microphone transducer. With gaseous samples, the periodic pressure change during irradiation is detected directly in the gas, whereas with solid samples the optoacoustic signal from the sample is detected "indirectly" by monitoring the periodic pressure change in the gaseous

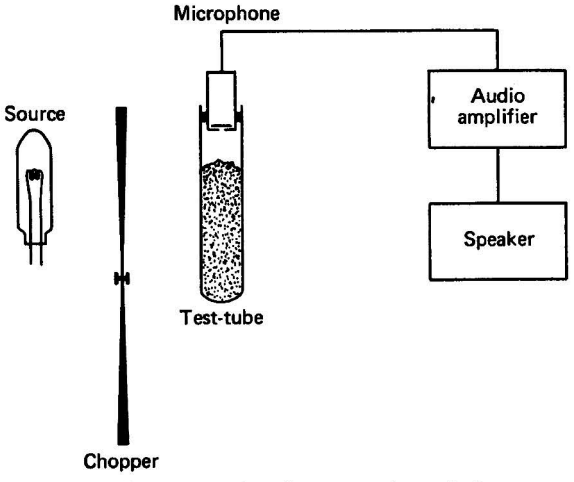

Fig. 1. Apparatus for demonstration of the optoacoustic effect.

environment surrounding the sample; the atmosphere around the gas becomes heated intermittently at the modulation frequency by heat transfer at the solid - gas interface. Despite the indirect nature of the detection for solid samples, as mentioned above some of the strongest optoacoustic signals observed have resulted from the observation of the effect in solid samples in this way. Indeed, in the original work of Bell,[1] using the sun as the source, distinctly audible signals were detected for various samples using only the unaided ear as the detector. It is apparent, even with the simple apparatus for the demonstration of the optoacoustic effect shown in Fig. 1, that the amplitude of the signal is directly proportional to the intensity of the source. In addition, the amplitude of the signal is inversely proportional to the modulation frequency, as at high operating frequencies the radiant energy supplied to the sample per pulse decreases and thus results in less heat energy per pulse being available after degradation to cause the pressure change. It is also observed that the amplitude of the optoacoustic signal is greatest with samples of large surface area, *e.g.*, fine powders, where the most efficient absorption of radiation by the solid and effective heat transfer to the surrounding gaseous atmosphere is possible.

The optoacoustic effect can be observed only when the incident radiation is absorbed by the sample. Thus, if the wavelength of the ultraviolet, visible or near infrared radiation incident upon the sample is varied, the amplitude of the optoacoustic signal observed at a given wavelength will provide a measure of the ability of the sample to absorb the incident radiation, *i.e.*, the absorption spectrum of the sample will be obtained. The optoacoustic power spectrum obtained by measurement of the signal amplitude *versus* the wavelength of the incident radiation should therefore resemble the electronic absorption spectrum of the sample and be complementary to the reflectance spectrum. The use of ultraviolet - visible optoacoustic spectrometry in this way for the examination of solid samples should have a number of advantages over conventional optical absorption or diffuse reflectance spectroscopy. These advantages include the following.

1. In contrast to optical absorption or reflectance spectroscopy, where the response of the photomultiplier or photocell detector employed is proportional to the photon flux, in the optoacoustic effect the microphone response is proportional to the optical power absorbed by the sample, *i.e.*, proportional to both the number of photons per unit area per second and to their energy (frequency). A photon at 200 nm can therefore result in twice as much heat energy after absorption, and therefore a proportional intermittent increase in pressure monitored by the microphone, as a photon at 400 nm. It is therefore a power spectrum that is obtained. This effect should be advantageous in the ultraviolet region, where difficulties can arise in absorption or reflectance spectroscopy if a rapid decrease in output intensity from the continuum source occurs at wavelengths of less than 300 nm.

2. Utilising optoacoustic spectrometry for gas analysis with laser sources, Kreuzer[7] has shown that, with a simple microphone and detector system, the absorption of 10^{-9} W of optical power can give a signal to noise ratio of greater than unity in the optoacoustic signal; an improvement in sensitivity of about 100-fold can be expected upon optimising the instrument and detector parameters. With a suitable continuum source and a monochromator of large aperture used with a spectral band pass of 10 nm, a power of 10^{-3} W should be attainable for sample illumination at all wavelengths in the visible and ultraviolet region. The detection of materials with high absorptivities at low concentrations, or as very small samples, should therefore be possible. Alternatively, satisfactory spectra should be measurable for materials with very low absorptivities. A low absorptivity may arise as a result of the low oscillator strength of the transitions involved or as a result of the highly reflecting nature of the sample surface. It can thus be expected that the technique should permit a higher detection sensitivity for fine powders and crystalline samples than is attained in reflectance or absorption spectroscopy and that spectra should be obtained when only very small amounts of samples are available.

3. Although radiation must be absorbed by the sample in order to obtain optoacoustic signals, unlike conventional absorption spectroscopy there is no need to detect radiation transmitted by the sample. Unlike reflectance spectroscopy, as only absorbed energy is detected, no problems arise from scattered source radiation as an acoustic rather than an optical transducer is employed. The difficulties encountered in diffuse reflectance spectroscopy owing to the variation in the relative contributions to the signal of specular reflectance (due to scattered radiation) and diffuse reflectance (due to radiation that has undergone some absorption) as the particle size varies should not be observed in optoacoustic spectrometry. The disadvantage encountered with fine powders of weakly absorbing species in diffuse reflectance spectroscopy, that only a small diffusely reflected component appears in the spectrum owing to failure of the incident radiation to penetrate the sample, should be offset in optoacoustic spectrometry by the ability to detect weak absorption effects and the increase in signal amplitude resulting from improved heat transfer efficiency between the sample and its gaseous environment as the particle size is reduced. For strongly absorbing powder samples, the latter effect should result in very strong optoacoustic signals for samples of very small particle size. Additionally, the freedom from problems with scattered light should make optoacoustic spectrometry suitable for the examination of other types of sample, such as hard and soft biological tissues, fibres and metallurgical samples.

4. For small solid samples, high absolute sensitivity should result without resort to the microscope illumination and viewing optics required in the examination of such samples by optical absorption or reflectance spectroscopy. Although the optical arrangement used to illuminate the sample is still important, owing to the need to ensure maximum energy absorption from the source, the requirement of wide solid-angle viewing of the sample by the detector should not be as important in optoacoustic spectrometry as in optical spectroscopy. In a sample cell of constant volume, it is necessary only to arrange to minimise the volume of gas in the cell in order to create the maximum pressure change for a given amount of energy transferred to it, and then to monitor this pressure change efficiently.

5. The technique should provide valuable information in the study of materials that are fluorescent or phosphorescent. In these instances, part of the absorbed energy is re-emitted radiatively and is not degraded into thermal energy by radiationless transitions as for most absorbing species. Hence, in the optoacoustic spectrometric power spectra of such materials, the absorption bands of longest wavelength that normally give rise to fluorescence or phosphorescence will be attenuated relative to those absorption bands at which radiationless transitions are responsible for de-excitation of the excited state. The technique should therefore prove complementary to spectrofluorimetry and phosphorimetry in the study of luminescence phenomena and for quantum efficiency measurements, ϕ, as it measures the complementary radiationless loss $(1-\phi)$.

6. As the observation of optoacoustic signals for solid samples depends on the transfer to the surrounding gaseous environment of energy released after absorption of radiation, optoacoustic spectrometry may prove useful in studies of heat transfer efficiency at solid - gas interfaces and in thermal conductivity measurements.

This paper reports the design and assembly of a simple single-beam spectrometer suitable for the study of the optoacoustic spectra of solid samples. The primary criteria for the

successful design of the sample cell for use in optoacoustic spectrometry have been established and the performance characteristics of the spectrometer evaluated by using simple types of sample. A preliminary assessment of the above potential advantages of optoacoustic spectrometry over conventional techniques of optical spectroscopy has been made.

Experimental

Apparatus

The single-beam optoacoustic spectrometer assembly constructed for this work is shown diagrammatically in Fig. 2. A 1 000-W mercury - xenon high-pressure continuum source (Oriel Corp., Stamford, Conn., USA, Model 6293) was employed. This source was operated in an air-cooled housing fitted with a UV-grade fused silica double-element condensing lens assembly and a spherical rear reflector. This optical arrangement provided for *f*/1.0 collection efficiency for radiation from the arc lamp.

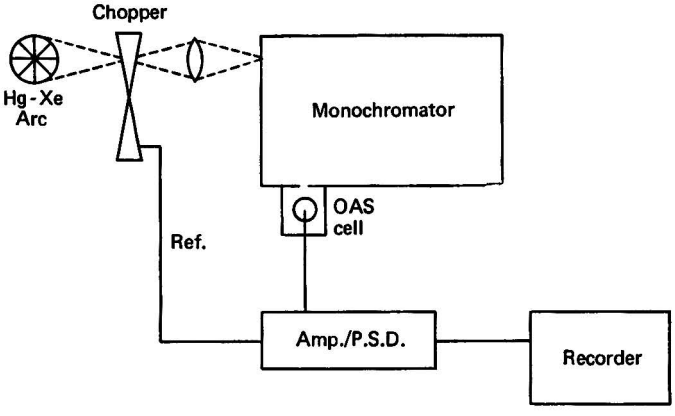

Fig. 2. Schematic diagram of the single-beam optoacoustic spectrometer.

The source radiation was focused on to the blades of a rotating chopper (Brookdeal Electronics Ltd., Bracknell, Berks., Model 9749) whose chopping frequency was variable between 1 and 1 000 Hz and which also generated a reference signal for the detector electronics at the chosen frequency by means of a simple source - photodiode assembly. The modulated radiation was collected by using a silica biconvex lens (40 mm diameter, 60 mm focal length) and focused on to the entrance slit of the grating monochromator employed. A small *f*/4 monochromator (Farrand Optical Co., New York) fitted with a plane grating (50 × 50 mm, 600 lines mm^{-1}) and interchangeable slits and a wavelength scanning motor were mounted on the optical rail of the system. The reciprocal linear dispersion obtained at the exit slit of the monochromator was 10 nm mm^{-1}. The optoacoustic sample cell and microphone transducer assembly were mounted directly at the exit slit of the monochromator.

The sample cell employed is shown diagrammatically in Fig. 3. The cell was machined directly from a single piece of stainless steel and took the form internally of a cylinder (25 mm diameter, 25 mm long), normal to which a silica window of 1 mm thickness was mounted and held in position on the cell body by a knurled and threaded cap and a PTFE compression gasket. The other side of the cylinder opposite the window was employed to locate the sample holder. This took the form of a polished stainless-steel tray (10 mm diameter, 0.75 mm thick) mounted on a screw mechanism so as to provide for fine adjustment of the positioning of the sample. One end of the cylindrical cell body was employed to locate the condenser microphone transducer. The microphone diaphragm effectively formed part of the cell wall and was mounted in a pressure-tight fitting to the body of the cell. A pressure release valve was also located in the side-wall of the cell body; this served to allow insertion of the sample without an increase in internal pressure in the cell. The whole assembly formed a pressure-tight cell; the cell walls were polished in order to reduce energy losses and stainless steel was employed in order to provide low thermal conductivity. In the cell design employed in this

work, and with the optical geometry used, the sample tray receives maximum irradiation from the source only when it is in the vertical position. For the purposes of this work, therefore, milligram powder samples were mounted on the sample tray utilising small pre-cut discs (7 mm diameter) of transparent double-sided adhesive tape. The transducer used was a 1-in diameter condenser microphone (Bruel and Kjaer, Model 4144) of sensitivity 5 mV μbar^{-1}, operated at a charging voltage of 200 V from a dry battery supply.

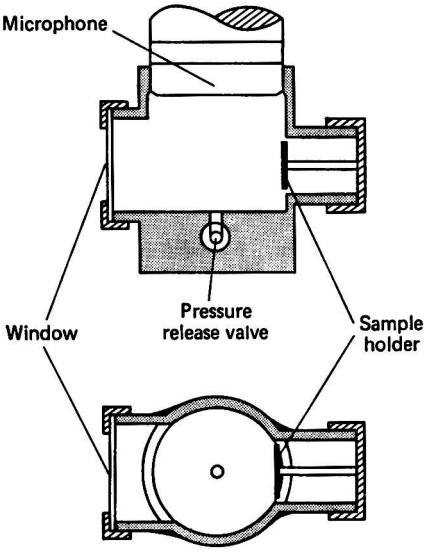

Fig. 3. The optoacoustic cell.

The optoacoustic signal from the microphone transducer was taken directly to a sensitive lock-in amplifier (Princeton Applied Research Corp., Model 186), which utilised the reference signal generated at the variable-speed chopper to extract the signal waveform and present this as a d.c. potential to a potentiometric chart recorder. Optoacoustic spectra were then obtained by recording the output of the lock-in amplifier *versus* the wavelengths of the incident radiation at the sample cell during wavelength scanning of the monochromator.

An Ideal Model for Prediction of the Strength of Optoacoustic Signals

The optoacoustic effect can be observed only after absorption of radiation by the sample. For a simple model system, for example a single absorbing particle or thin absorbing layer of homogeneous composition, the power absorbed can readily be calculated from the classical relationships that govern the absorption of electromagnetic radiation by matter. In order to obtain an estimate of the optoacoustic signal power, it is then necessary to quantify the fraction of this absorbed radiation that is lost by the excited state in its return to the ground state by radiationless transitions. Thus,

$$\begin{matrix}\text{Optoacoustic signal} \\ \text{power (W)}\end{matrix} = \begin{matrix}\text{Power absorbed} \\ \text{from source (W)}\end{matrix} \times \begin{matrix}\text{Efficiency of} \\ \text{radiationless} \\ \text{conversion}\end{matrix}$$

For a simple absorbing layer of thickness l of a species of molar absorptivity ϵ and concentration c in the sample matrix, the power absorbed at wavelength λ, $P_{abs\lambda}$, is given by Beer's law as

$$\begin{aligned} P_{abs} &= P_{0\lambda} - [P_{0\lambda}\exp(-2.3\epsilon_\lambda cl)] \\ &= P_{0\lambda}\,[1-\exp(-2.3\epsilon_\lambda cl)] \quad .. \quad .. \quad .. \quad .. \quad (1) \end{aligned}$$

where $P_{0\lambda}$ is the power of the incident radiation at wavelength λ.

The optoacoustic signal power, $P_{OAS\lambda}$ (watts), is then obtained by multiplying $P_{abs\lambda}$ by an

efficiency factor, β, which is a measure of the conversion efficiency of absorbed power to heat by radiationless processes, *i.e.*

$$P_{OAS\lambda} = P_{0\lambda}\,[1-\exp(-2.3\epsilon cl)]\beta \quad .. \quad .. \quad .. \quad .. \quad (2)$$

For low absorption conditions, where the power absorbed is small, the higher terms in the expansion of $1-\exp(-2.3\epsilon cl)$ can be neglected, and we can write

$$P_{OAS\lambda} = P_{0\lambda}(2.3\epsilon cl)\beta \quad .. \quad .. \quad .. \quad .. \quad (3)$$

From this expression, it is evident that the optoacoustic signal power under ideal conditions is directly proportional to the available power of the source at a given wavelength, the molar absorptivity of the absorbing species at this wavelength (ϵ) and the concentration, path length and power conversion efficiency.

It can be seen that when the optoacoustic signal is plotted against wavelength for a source whose output power does not vary with wavelength, the spectrum obtained will give a direct measure of the variation of ϵ with wavelength, *i.e.*, the electronic absorption spectrum will be obtained.

It is also apparent from equation (3) that for weakly absorbing species, the amplitude of the optoacoustic signal will be directly proportional to the concentration of the absorbing species, so that linear calibration graphs can be expected. In addition, the direct proportionality between $P_{OAS\lambda}$ and the absorption path length (l) will affect the manner in which the amplitude of the signal varies for strong and weakly absorbing species with sample thickness and/or particle size (for powdered samples).

For absorbing species that luminesce by fluorescence or phosphorescence, where a fraction of the absorbed energy is lost by radiative transitions rather than radiationless internal conversion and collisions, the optoacoustic signal power expected might be written as

$$P_{OAS\lambda} = P_{0\lambda}(2.3\epsilon cl)(1-\phi) \quad .. \quad .. \quad .. \quad .. \quad (4)$$

where ϕ is the luminescence quantum efficiency, which is complementary to β.

In a real experimental system, a number of factors relating to the instrument arrangement employed and to the characteristics of the sample will lead to modification of the ideal expression of equation (3). Thus, for the continuum source used in optoacoustic spectrometry, the power incident upon the sample, $P_{0\lambda}$, is given by

$$P_{v\lambda} = I_{0\lambda}\omega H T_\lambda s\Omega/4\pi \quad .. \quad .. \quad .. \quad .. \quad (5)$$

where $I_{0\lambda}$ W cm^{-2} nm^{-1}, is the spectral irradiance of the source, ω cm is the monochromator slit width, H is the slit height, s nm is the spectral band width employed, T_λ is the transmittance of the monochromator at wavelength λ and Ω sr is the solid angle, for sample illumination available from the particular source and monochromator assembly.

Thus the optoacoustic signal power becomes

$$P_{OAS} = I_{0\lambda}\omega H T_\lambda s\,\frac{\Omega}{4\pi}\,(2.3\epsilon cl)\beta \quad .. \quad .. \quad .. \quad .. \quad (6)$$

In contrast to fluorescence or reflectance spectroscopy, in which the re-emitted or reflected optical power received at the radiation detector is further dependent on the optical viewing geometry (solid angle), in optoacoustic spectrometry in the ideal case, all of the absorbed power that appears as kinetic energy after radiationless de-excitation is available to cause an increase in pressure in the cell and to generate the optoacoustic signal at the microphone transducer. In practice, however, a power transfer efficiency from sample to transducer of unity is difficult to achieve owing to loss of energy at the cell walls. For a real experimental system, therefore, it is necessary to introduce an additional power transfer efficiency factor, α, into equation (6) in order to account for this loss and for any loss in efficiency at the transducer.

In addition, for solid samples, the optoacoustic signal power may be expected to vary with particle size, for two reasons: (a) when the particle size (or surface area) varies, the power absorbed will vary owing to changes in the average path length for absorption and the reflectivity of the sample, and (b) as the particle size (surface area) varies, the efficiency of power transfer to the surrounding gas may vary. The power transfer at the solid - gas interface may also be influenced by the thermal conductivity of the sample and the filler gas; this would

then also be expected to affect the manner in which the observed optoacoustic signal varies with sample characteristics. The amplitude of the signal would also be expected to be inversely proportional to the heat capacity of the filler gas.

As part of our preliminary studies on optoacoustic spectrometry, we have undertaken a number of experiments with the instrument assembly described here in order to investigate the predicted variation in optoacoustic signal strength with the sample and instrument characteristics outlined above.

Results and Discussion

In order to evaluate the performance characteristics of the optoacoustic spectrometer, and the fundamental instrument and sample parameters that govern the analytical application of the optoacoustic effect to solid samples, it was necessary initially to choose a "standard" sample of well defined absorption characteristics whose optoacoustic spectrum could be studied. Carbon black was chosen for this purpose, as it is readily obtainable, can be employed as a black-body reference absorber of known absorptivity at different wavelengths and is a strong absorber for which optoacoustic signals are easily attainable. This material was therefore used to demonstrate the relationships between the optoacoustic signals obtained and the instrument and sample parameters.

Optoacoustic Spectrum of Carbon Black

With the instrument assembly described above, the amplitude of the optoacoustic signal *versus* the excitation wavelength from the mercury - xenon source was obtained for particulate carbon black (particle size less than 76 μm) utilising a source modulation frequency of 86 Hz and a broad spectral band pass at the monochromator exit slit (40 nm). The optoacoustic spectrum obtained is shown in Fig. 4, A. An optoacoustic signal, caused by absorption of the source radiation by the sample, was observed at all wavelengths between 200 and 650 nm selected by the monochromator. The optoacoustic spectrum exhibits broad peaks at those wavelengths which correspond to the intense mercury line emission from the source superimposed on the continuum background of xenon. Fig. 4, B, shows the spectrum obtained when a thermocouple detector was positioned at the monochromator exit slit in place of the optoacoustic sample cell and microphone transducer. In this way, the variation with

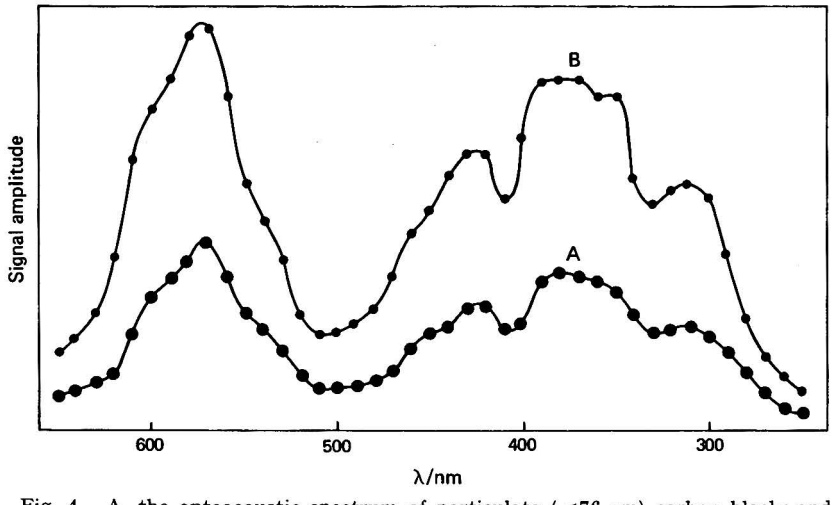

Fig. 4. A, the optoacoustic spectrum of particulate (<76 μm) carbon black; and B, the power spectrum from the 1000-W mercury - xenon lamp employing a thermopile detector.

wavelength of the integrated incident power per unit time (in millijoules) from the source was measured. The source power spectrum obtained is seen to be virtually identical with the optoacoustic spectrum of the carbon black and clearly indicates that power spectra are

obtained by optoacoustic spectrometry. These results also confirm the suitability of carbon black as a reference absorption material whose optoacoustic spectrum can be used to correct the observed spectra of other samples for the variation of source power with wavelength. This correction procedure for the optoacoustic spectra can be effected either manually, as with the spectra obtained in the work reported here with the single-beam spectrometer, or automatically in a double-beam spectrometer in which the carbon black absorber is incorporated into the reference beam.

Effect of Source Power and Modulation Frequency

The predicted proportionality between the amplitude of the optoacoustic signal and the incident source power was readily confirmed using a carbon black sample by varying the operating current of the mercury - xenon lamp source. The results illustrated in Fig. 5 were obtained utilising a modulation frequency of 85 Hz and a peak excitation wavelength of 570 nm selected at the monochromator.

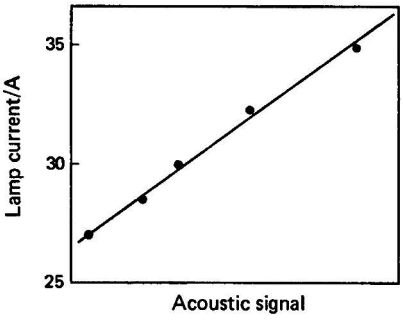

Fig. 5. Variation in the amplitude of the optoacoustic signal for carbon black at 570 nm with source lamp current.

The variation of the amplitude of the optoacoustic signal with the source modulation frequency was studied for carbon black (particle size less than 76 μm) at several different excitation wavelengths over the frequency range 10–460 Hz. Essentially similar results were obtained at each excitation wavelength employed. The variation of the optoacoustic signal amplitude at 570 nm with modulation frequency is shown in Fig. 6, (*a*). As expected, the signal is inversely proportional to the modulation frequency and the graph of signal amplitude *versus* the reciprocal of the frequency is linear [see Fig. 6, (*b*)]. This relationship follows from the direct proportionality obtained between signal amplitude and source power.

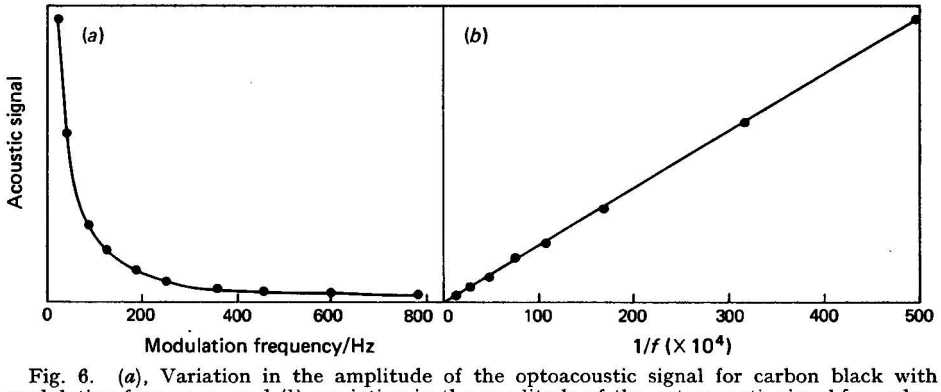

Fig. 6. (*a*), Variation in the amplitude of the optoacoustic signal for carbon black with modulation frequency; and (*b*), variation in the amplitude of the optoacoustic signal for carbon black with the reciprocal of the modulation frequency.

Thus, as the modulation frequency increases, the power per pulse available for absorption by the sample decreases. All further studies reported here were conducted at modulation frequencies of less than 200 Hz, in order to maintain an adequate signal amplitude and to optimise the signal to noise ratio.

Effect of Nature of Filler Gas Used in Sample Cell

As optoacoustic signals for solid samples are obtained "indirectly" by monitoring the periodic pressure change in the gaseous environment surrounding the sample in the constant-volume cell, it might be expected that the amplitude of the optoacoustic signals observed would depend on the physical properties of the gas in the sample cell. The particular properties of interest are the heat capacity of the filler gas at constant volume (C_v) and its thermal conductivity. The effect of using different filler gases on the spectrum observed for carbon black in the region 500–650 nm was therefore investigated. The spectra shown in Fig. 7 were obtained for a carbon black sample in a closed sample cell that contained helium, argon, nitrogen or carbon dioxide at atmospheric pressure. The corresponding heat capacity and thermal conductivity values for these gases are shown in Table I. It might be expected that

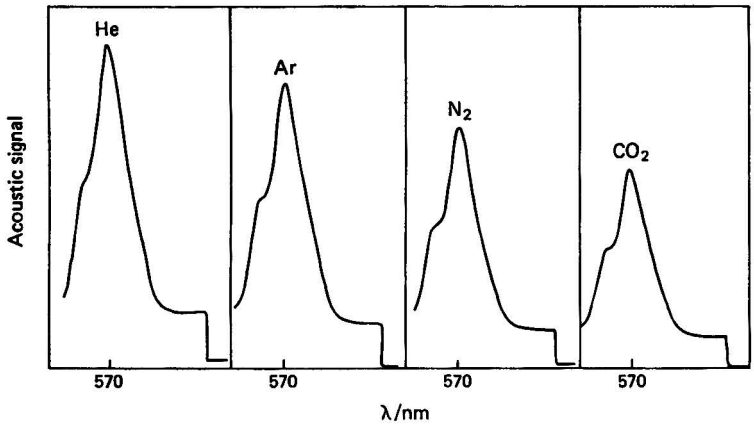

Fig. 7. Variation in the optoacoustic signal for carbon black with the nature of the cell filler gas.

the use of a filler gas of high thermal conductivity would lead to efficient heat transfer at the sample - gas interface and that this would be beneficial to the amplitude of the optoacoustic signal but that correspondingly greater energy losses to the cell walls might then offset this effect. At the low source modulation frequencies employed in this work, the results obtained indicate that the rate of heat transfer at the sample - gas interface does not limit the amplitude of the optoacoustic signal observed; with the stainless-steel cell employed, no relationship is observed between the thermal conductivity of the filler gas and the amplitude of the signals obtained. A comparison of the results shown in Fig. 7 with the heat capacities of the gases employed, however, reveals an apparent correlation: as the heat capacity of the gas increases, the amplitude of the optoacoustic signal decreases. This results from the fact that, under otherwise constant conditions, the energy absorbed by the sample can produce only a small change in temperature and pressure (and therefore a small signal amplitude) in the constant volume of gas in the cell when a gas of large heat capacity is employed.

TABLE I

HEAT CAPACITIES (C_v) AND THERMAL CONDUCTIVITIES (k) OF GASES

Gas	C_v/J K^{-1} mol^{-1}	k/W m^{-1} K^{-1}
Helium	12.48	0.150
Argon	12.58	0.017
Nitrogen	20.70	0.025
Carbon dioxide	28.27	0.016

It is apparent that no significant practical advantage or significantly higher sensitivity would accrue from the use of filler gases other than air with the sample cell and detector assembly used in this work.

Effect of Particle Size of Sample

The effect of the particle size of the sample for a strongly absorbing material was investigated, utilising samples of carbon black and a source modulation frequency of 85 Hz and examining the optoacoustic spectrum in the region 500–650 nm. Fig. 8 shows the spectra obtained using a set of standard test sieves for three particle size ranges: A, less than 76 μm, B, 76–150 μm and C, 150–250 μm. It is clear that the amplitude of the optoacoustic signal increases at all wavelengths in the range examined as the particle size of the sample decreases. This effect is not a mass effect, as the sample mass increases as the particle size increases.

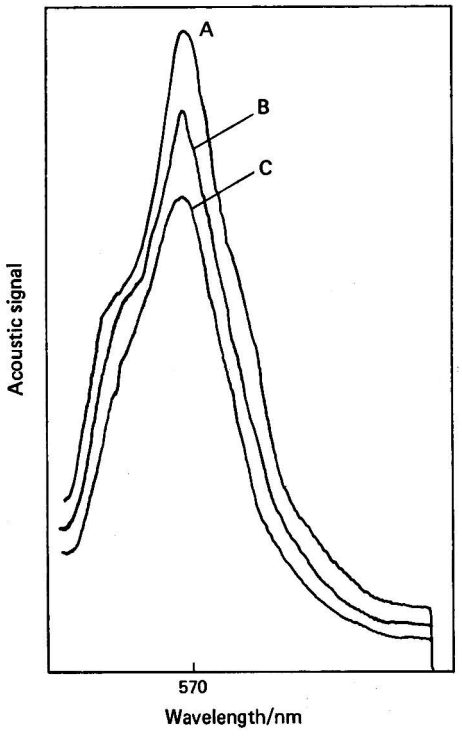

Fig. 8. Effect of particle size of the sample on the amplitude of the optoacoustic signal for carbon: A, <76 μm; B, 76–150 μm; and C, 150–250 μm.

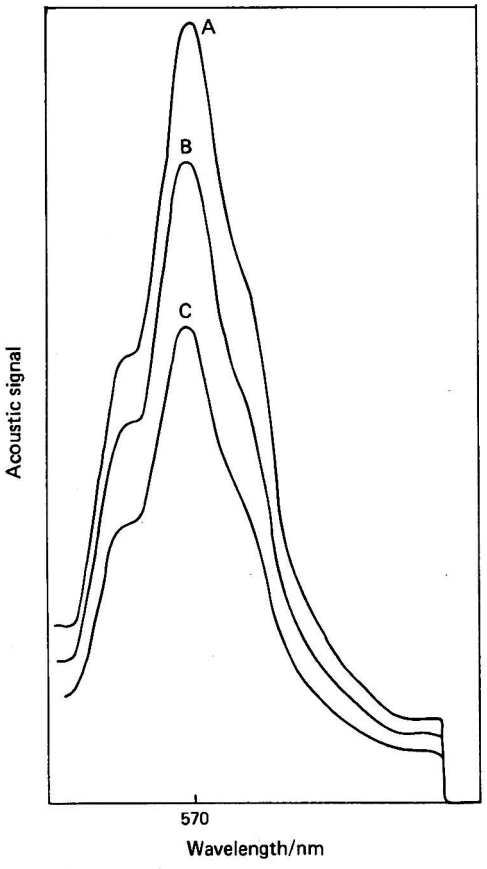

Fig. 9. Effect of particle size of the sample on the amplitude of the hydrated copper(II) sulphate optoacoustic signal: A, <76 μm; B, 76–150 μm; and C, 150–250 μm.

As the surface area increases, the power absorbed (which alone gives rise to the optoacoustic signal) thus also increases. The implication is that as the particle size decreases the absorbed power increases, owing to an increase in the mean effective absorbing path length [l in equation (3)]. It is also possible that the power transfer efficiency at the solid - gas interface increases as the particle size decreases.

The variation of the amplitude of the optoacoustic signal with particle size was also investigated for a weakly absorbing species. Crystalline hydrated copper(II) sulphate was employed

in these experiments using the same particle size ranges as those of the carbon black samples. Fig. 9 shows the uncorrected optoacoustic spectra obtained in the wavelength range 550–650 nm for these samples. The signal amplitude is again seen to increase as the particle size decreases, although the effect observed is not as pronounced as with carbon black.

It is apparent that for powdered samples, control of particle size will be important in quantitative applications to optoacoustic spectrometry. The effect on the analytical signal of variation in particle size, however, is less complex than that encountered in diffuse reflectance spectroscopy. In the latter technique it has commonly been observed that either an increase or decrease in the magnitude of the observed reflectance at different wavelengths may be obtained, depending on whether the sample is a weak or strong absorber. The complicating factor is that both the diffuse reflectance component of the measured intensity (which has experienced absorption by the sample) and the specular (non-absorbed) reflectance component may vary independently with particle size and the molecular absorptivity for the species studied at different wavelengths; the measured reflectance, however, indicates only the observed net effect for both of these components. Thus the effect of particle size and sample absorptivity in optoacoustic spectrometry is fundamentally simpler to interpret owing to the fact that it is only the portion of the incident radiation that is absorbed that gives rise to the optoacoustic signal; no complications arise from the specular (non-absorbed) reflected radiation, which is not measured.

Effect of Amount of Sample and Concentration of the Absorbing Species

The variation of signal amplitude with the sample size was investigated for a carbon black sample of particle size less than 76 μm. The carbon powder was spread uniformly on to a 7 mm diameter disc of double-sided clear adhesive tape. The mass of the sample was determined by weighing the adhesive tape with and without the powder sample. The amplitude of the optoacoustic signal was measured for this sample in the wavelength range 500–650 nm. The mass of the sample was then progressively decreased by removing sections of the 7-mm disc of tape and re-weighing. The optoacoustic signal was recorded in each instance. Fig. 10 shows the variation in signal amplitude at 570 nm with sample mass. A linear relationship is obtained; as the sample mass and surface area decrease, the power absorbed from the incident beam of radiation becomes less so that the optoacoustic amplitude is decreased. The minimum detectable mass of sample for carbon black, based on an estimation of the signal to noise ratio observed for the small background signal produced by the stainless-steel sample holder, was about 10 μg.

The effect of the concentration of the absorbing species was investigated for a strong absorber using milligram samples of mixtures of carbon black in magnesium oxide of particle size less than 76 μm. Fig. 11 shows the variation in the amplitude of the optoacoustic signal at 570 nm with the concentration of carbon black in magnesium oxide covering the range 0–100%. The graph obtained is linear at low concentrations, *i.e.*, under conditions of low power absorption, but deviates towards the concentration axis at high concentrations when the simple form of equation (3) is not valid.

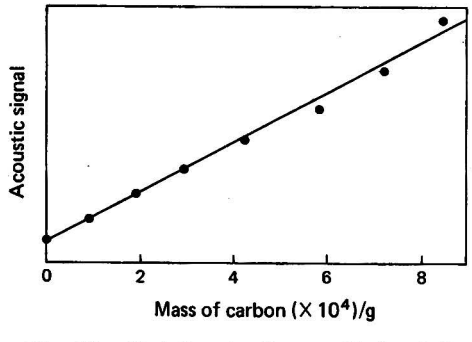

Fig. 10. Variation in the amplitude of the optoacoustic signal with the mass of sample, for carbon (<76 μm) at 570 nm.

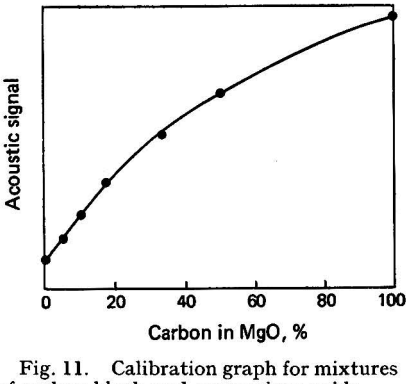

Fig. 11. Calibration graph for mixtures of carbon black and magnesium oxide.

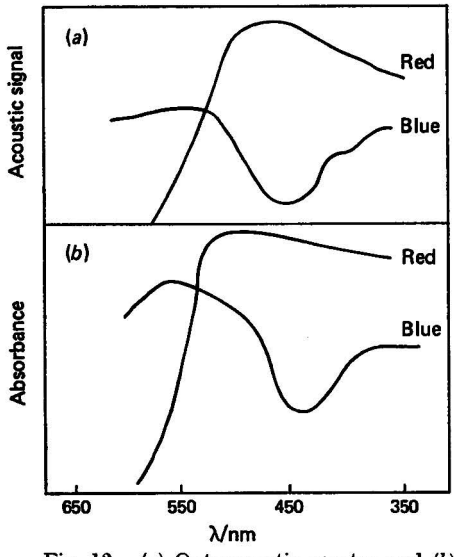

Fig. 12. (*a*) Optoacoustic spectra and (*b*) reflectance spectra of glossy red and blue papers.

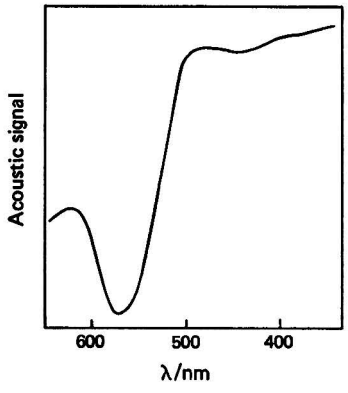

Fig. 13. Optoacoustic spectrum of a 1 + 9 cadmium sulphide - magnesium oxide mixture.

Preliminary Optoacoustic Spectra of Different Types of Sample

Optoacoustic spectrometry shows considerable promise for the characterisation and quantitative determination of a wide range of molecular species present in different types of solid samples. Investigation of the analytical application of optoacoustic spectrometry to materials of inorganic and biological origin is at present in process; the results of these studies will be reported in later papers. In order to demonstrate that "real" spectra are obtained, and that these spectra give information relating to the molecular absorption characteristics of samples, however, some representative spectra of different samples are shown in Figs. 12–14. The

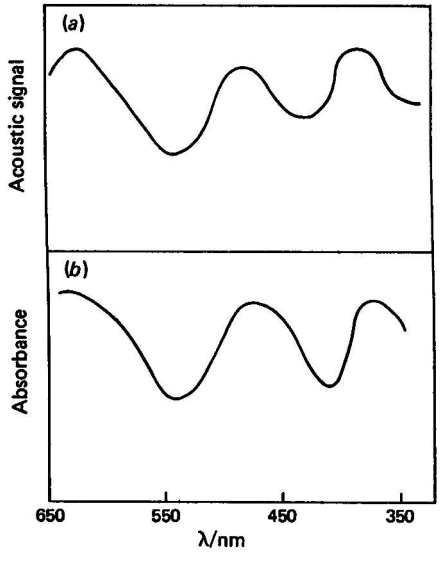

Fig. 14. (*a*) Optoacoustic spectrum and (*b*) reflectance spectrum of a 1 + 9 chromium(III) oxide - magnesium oxide mixture.

spectra shown have been manually corrected for variation in output power of the source with wavelength using the optoacoustic spectrum of carbon black as reference.

Fig. 12, (*a*) and (*b*), shows the spectra of samples of highly reflecting artists' gummed paper. These spectra are compared with the corresponding reflectance spectra and are clearly virtually identical. Although the highly reflecting nature of the papers gave rise to relatively weak absorption, and some degradation in the signal to noise ratio was observed in the reflectance spectra, the optoacoustic signal for these samples was readily measured. Fig. 13 shows the optoacoustic spectrum of a 1 + 9 (*m/m*) mixture of cadmium sulphide and magnesium oxide. Cadmium sulphide is a direct-band semiconductor whose band-edge occurs at 2.4 eV.[9] The band-edge measured from the optoacoustic spectrum occurs at 500 nm, which corresponds to 2.48 eV; this value is thus in fair agreement with the literature value and with a previous value obtained by optoacoustic spectrometry by Rosencwaig.[10] Fig. 14 shows the optoacoustic and reflectance spectra of chromium(III) oxide powder. The resolution attainable is similar to that obtained in earlier measurements by Rosencwaig and the Cr^{3+} ion crystal field bands are readily observed. The sample size taken for the optoacoustic measurements was 100 μg of chromium(III) oxide, diluted to 1 mg with magnesium oxide, whereas the attachment for the spectrophotometer employed to obtain the reflectance spectra required a sample size of about 750 mg.

Modifications to the simple optoacoustic spectrometer described here so as to permit the automatic correction of the optoacoustic spectra for variation of the source power with wavelength are at present in progress; this improved system, and the results of its application to different types of sample, will be described in a later paper.

We are grateful to the Analytical Chemistry Trust of the former Society for Analytical Chemistry (now the Analytical Division of the Chemical Society) for the award of a Studentship to one of us (A.A.K.) and to the Royal Society for an equipment grant for the assembly of the spectrometer.

References

1. Bell, A. G., *Phil. Mag.*, 1881, **11**, 510.
2. Tyndall, J., *Proc. R. Soc.*, 1881, **31**, 307.
3. Pfund, A. H., *Science, N.Y.*, 1939, **90**, 326.
4. Luft, K. F., *Z. Tech. Phys.*, 1943, **24**, 97.
5. Read, A. W., *Adv. Molec. Relaxation Processes*, 1967, **1**, 257.
6. Cottrell, T. L., Macfarlane, I. M., Read, A. W., and Young, A. H., *Trans. Faraday Soc.*, 1966, **62**, 2655.
7. Kreuzer, L. B., *J. Appl. Phys.*, 1971, **42**, 2934.
8. Harshbarger, W. R., and Robin, M. R., *Accts Chem. Res.*, 1973, **6**, 329.
9. Pankove, J. I., "Optical Process in Semiconductors," Prentice Hall, Englewood Cliffs, N.J., 1971.
10. Rosencwaig, A., *Analyt. Chem.*, 1975, **47**, 592A.

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Observations on the Limitation Imposed by Interferences in Flame Atomic-absorption Spectrometry at High Analyte Concentrations

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When burner rotation or an absorption line of poorer sensitivity is used in flame atomic-absorption spectrometric analysis, care must be taken to establish the absence of fresh or increased interferences at higher concentrations of the analyte element. At high concentrations, sulphate was found to cause severe depressions in the determinations of magnesium, cobalt and nickel, although under normal conditions the interference is negligible. The risk of substantial error can be reduced either by dilution of samples and standards, or by taking measurements by using the upper part of a fuel-lean flame that is burning on a slot burner with a triangular cross-section, or by adding a suitable releasing agent.

An inherent limitation of atomic-absorption spectrometry is the incidence of curvature of calibration graphs at high concentrations of analyte elements. In practice, the useful working range of the technique is often extended by the use of an alternative absorption wavelength, or, when flame atomisation is employed, by rotating the burner to give a shorter absorption path length. We have recently found in our laboratory, however, that when magnesium is determined over the range 0–15 μg ml^{-1}, using burner rotation to attain higher (poorer) sensitivity, very substantial interference was encountered from sulphate, although under normal working conditions, over the concentration range 0–2 μg ml^{-1}, the interference from this anion was negligible in the air - acetylene flame. The depression of calcium absorbance by phosphorus is known to decrease with decreasing calcium concentration, a fact which leads to increased curvature of calibration graphs in the presence of phosphate.[1] Very little work has been carried out on the effect of the concentration of the analyte element on the incidence and extent of interferences for other elements, however.

According to Aldous and Reynolds,[2] the sensitivity of the determination of magnesium is slightly diminished when sulphate, rather than chloride or nitrate, is used to prepare magnesium standards for atomic-absorption analysis; most books on atomic absorption do not mention this possible interference. As we observed a very substantial depression at higher magnesium concentrations, it was decided to investigate this interference further, and to search for further instances of enhanced or fresh interferences occurring at high analyte concentrations.

Experimental

Apparatus

Atomic-absorption spectrophotometers. The instruments used were: an EEL, Model 240, equipped with either a conventional 100-mm air - acetylene burner or a laboratory-built 50-mm brass slot burner with a triangular cross-section, constructed as shown in Fig. 1, and a Shandon Southern Instruments A3400 with a standard air - acetylene burner.

Standard Solutions

Solutions containing 1000 μg ml^{-1} of magnesium, nickel and cobalt were prepared from the analytical-reagent grade chlorides and sulphates. The magnesium solutions were standardised by complexometric analysis before further dilution. The magnitude of the effects observed was so substantial that standardisation of the other stock solutions was unnecessary.

Results and Discussion

For the EEL, Model 240, instrument, the effects of burner type, fuel flow-rate (at a constant air flow-rate for both burners) and height of measurement on the change in magnesium absorbance at 285·2 nm caused by nebulising 10 μg ml^{-1} of magnesium, as the sulphate

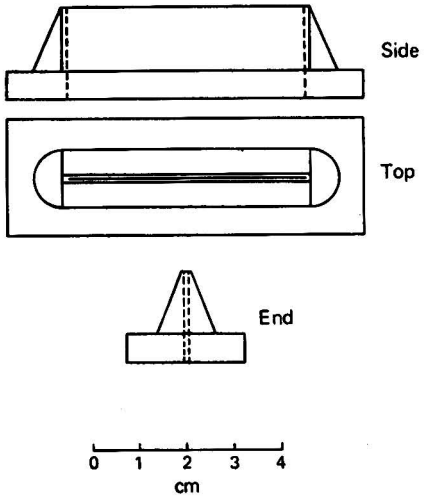

Fig. 1. Design of burner with triangular cross-section.

rather than the chloride, are shown in Fig. 2. Both burners were rotated through an angle of 90° in order to increase the sensitivity for 1 per cent. absorption. The interference became greater for both burners as the ratio of fuel to oxidant was increased, or as measurements were made at lower heights in the flame. The interference was significantly reduced when the burner with a triangular cross-section was used, and with this burner could be eradicated completely over a wide range of burner heights and fuel to oxidant ratios.

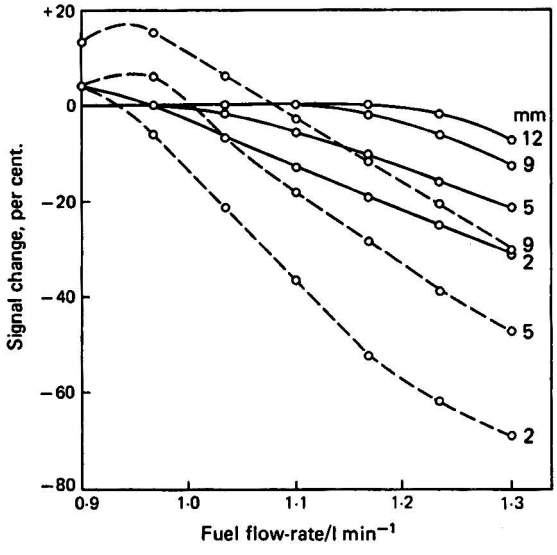

Fig. 2. Effect of fuel flow-rate on the change in magnesium absorbance caused by using sulphate in place of chloride at various heights above a flat-topped, 100-mm burner (broken lines) and a triangular cross-section, 50-mm burner (solid lines), with burners rotated through an angle of 90°. Air flow-rate, 6·5 l min^{-1} for both burners.

The extent of the interference varied significantly with magnesium concentration: it was negligible at 2 μg ml^{-1} of magnesium, but rose to a 30 per cent. depression for 15 μg ml^{-1} of magnesium under the routine operating conditions used in our laboratory (*i.e.*, wavelength, 285·2 nm; air flow-rate, 6·5 l min^{-1}; acetylene flow-rate, about 1 l min^{-1}; and burner height about 4 mm).

The atomisation of magnesium sulphate proceeds, at least in part, via the formation of magnesium oxide. Magnesium sulphate decomposes at 1397 K, whereas the oxide melts and boils at 3073 and 3873 K, respectively. The chloride, on the other hand, boils at 1685 K, so that while the chloride is readily volatilised, and hence atomised, the sulphate tends to form stable oxide particles, the size of which depends primarily upon the droplet size distribution produced by the nebuliser, and the magnesium concentration in solution. Larger particles, which secure the magnesium atoms more efficiently, are formed as the magnesium concentration is increased. It should be emphasised that as the droplet size distribution varies between instruments and between nebulisers, the precise analyte concentration at which such an interference becomes significant will also vary between instruments.

The effect and trends described above were still observed when an A3400 atomic-absorption spectrophotometer was used in place of the EEL, Model 240, instrument, for example, but the extent of the effect was much smaller. Even when measurements were made at a low height in a fuel-rich flame, the use of magnesium sulphate instead of the chloride reduced the absorbance by only about 20 per cent. If, however, the impact bead was displaced from its normal, optimised position, the effect became more pronounced, which indicates that a finer mist is normally produced by the A3400 nebuliser, although the higher oxidant and fuel flow-rates used with this instrument may also contribute to the improvement in selectivity.

Magnesium calibration graphs for the concentration ranges 0–15 and 0–25 μg ml^{-1} exhibited far greater curvature when sulphate rather than chloride solutions were employed, as would be expected under these conditions. Typical curves for the EEL, Model 240, instrument, are shown in Fig. 3.

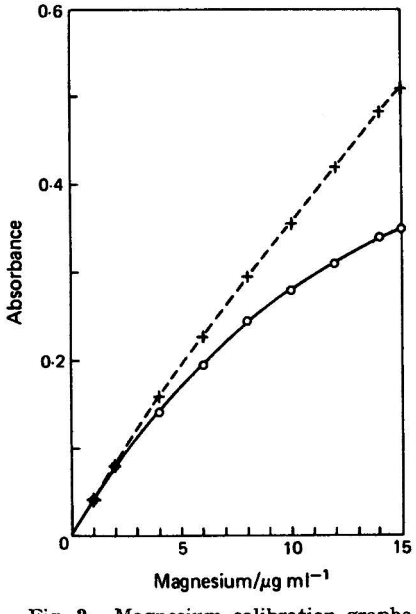

Fig. 3. Magnesium calibration graphs at 202·5 nm: broken line, $MgCl_2$; and solid line, $MgSO_4$.

The advantages of the burner with a triangular cross-section must arise from the fact that burners of this design give a stiffer, narrower flame, because of the different pattern of air entrainment. The burner with a triangular cross-section required a slightly higher acetylene

flow-rate in order to give a luminous flame, which indicates that more air is entrained by the stiffer flame. This effect would make the flame leaner and hotter, and could result in the observed decrease in the extent of the interference when this burner was used. The increase in the extent of the interference with burner rotation is probably attributable to the effects of lateral diffusion interference,[3–5] which might be expected to occur under these conditions, although they are not normally observed in air - acetylene flames. A brief investigation of the absorption profiles showed a small but significant effect in this instance, but it would be difficult to relate it quantitatively to the increase in interference when burner rotation is used.

It was found that the interference effect of sulphate on the absorbance of magnesium could readily be overcome by the addition of a suitable excess of one of the commonly used releasing agents, such as lanthanum chloride or strontium chloride. The main risk of unsuspected error arising at higher concentrations of the analyte element will therefore be in analyses in which the addition of a releasing agent is not normally regarded as essential. However, in view of the extent of the effect in the determination of magnesium, it is surprising that a more widespread occurrence of sulphate interference has not been reported. Nickel chloride, for example, sublimes[6] at 1246 K, whereas the sulphate decomposes at 1121 K, and the oxide melts at 2263 K, so that the effect should be observed, particularly at a low height in the flame, for nickel. Cobalt chloride melts and boils at 997 and 1322 K, respectively, while the sulphate decomposes at 1008 K, and the oxide only melts at 2208 K.

It has been stated in the literature,[2] however, that nickel chloride and sulphate and cobalt chloride and sulphate will give the same responses. It was found in practice, however, that considerable depressions could be observed when sulphates were used to prepare standard solutions at higher concentrations than those normally employed under the most sensitive conditions for the determinations of these two elements. The extents of the effects for 50 μg ml^{-1} solutions of cobalt and nickel are shown in Fig. 4 for various observation heights as functions of the fuel flow-rate. The same trends were observed as for magnesium: the degree of interference became greater at lower heights in the flame, and as the fuel flow-rate

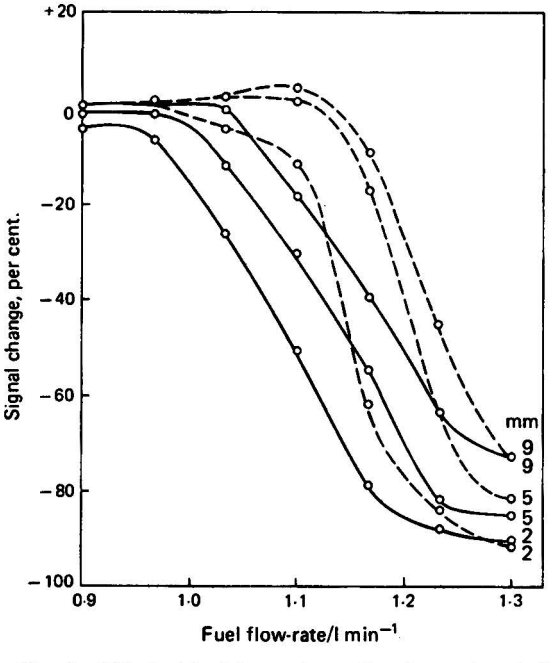

Fig. 4. Effect of fuel flow-rate on the change in cobalt absorbance at 341·3 nm (broken lines) and nickel absorbance at 234·8 nm (solid lines) caused by using sulphate in place of chloride, at various heights above a 100-mm, flat-topped burner in line with the optical axis.

was increased. The effects were slightly less pronounced when the burner with a triangular cross-section was used, but became more pronounced when either burner was rotated, and as the concentrations of the analyte element increased.

With nickel, it is perhaps worth mentioning here that although under normal working conditions the effect of using sulphate rather than chloride to prepare standard solutions was negligible for 1 and 5 μg ml^{-1} concentrations, and only an 8 per cent. depression occurred for 50 μg ml^{-1} concentration, if measurements were made at a low height in a fuel-rich flame depressions of 48, 72 and 90 per cent., respectively, could be observed for these three concentrations.

There can be little doubt that many other instances will be found when the incidence and extent of interferences increases at higher concentrations of the analyte element. The effect is not confined to sulphate, and may be observed for other oxy-anions. Thus, for example, the depression of the absorbance of magnesium by the addition of different excess amounts of phosphate was found to vary with magnesium concentration (see Table I).

TABLE I

EFFECT OF PHOSPHATE ON MAGNESIUM ABSORBANCE AT A LOW HEIGHT IN A FUEL-RICH FLAME

Magnesium (as $MgCl_2$)/mg ml^{-1}	Change in absorbance, per cent., with phosphate (PO_4^{3-}) concentrations of—		
	2 μg ml^{-1}	20 μg ml^{-1}	200 μg ml^{-1}
0·5*	0	0	0
5·0†	4	9	10
50·0‡	12	29	46

* 285·2 nm, burner aligned.
† 285·2 nm, burner rotated through an angle of 90°.
‡ 202·5 nm, burner rotated through a small angle.

When possible cationic interferences are being investigated, care must be taken to ensure that the associated anion does not cause a variation in the incidence or extent of apparently simple cationic interferences. Thus, for example, 50 μg ml^{-1} of magnesium (as sulphate) interfered considerably in the determination of 2 μg ml^{-1} of cobalt or nickel, whereas the same concentration of magnesium as the chloride caused no interference.

It can be concluded that care should be taken to establish the absence of additional or increased interferences from concomitant elements and ions when employing burner rotation or an absorption line of poorer sensitivity for analysis at high concentrations of the analyte element. The risk of increased interference can be reduced by making measurements by using the upper part of a fuel-lean flame, particularly if a burner with a triangular cross-section is used.

Although the results obtained with one particular instrument provide an indication of interference trends, significant variation can be expected to occur between different instruments and even between different nebulisers, so that it is essential to check for interferences on the instrument to be used for the analysis.

The authors are indebted to Messrs. G. Wilson and D. Strath, for the construction of the burner with a triangular cross-section, and to Mrs. S. Reid, for assistance with some of the experimental work.

References

1. Kirkbright, G. F., and Sargent, M., "Atomic Absorption and Fluorescence Spectroscopy," Academic Press, London, New York and San Francisco, 1974.
2. Aldous, K., and Reynolds, R. J., "Atomic Absorption Spectroscopy," Charles Griffin & Co. Ltd., London, 1970.
3. Koirtyohann, S. R., and Pickett, E. E., *Analyt. Chem.*, 1968, **40**, 2068.
4. West, A. C., Fassel, V. A., and Kniseley, R. N., *Analyt. Chem.*, 1973, **45**, 1586.
5. West, A. C., Fassel, V. A., and Kniseley, R. N., *Analyt. Chem.*, 1973, **45**, 2420.
6. "Handbook of Chemistry and Physics," 53rd Edition, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1972–1973.

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An Improved Digestion Method for the Extraction of Mercury from Environmental Samples

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An improved digestion procedure for the extraction of mercury from environmental material is reported. The method involves the digestion of the sample at 60 °C with sulphuric acid - nitric acid (2 + 1), containing a trace amount of hydrochloric acid, and subsequent oxidation with permanganate and persulphate solutions. With this procedure mercury is successfully recovered from organic matter and resistant inorganic forms such as mercury(II) sulphide. Unlike digestion with aqua regia, this procedure is simple and safe, and is applicable to the digestion of a large number of samples simultaneously. The method can be adapted to the automated cold-vapour and flame atomic-absorption techniques and is therefore ideal for routine monitoring.

Agemian and Chau[1] reported a method for the determination of mercury in sediments, in which a comprehensive manual digestion method developed by Iskandar *et al.*[2] was adapted to the automated cold-vapour atomic-absorption technique. The extraction technique involved the digestion of the sediment with sulphuric acid - nitric acid (2 + 1) at 60 °C and subsequent oxidation of the organomercury compounds with permanganate and persulphate solutions. Complete recovery[2] of several organomercury compounds was obtained by using this technique.

Jacobs and Keeney[3] showed that this procedure does not adequately dissolve mercury(II) sulphide (cinnabar), which may be formed under reducing conditions. They suggested treating the sediment with boiling aqua regia. However, we found that this treatment is hazardous, impractical and unnecessary for routine analysis of a large number of samples. Moreover, Jonasson *et al.*[4] have reported that the presence of excessive amounts of hydrochloric acid should be avoided as the consequent generation of chlorine[5] may cause the loss of volatile mercury chlorides. They proposed the use of a solution of nitric acid plus a trace amount of hydrochloric acid, which technique enables mercury sulphides to be satisfactorily dissolved, and is suitable for application to geological samples.

Agemian *et al.*[6] showed the adaptability of both sulphuric acid - nitric acid (2 + 1) and hydrochloric acid - nitric acid (1 + 9) digestion mixtures to the automated cold-vapour atomic-absorption technique for mercury determination. They compared these extraction methods for a number of rock, soil and sediment samples and obtained identical results, presumably owing to the absence of cinnabar in the samples analysed.

Samples that contain substantial amounts of this mercury compound are not commonly analysed in this laboratory. However, in this study, the intention was to obtain a comprehensive method that is applicable to all types of samples, including those containing mercury in forms such as mercury(II) sulphide. Cinnabar is resistant to attack by sulphuric and nitric acids.[4] However, the inclusion of the minimum[4] amount of hydrochloric acid promotes its rapid decomposition. Thus, a slight modification of the digestion method of Iskandar *et al.*,[2] by the addition of a trace amount of hydrochloric acid, enables large amounts of mercury(II) sulphide, at levels much higher than are found in natural samples, to be recovered.

The proposed method is simple, rapid and adaptable to the determination of all organic and inorganic forms of mercury in a large number of samples by the automated cold-vapour atomic-absorption technique. The method can be suited to the digestion of biological (fish)[7] or geological (rocks, soils and sediments) samples by using the procedure with or without the inclusion of hydrochloric acid.

The extraction medium is especially suitable for sediments and soils as its oxidising nature enables the large amounts of organic matter frequently found in these samples to be oxidised;

also, the strongly acidic medium, in the presence of a trace amount of hydrochloric acid, extracts inorganic forms of mercury including that found in cinnabar.

Experimental

Apparatus

Samples were digested in 100-ml calibrated flasks in a temperature-controlled shaker bath (Precision Scientific Co., Model 75).

The equipment used for the automated cold-vapour analysis consisted of (*a*) an automatic sampler (Technicon AutoAnalyzer II sampler with 20–1/5 cam); (*b*) a proportionating pump (Carlo Erba, Model 08-59-10202); (*c*) Technicon AutoAnalyzer tubing of specified dimensions; (*d*) a gas separator, as used by Agemian and Chau[1]; (*e*) a mercury monitor (Pharmacia Fine Chemicals); and (*f*) a strip-chart recorder (Hewlett-Packard, Model 7101B). The system is similar to that used by Agemian and co-workers.[1,6]

For high levels of mercury, a Perkin-Elmer 503 atomic-absorption spectrophotometer, equipped with an Intensitron lamp, was used with an air - acetylene flame.

Reagents

High-purity certified reagents were used for all analyses.

Sulphuric acid, 36 N.
Nitric acid, 16 N.
Hydrochloric acid, 12 N.
Potassium permanganate solution, 6 *per cent.* m/V.
Potassium persulphate solution, 5 *per cent.* m/V.
Tin(II) sulphate solution, 10 *per cent.* m/V *in* 2 N *sulphuric acid.*
Hydroxylammonium sulphate (6 *per cent.* m/V) - *sodium chloride* (6 *per cent.* m/V) *solution.*

Procedure

Determine the water content of the wet sediment by drying it overnight to constant mass at 110 °C. Weigh a representative sample of wet sediment, equivalent to 0·1–2 g of the dry mass, into a 100-ml calibrated flask. Wash the sediment down to the bottom of the flask with mercury-free distilled water, place the flask in an ice - water bath and slowly add 15 ml of sulphuric acid - nitric acid (2 + 1). After cooling, add 2 ml of hydrochloric acid. Shake the mixture and let it stand for 5 min.

After expelling the acid fumes from the flask, place it in a shaking water-bath at a temperature of 50–60 °C and digest for 2 h. Then allow the flask to cool for 30 min and carefully add 10 ml of potassium permanganate solution while cooling in an ice - water bath. If the colour does not persist for 15 min, add a further amount of potassium permanganate solution. After 30 min, add 5 ml of potassium persulphate solution, with gentle stirring, and allow the mixture to stand overnight. If all of the permanganate is reduced, as witnessed by the absence of the purple colour, add potassium permanganate solution until the colour persists.

Add 10 ml of hydroxylammonium sulphate - sodium chloride solution and stir the mixture gently until the solution becomes clear and all of the precipitated manganese(IV) oxide has dissolved. Make the solution up to volume and centrifuge an aliquot at 2500 rev min^{-1} for 5 min. Transfer an aliquot of the clear supernatant liquid into a glass sample cup and place it in the automatic sampler for analysis. Use a cam designed for 20 samples per hour and a sample to wash ratio of 1:5, corresponding to a sampling time of 30 s and a wash time of 2·5 min. For concentrated solutions of mercury use the flame technique.

The linear concentration range in solution is 0·0002–0·006 mg l^{-1} for the non-flame detection system[1] and 10–300 mg l^{-1} for the flame detection system.[8] For sample concentrations of 0·1–2 g per 100 ml, the non-flame detection system has a range of 0·01–6 mg kg^{-1} and the flame method 5–300 mg kg^{-1} of mercury in the sediment. Further dilution of the extracts could extend the upper limit of both detection systems.

Treat all standards exactly as for the above samples.

Results and Discussion

Sulphuric acid is used extensively for the extraction of mercury from biological materials, either alone[7,9,10] or with nitric acid.[11] It has also been used separately[11–13] or together with

nitric acid[2,14,15] for sediments and rocks. Iskandar *et al.*[2] also showed that a mixture of sulphuric and nitric acids is necessary for the adequate digestion of organic matter in sediments and soils and for the subsequent liberation of mercury.

As already indicated, the presence of hydrochloric acid is necessary for the decomposition of cinnabar. Initially, an attempt was made to use large amounts of hydrochloric acid, as suggested by Jacobs and Keeney,[3] but the procedure proved to be very impractical and difficult and gave rise to low recoveries of mercury from sediments. The use of a fume hood in which to perform the digestion is essential when hydrochloric acid is heated, even to 60 °C. Further, on adding potassium permanganate in order to oxidise the organomercurials, violent frothing of the solution occurs, with evolution of chlorine, which makes the analysis very difficult. In addition, the decomposition[5] of the permanganate to manganese(IV) oxide caused by the hydrochloric acid, renders it ineffective as an oxidant for organomercurials, and a low recovery of mercury may therefore result.

We found that as little as 5 ml of hydrochloric acid caused the rapid decomposition of 25 ml of a 5 per cent. *m*/*V* potassium permanganate solution. Table I shows the effect of excess of hydrochloric acid on the recovery of mercury from sediments. The low results obtained (third column) are attributed to the loss of mercury due to violent frothing of the solution and possible volatilisation, and also to the reduced efficiency of oxidation of the organic matter by permanganate owing to its decomposition by hydrochloric acid. The analyses were performed by using the automated method reported by Agemian and co-workers.[1,6] The samples examined were ordinary samples as analysed in our laboratory and therefore did not give any indication of the presence of cinnabar. Consequently, the method of Iskandar *et al.*[2] gave results for recovery that are similar to those given by the proposed method.

TABLE I

EXTRACTION OF MERCURY FROM SEDIMENT SAMPLES BY USING DIFFERENT EXTRACTION MEDIA

Results are expressed in μg kg^{-1}.

	Extraction medium		
Sample	H_2SO_4 - HNO_3 (2 + 1)*	H_2SO_4 - HNO_3 - HCl (10 + 5 + 2)†	H_2SO_4 - HNO_3 - HCl (2 + 1 + 1)‡
Silt	310	320	250
Silty clay	600	600	450
Clay	970	960	600
Clay	1000	1000	800
Clay	1600	1600	1400

* Method of Iskandar *et al.*[2]
† Present method.
‡ Contains an excessive amount of hydrochloric acid.

In order to check the efficiency of the method, sediment samples were spiked with mercury(II) sulphide powder and the recovery of the mercury was determined. As only milligram amounts could reliably be weighed, the analysis had to be performed by the flame atomic-absorption method; the results obtained are given in Table II and show a satisfactory recovery of 100 ± 5 per cent. of mercury added as mercury(II) sulphide. The small amount of hydrochloric acid added in the digestion procedure causes the decomposition of the cinnabar to become visually apparent, the disappearance in a few seconds of the bright red colour indicating its complete dissolution.

TABLE II

RECOVERY OF MERCURY FROM MERCURY(II) SULPHIDE BY THE PROPOSED METHOD

Mercury added (as HgS)/g	0·0018	0·0071	0·0103	0·0222	0·0291
Recovery, per cent.	102	98	105	95	101

The levels of the spikes used for the recovery tests are much higher than would be found in any real samples, the mercury contents[16] of most uncontaminated solid earth materials being in the range 10–500 ng kg^{-1}. Based on 1-g samples, the results shown in Table II correspond

to levels of 1000 mg kg^{-1} and above, which are much higher than those reported for most contaminated samples; Konrad[17] reported levels of 700–800 mg kg^{-1} for samples from chlor-alkali plants in Wisconsin. Therefore, the satisfactory recovery of amounts of mercury that are much larger than those encountered in highly contaminated samples indicates that the proposed method is adequate. As confirmed by Jacobs and Keeney,[3] use of the method of Iskandar *et al.*[2] did not permit the recovery of any of the mercury introduced as mercury(II) sulphide, which was completely resistant to the sulphuric acid - nitric acid mixture.

Table III shows the effect of hydrochloric acid on the recovery of mercury from geological samples that contain large amounts of sulphide. The results given in this table show the superiority of the proposed method, using hydrochloric acid, for determining low levels of mercury. The precisions of the two methods are similar and the coefficient of variation[6]

TABLE III

EXTRACTION OF MERCURY FROM GEOLOGICAL SAMPLES THAT HAVE HIGH SULPHIDE CONTENTS

Results are expressed in mg kg^{-1}; all samples were analysed in triplicate.

Sample	Extraction medium: H_2SO_4 - HNO_3 (2 + 1)*	Extraction medium: H_2SO_4 - HNO_3 - HCl (10 + 5 + 2)†	Difference, per cent.
Sphalerite	11·1	12·5	+11·2
Copper concentrate	0·30	0·31	+3·2
Pyrite concentrate	0·19	0·33	+42·4
Ore head	29·7	29·3	−1·4
Tailing	16·8	16·5	−1·8
Tailing	8·6	8·7	+1·1
Lead concentrate	32·5	35·7	+9·0
Ore head	6·2	6·7	+4·5
Copper concentrate	5·2	5·2	0
Oxidised tailing	0·9	0·9	0

* Method of Iskandar *et al.*[2]
† Present method.

varies with the concentration of mercury as follows: 14, 2 and 2 per cent. for 0·1, 0·6 and 2 mg kg^{-1} of mercury, respectively, levelling off at values of about 2 per cent. above this concentration range. Thus, from Table III it can be seen that the first, third, seventh and eighth samples statistically show higher levels of mercury by the proposed method. This evidence is consistent with the hypothesis that in these samples some of the mercury is in the form of mercury(II) sulphide. In the remaining samples there is again, apparently, no mercury(II) sulphide in spite of the high sulphide content.

Therefore, the above results show that use of the proposed method is advantageous and convenient for the safe digestion of a large number of samples. In addition, the proposed method is directly applicable, without modification, to the digestion of organic and biological tissues. We have not shown recoveries for organomercury compounds because both Iskandar *et al.*[2] and Jacobs and Keeney[3] have shown that with their methods the mercury in these compounds can be successfully recovered. Their methods represent the two extremes of the proposed method, that is, our method is intermediate between the two digestion techniques and was found to give similar recoveries.

Conclusion

A digestion method applicable to biological and geological samples for the extraction of mercury has been shown to enable mercury to be satisfactorily recovered from mercury(II) sulphide. The method permits the decomposition of all forms of mercury and is simple, rapid, safe and adaptable to the automated cold-vapour and flame atomic-absorption techniques for the determination of mercury.

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References

1. Agemian, H., and Chau, A. S. Y., *Analytica Chim. Acta*, 1975, **75**, 297.
2. Iskandar, I. K., Syers, J. K., Jacobs, L. W., Keeney, D. R., and Gilmour, J. T., *Analyst*, 1972, **97**, 388.
3. Jacobs, L. W., and Keeney, D. R., *Envir. Sci. Technol.*, 1974, **8**, 267.
4. Jonasson, I. R., Lynch, J. J., and Trip, L. J., *Geol. Surv. Pap. Can.*, 1973, Paper 73–21.
5. Lingane, J. J., "Analytical Chemistry of Selected Metallic Elements," Reinhold Publishing Corporation, New York, 1966.
6. Agemian, H., Aspila, K. I., and Chau, A. S. Y., *Analyst*, 1975, **100**, 253.
7. Uthe, J. F., Armstrong, F. A. J., and Stainton, M. P., *J. Fish. Res. Bd Can.*, 1970, **27**, 805.
8. "Analytical Methods for Atomic Absorption Spectrophotometry," Perkin-Elmer Corp., Norwalk, Connecticut, 1973.
9. Polley, D., and Miller, V. L., *Analyt. Chem.*, 1955, **27**, 1162.
10. Thorpe, V. A., *J. Ass. Off. Analyt. Chem.*, 1971, **54**, 206.
11. Jeffus, M. T., and Elkins, T. S., *J. Ass. Off. Analyt. Chem.*, 1970, **53**, 1172.
12. Hatch, W. R., and Ott, W. L., *Analyt. Chem.*, 1968, **40**, 2085.
13. Head, P. C., and Nicholson, R. A., *Analyst*, 1973, **98**, 53.
14. Cranston, R. E., and Buckley, D. E., *Envir. Sci. Technol.*, 1972, **6**, 274.
15. Melton, J. R., Hoover, W. L., and Howard, P. A., *Proc. Soil Sci. Soc. Am.*, 1971, **35**, 850.
16. "Mercury in the Environment," *Prof. Pap. U.S. Geol. Surv.*, 1970, Paper 713.
17. Konrad, J. G., Research Report 74, Wisconsin Department of Natural Resources, Madison, Wis., 1971.

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The Application of a Wide-slot Nitrous Oxide - Nitrogen - Acetylene Burner for the Atomic-absorption Spectrophotometric Determination of Aluminium, Arsenic and Tin in Steels by the Single-pulse Nebulisation Technique*

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Single-pulse nebulisation of 10 per cent. *m/V* iron or steel solutions into a nitrogen-diluted nitrous oxide - acetylene flame maintained on a specially designed wide-slot burner is a useful technique for the determination of tin, arsenic and soluble aluminium in iron and steels. Use of this method avoids the need for prior separation of the analyte. A deuterium lamp was found to be unsatisfactory for measuring the background (non-specific) absorption when determining aluminium and tin, the explanation for which is postulated.

Atomic-absorption flame spectrophotometry has traditionally depended on the continuous introduction of the sample into the flame during the measurement period. The nebulisation of steel solutions containing more than 1–2 per cent. *m/V* of steel into a conventional nitrous oxide - acetylene flame may result in a rapid partial blockage of the burner slot. This effect can be overcome by nebulising discrete sample aliquots, typically 25–200 μl, and recording the resulting pulse absorption signal.[1–3] Single-pulse nebulisation studies in flames have also been reported for the analysis of microlitre samples by flame-emission and atomic-fluorescence spectroscopy[4] and in conjunction with an ultrasonic nebuliser.[5]

Other workers[6,7] have shown that the addition of air or argon to the nitrous oxide - acetylene flame increases the operating safety margin and minimises inter-element effects in the determination of magnesium[6] and strontium.[7] Conventional atomic-absorption methods for the determination of low levels of aluminium and some other metals in steels usually require the prior extraction of the iron.[8,9] Shaw and Ottaway[10] have proposed the use of electrothermal atomisation using a graphite tube to overcome this problem.

This paper reports the application of the nitrogen-diluted nitrous oxide - acetylene flame, in conjunction with a wide-slot burner and pulse nebulisation of the sample, to the determination of arsenic, tin and soluble aluminium in steels. This study also shows that the use of a deuterium hollow-cathode lamp for background correction can lead to erroneous results for aluminium and tin. The reason for this behaviour is postulated.

Experimental

Results were obtained by using a Shandon Southern Instruments A3400 atomic-absorption spectrophotometer with an A3429 air - nitrous oxide change-over valve. The output was monitored on a Shandon Southern Autograph potentiometric recorder. A nebuliser with a platinum - iridium capillary was used. The nitrogen supply to the burner was fed, via a non-return valve, into a 2·5-l metal reservoir. The exit of this reservoir was connected to the inlet of the supplementary air flow meter. The needle valve of this flow meter was permanently set to give a nitrogen flow-rate of 2 l min^{-1} at a nitrogen pressure of 20 p.s.i.g. (138 kN m^{-2}). A pressure-sensing device was incorporated into the reservoir such that if the nitrogen pressure in the reservoir fell below 16 p.s.i.g. (110 kN m^{-2}) a cut-off valve (Dewrange Controls Ltd.) in the acetylene line to the A3400 was activated.

Tests showed that if the nitrogen supply to the unit failed during operation the flame was always extinguished without explosive flashback. The system is depicted in Fig. 1. The design of the wide-slot burner grid is shown in Fig. 2.

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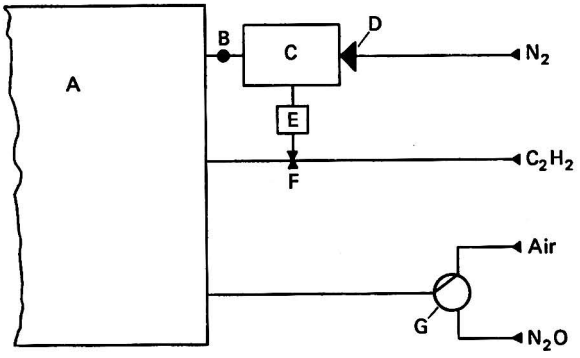

Fig. 1. Gas arrangement. A, A3400 spectrophotometer; B, flow meter + needle valve; C, 2·5-l reservoir; D, non-return valve; E, pressure sensor; F, cut-off valve; and G, A3429 change-over valve.

An air - acetylene mixture, with nitrogen flowing at the rate of 2 l min^{-1}, was ignited and the acetylene flow-rate set to give a fuel-rich flame. The change-over valve was then operated so as to substitute nitrous oxide for the air. A nitrous oxide flow-rate of 11·5 l min^{-1} and a nitrogen flow-rate of 2 l min^{-1} were used for all studies; the acetylene flow-rate was optimised for each element.

The burner was removed and washed out with dilute hydrochloric acid after operating for about 2 h. Occasionally the burner slot was polished with a very fine grade of emery paper, which was found to minimise carbon build-up on the jaws of the burner.

Tests showed that even if a severe reduction in the nitrous oxide flow-rate occurred, the acetylene supply could be turned off without risk of explosive flashback. This is not true for the standard burner (without nitrogen) with which, if the nitrous oxide flow-rate is reduced by 30 per cent. or more, the nitrous oxide must be turned off prior to the acetylene in order to prevent an explosive flashback. With the wide-slot burner it was possible to nebulise a 5 per cent. m/V steel solution continuously for 15 min before signs of burner clogging became evident. If 5 per cent. m/V steel solutions were nebulised for 15 s, with an equal nebulisation period for distilled water between samples, partial blockage of the

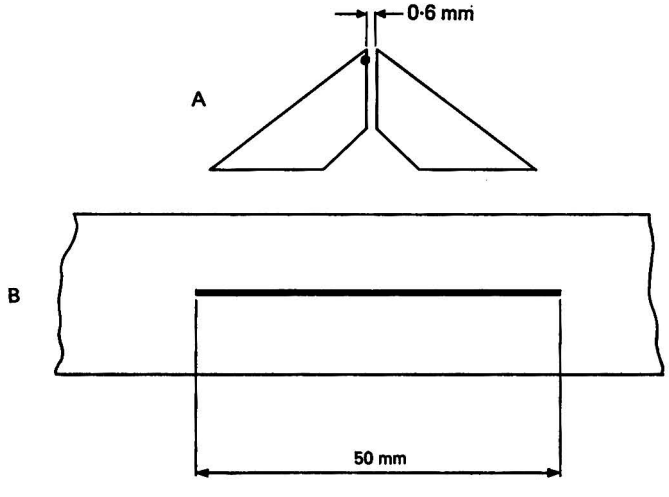

Fig. 2. Wide-slot nitrous oxide - nitrogen - acetylene burner. A, Section (twice full size); and B, top view (full size).

burner slot occurred after 40–45 min of operation. The burner was allowed to warm up for 5 min before any steel solutions were nebulised, otherwise partial clogging of the burner slot occurred more rapidly.

Optimisation of Operating Conditions

Nitrogen flow-rate

For most elements tested the sensitivity decreased with increasing nitrogen flow-rate. A nitrogen flow-rate of 2 l min^{-1} gave a satisfactory safety margin with respect to flashback, and adequate sensitivity. In Table I the sensitivity of the wide-slot burner (slot width 0·60 mm) is compared with that of the standard burner (slot width 0·43 mm). It can be seen that for most elements tested the use of the wide-slot burner results in an improvement in sensitivity even though the flame temperature must be lower. This effect was attributed to a larger flame volume where the breakdown of refractory oxides can occur. The burner height setting and acetylene flow-rate were not so critical with the wide-slot burner, and the optimum burner height setting tended to be 2–3 mm lower than that of the standard burner. The optimum acetylene flow to the wide-slot burner was not dependent on the nitrogen flow-rate. Although it was possible to use air[6] instead of nitrogen, this change reduced the safety margin and the optimum acetylene flow was then very dependent on the air flow-rate.

TABLE I

COMPARISON OF SENSITIVITY OF STANDARD AND WIDE-SLOT BURNER

		Characteristic concentration (continuous nebulisation)/μg ml^{-1}		
Element	Wavelength/nm	Standard burner (normal operating conditions)	Standard burner (+2 l min^{-1} of nitrogen)	Wide-slot burner (+2 l min^{-1} of nitrogen)
Al	309·3 (doublet)	1·0	1·2	0·75
Al	396·2	—	—	0·84
As	193·7	1·7	1·5	1·1
Ba*	553·6	0·37	0·41	0·30
Si	251·6	2·0	3·5	2·1
Sn	235·5	—	—	1·2
Sn†	286·3	2·6	2·4	1·9
Ti	364·3	1·9	3·5	2·1
V	318·4	1·5	1·8	1·3

* +1000 μg ml^{-1} of potassium.
† Better signal to noise ratio at 286·3 nm than at 235·5 nm.

Optimum sample volume for pulse nebulisation

A sample volume of 200 μl was found to give the best compromise with respect to the signal to noise ratio and absence of blockage of the burner slot when nebulising 10 per cent. *m/V* steel solutions, which is in agreement with other studies.[1–3]

Damping

In order to attain the optimum signal to noise ratio the A3400 spectrophotometer was operated at a time constant of 2 s.

Spectral bandpass and wavelengths

The resonance lines, background correction wavelengths and spectral bandpasses used in this study are listed in Table II.

Sample dissolution

The steel sample (5 g) was carefully dissolved by slowly adding to it 50 ml of aqua regia. The solution obtained was then boiled for 15 min, allowed to cool and filtered into a 50-ml (for a 10 per cent. *m/V* solution) or 100-ml (for a 5 per cent. *m/V* solution) calibrated flask. The filter was washed with a small volume of 10 per cent. aqua regia solution and the combined filtrate and washings were diluted to volume with water. Calibration was carried out by the method of standard additions. The aluminium, arsenic and tin contents of the acid blank were below the detection limits of the technique.

TABLE II

RESULTS FOR BACKGROUND CORRECTION

Analyte		Background correction					
Element	Wavelength/nm	Element	Wavelength/nm	Spectral bandpass/nm	Lower energy level of background line/eV	Background absorption* from 200 μl of 10^5 μg ml^{-1} steel† solution	Signal* from 200 μl of a 10^3 μg ml^{-1} solution of background correction element
Al	309·3 (doublet)	D_2	309·3	0·3	—	0·0012	—
		Pd	311·4	0·18	0·96	0·000 25	0·017
		Mg	309·3	0·18	2·72	0·000 25	0·0015
		Cu	309·4	0·18	1·39	0·0003	0·0012
Al	396·2	Pd	395·9	0·18	1·45	0·000 25	0·003
As	193·7	D_2	193·7	0·6	—	0·002	—
Sn	286·3	D_2	286·3	0·3	—	0·005	—
		D_2	286·3	0·6	—	0·004	—
		Pd	285·5	0·3	4·00‡	0·001§	0·011

* Expressed as per cent. of analyte in steel.
† BCS 456.
‡ Ionic line.
§ Probably caused by stray light from very intense 276·3-nm palladium resonance line.

Measurement Procedure

The burner was always allowed to run for 5 min in order to attain the normal operating temperature prior to nebulising the steel solutions; 200 μl of the sample were pipetted into a 20-ml disposable polystyrene beaker. The plastic capillary tube was removed from the blank solution and placed in the 200-μl sample until the latter had completely disappeared from the beaker; the capillary tube was then replaced in the blank solution. A blank solution of 0·1 M hydrochloric acid was continuously nebulised between samples at all times. Some typical traces are shown in Fig. 3.

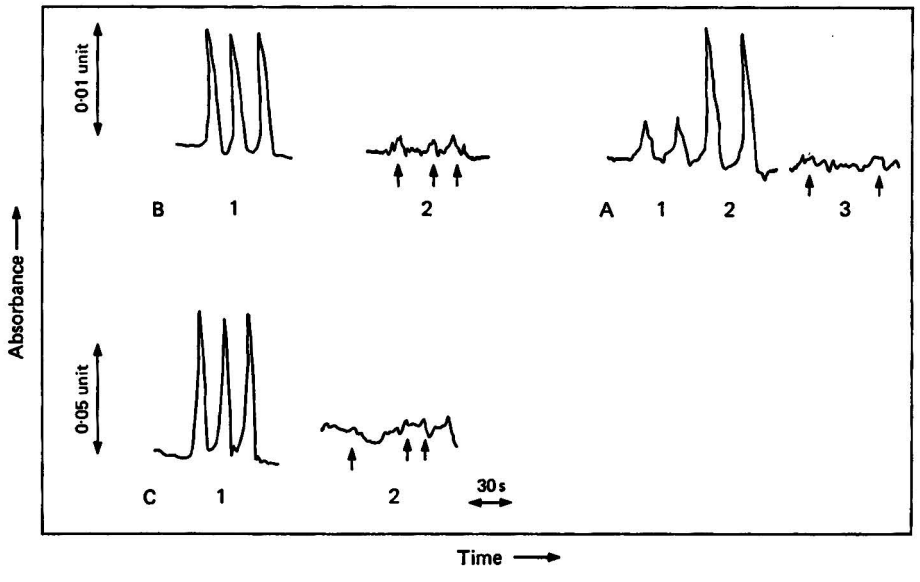

Fig. 3. Typical traces (10 per cent. m/V mild steel solutions, 200-μl pulse nebulisation). A, Aluminium, 396·2 nm: 1, sample (0·0008 per cent. of Al); 2, as for (1) + 2·5 μg ml^{-1} of Al; and 3, background (Pd 395·9 nm). B, Tin 286·3 nm: 1, sample (0·0075 per cent. of Sn); and 2, background (Pd 285·6 nm). C, Arsenic, 193·7 nm: 1, sample (0·032 per cent. of As); and 2, background (D_2 193·7 nm).

Results

Background Absorption Measurements

When concentrated solutions (5–10 per cent. *m/V*) are nebulised it is essential to check for non-specific background absorption caused by the sample matrix. Initially, background absorption measurements were made by using a deuterium hollow-cathode lamp. However, for steel samples that contained very low levels of aluminium, the background signals from both 5 and 10 per cent. *m/V* steel solutions were larger than those observed by using the aluminium and tin lamps at 309·3 and 286·3 nm, respectively. This behaviour was reproducible and was also observed, to a slightly lesser degree, if the spectral bandpass was increased from 0·3 to 0·6 nm. The background absorption was also monitored by using the non-resonance lines of various elements. These lines are listed in Table II, which also gives the lower energy level of the transition,[11,12] the absorption signal for a 200-μl sample of a 1000 μg ml^{-1} solution of the non-resonance line element and the background absorption signal expressed as a concentration of the analyte. The deuterium lamp had too low an intensity to be satisfactorily used at the aluminium wavelength of 396·2 nm.

This curious behaviour by which the background absorption (deuterium lamp) was apparently higher than the sum of atomic plus background absorption (element lamp) was attributed to weak atomic absorption by the large concentration (about 10^5 μg ml^{-1}) of iron. It was not considered to be justified to ignore the absorption by the iron non-resonance lines over the monochromator spectral bandpass. A typical absorption line half-width in the nitrous oxide - acetylene flame is about 0·005 nm.[13] Assuming a triangular line profile, a spectral bandpass of 0·3 nm and complete absorption over the absorption line profile, then (0·005/0·3) $\times$ 100 = 1·7 per cent. of the radiation of the deuterium lamp will be absorbed for a single absorption line that falls within the monochromator spectral bandpass (ignoring any additional absorption from the wings of the line).

In Table III the iron lines[12] that are within 0·15 nm of the aluminium and tin lines used in this work are listed. It can be seen that this explanation would account for the anomalously high absorbance values observed when using the deuterium lamp at 286·3 and 309·3 nm, and was further substantiated by the fact that very large background absorption signals at 248·3 and 279·6 nm were observed when using a deuterium lamp and nebulising a 5 per cent. *m/V* solution of a manganese steel sample.

TABLE III

IRON (I) LINES WITHIN $\pm$ 0·15 nm OF THE ALUMINIUM, ARSENIC AND TIN RESONANCE LINES

Analyte			
Element	Wavelength/nm	Iron lines[12]/nm	Lower energy level of iron[12] line/eV
Al	309·271 } doublet	309·158	1·02
	309·284 }	309·278	2·96
		309·336	—
		309·381	1·61
		309·388	2·57
Al	396·153	396·029	3·64
		396·115	2·85
		396·235	3·27
As	193·696	None	—
Sn	286·333	286·250	1·01
		286·344	1·48
		286·386	0·09

The deuterium lamp had a molybdenum cathode. However, a 1000 μg ml^{-1} molybdenum solution (equivalent to 1 per cent. of molybdenum in steel for 10 per cent. *m/V* solutions) gave no response at any of the deuterium background wavelengths used. A hydrogen hollow-cathode lamp with a nickel cathode gave background absorption results that were similar to those given by the deuterium lamp. The outputs from both lamps were scanned in the emission mode using a spectral bandpass of 0·18 nm. The 248·3-nm iron line and the 279·6-nm manganese line could not be detected above the continuum emission.

Wagenaar and de Galan[13] have shown that the profile of the 396·2-nm aluminium absorption

line in the nitrous oxide - acetylene flame has a half-width of 0·0048 nm. The line half-width of the 396·2-nm resonance line from the aluminium hollow-cathode lamp was quoted as being 0·0013 nm. If it is assumed that the iron lines given in Table III have a similar absorption line half-width, spectral overlap of the profiles of the iron absorption lines with the aluminium 396·2-nm resonance line or the palladium non-resonance lines used in this work should not occur. There could be slight overlap of the aluminium 309·271/309·284 and iron 309·278-nm lines, but as similar analytical results were obtained by using the 309·3 and 396·2-nm aluminium resonance lines, this was not thought to be of any practical significance. (Also the lower energy level of the iron 309·278-nm line is 2·96 eV above the ground state.[12])

There could be weak overlap of the tin 286·333-nm and iron 286·344-nm lines, but the steel sample (BCS 456) gave an identical (very small) signal at the tin resonance and palladium background wavelengths, which would indicate that iron atoms are not absorbing radiation at the wavelength of the tin resonance line. Also tin measurements made at the 235·485-nm tin resonance line, with background correction measurements made using the palladium 235·134-nm line, gave similar results. For arsenic measurements the deuterium lamp gave satisfactory results. This is to be expected as no iron lines are listed[11,12] in the wavelength region 191–198 nm.

It can be seen that great care must be exercised in the choice of non-resonance lines for background correction. The response (0·006 absorbance unit) for a 1000 μg ml^{-1} magnesium solution at the 309·3-nm magnesium non-resonance line was found to be caused by stray light from the magnesium 285·2-nm resonance line (the intensity of the 309·3-nm line was only 1·5 per cent. of that of the 285·2-nm line). Thus the use of this line for background correction would be invalid if the sample contained minor amounts of magnesium. If an OX9 filter (Barr & Stroud Ltd.), which is effectively opaque at 285·2 nm but transmits at 309·3 nm, is placed between the flame and the monochromator, no response is observed from the 1000 μg ml^{-1} magnesium solution. Thus, when selecting a non-resonance line for background correction in complex matrices it is essential to check for a response using a solution containing the maximum concentration of the non-resonance lamp element that is likely to be encountered. If the cathode is an alloy (*e.g.*, brass) all the major elements of the alloy should similarly be checked. It is also advisable to check that the selected non-resonance line does not overlap any atomic line profiles of the main components of the analyte.

A palladium lamp was used for all background correction measurements for aluminium and tin, while for arsenic a deuterium lamp was used. It was found that the noise level and drift of the output from the deuterium lamp were greater than those from the aluminium, tin and palladium lamps.

Analysis of Steel Samples

Preliminary studies were performed using 200-μl aliquots of 5 per cent. m/V solutions. However, subsequent work showed that there were no burner clogging problems with 200-μl aliquots of 10 per cent. m/V solutions and the latter were utilised in all further work. The response for a given amount of aluminium from the 10 per cent. m/V steel solution was 80 per cent. of that from a 5 per cent. m/V steel solution. The calibration graphs were linear up to concentrations 50 times greater than the detection limits (see Table IV). Higher concentrations were not studied.

TABLE IV

DETECTION LIMITS FOR ARSENIC, TIN AND SOLUBLE ALUMINIUM IN STEEL

Element	Line/nm	2σ detection limit, per cent.
Al	309·3	0·000 25
Al	396·2	0·000 25
As	193·7	0·002
Sn	286·3	0·0008

Table IV shows the 2σ detection limits obtained, and Table V some results obtained for arsenic, tin and soluble aluminium in standard steel samples. The BCS 494 manganese steel contained 13 per cent. of manganese, but a 15 000 μg ml^{-1} manganese solution gave negligible background absorption at all of the analytical wavelengths used.

The relative standard deviation for a solution containing 2·5 μg ml^{-1} of aluminium (396·2 nm) in 10 per cent. m/V steel solution (20 measurements) was 3·1 per cent.

Conclusions

The single-pulse nebulisation technique in conjunction with a nitrogen-diluted nitrous oxide - acetylene flame maintained on a wide-slot burner allows the direct nebulisation of 10 per cent. *m/V* steel solutions, thus avoiding the need to carry out a prior separation of the analyte from the matrix. The method is also very useful if the amount of sample available is limited.

TABLE V

DETERMINATION OF ARSENIC, TIN AND SOLUBLE ALUMINIUM IN IRON AND STEEL

Sample	Element	Concentration, per cent.	
		Pulse nebulisation	Other methods
BCS 456 mild steel	Al	0·0008	0·0007*
BCS 494 manganese steel ..	Al	0·000 85	0·0007*
			0·001†
BCS 260/3 high-purity iron ..	Al	0·000 55	0·000 42‡
BCS 451 mild steel	Sn	0·0075	0·008§
BCS 453 mild steel	Sn	0·0185	0·019§
BCS 451 mild steel	As	0·032	0·031§
BCS 453 mild steel	As	0·056	0·052§

* Results obtained by Mr. R. C. Rooney using a method based on the extraction of iron with isobutyl acetate.
† Single BCS value.
‡ Results obtained by Shaw and Ottaway.[10]
§ BCS standard values.

A deuterium hollow-cathode lamp was found not to be satisfactory for making background correction measurements at wavelengths 286·3 and 309·2 nm when nebulising 10 per cent. *m/V* steel solutions, which was attributed to atomic iron lines within the monochromator spectral bandpass, which absorb radiation from the deuterium lamp. Care should be exercised when using a deuterium lamp for background correction measurements with this type of analysis.

A better technique for background correction is to utilise a non-resonance line from an element that is unlikely to be encountered in the steel samples. Ideally, the chosen background correction line and analyte resonance line should not overlap any atomic line profiles of the major elements in the sample.

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References

1. Sebastiani, E., Ohls, K., and Riemer, G., *Z. Analyt. Chem.*, **1973**, **264**, 105.
2. Berndt, H., and Jackwerth, E., *Spectrochim. Acta*, 1975, **30B**, 169.
3. Manning, D. C., *Atom. Absorption Newsl.*, 1975, **14**, 99.
4. Sarbeck, J. R., St. John, P. A., and Winefordner, J. D., *Mikrochim. Acta*, 1972, 55.
5. Korte, N. E., Moyers, J. L., and Denton, M. B., *Analyt. Chem.*, **1973**, **45**, 530.
6. Fleming, H. D., *Spectrochim. Acta*, 1967, **23B**, 207.
7. Fulton, A., and Butler, L. R. P., *Spectrosc. Lett.*, 1968, **1**, 317.
8. Headridge, J. B., and Sowerbutts, A., *Analyst*, **1973**, **98**, 57.
9. Jenkins, R. H., and Jones, C. P., British Steel Corporation Research Report No. SM/464/A, 1972.
10. Shaw, F., and Ottaway, J. M., *Analyst*, 1975, **100**, 217.
11. Meggers, W. F., Corliss, C. H., and Scribner, B. F., "Table of Spectral Line Intensities," NBS Monograph 32, Part 1, 1961.
12. Zaidel, A. N., Prokof'ev, V. K., and Raiskii, S. M., "Tables of Spectrum Lines," Pergamon Press, London, 1961.
13. Wagenaar, H. C., and de Galan, L., *Spectrochim. Acta*, **1973**, **28B**, 157.

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The Determination of Mobile Nitrogen in Steel Using an Ammonium Ion-selective Electrode

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An absorption cell containing an ammonium ion-selective electrode has been constructed and used for the determination of mobile nitrogen in steel; this nitrogen is released as ammonia when the steel is heated at 500 °C in a stream of hydrogen. The cell was used in conjunction with a digital voltmeter and a recorder in order to obtain a continuous record of the progress of the reaction between mobile nitrogen and hydrogen. Results are presented for the determination of 0·0005–0·0108 per cent. of mobile nitrogen in 10 steels using the new equipment and are compared with those obtained by using a spectrophotometric finish based on indophenol blue. The method, with relative standard deviations of 0·0001–0·0003 per cent., is more precise than that with the spectrophotometric finish, with relative standard deviations of 0·0002–0·0006 per cent.

The mechanical properties of steel are greatly affected by the content of nitrogen, which is usually present within the range 0·001 to 0·05 per cent. Its presence can be harmful, causing age-hardening and flaws in pressings, and the presence of aluminium nitride can result in inter-granular fracture. The presence of nitrogen can also be beneficial by improving the strength and creep properties of steels.[1] Usually nitrogen occurs in steels both as mobile nitrogen and as stable nitrides of elements such as aluminium, silicon, titanium, zirconium, vanadium, niobium and chromium; the nitrogen in stable nitrides is referred to as combined nitrogen. The mobile nitrogen is less strongly bound in steel, occurring as atomic nitrogen or as less stable nitrides of iron and manganese. The ratio of mobile to combined nitrogen, and thus the properties of a steel, can be changed by heat treatment. Hence, for the control of heat treatments, a knowledge of the mobile and combined nitrogen contents is most helpful.

The total nitrogen content of a steel can be determined by use of a Kjeldahl method, in which the nitrogen is converted into ammonia and determined by a suitable titrimetric or colorimetric procedure. The combined nitrogen content of a steel can be determined by using a similar procedure after separation of stable nitrides and other compounds from the steel, following dissolution of the metals, by using a methyl acetate - bromine mixture. The difference between the total and combined nitrogen values is the mobile nitrogen. However, a more convenient way to determine mobile nitrogen is to pass hydrogen over steel millings at 500 °C. The mobile nitrogen is thus converted into ammonia, which is absorbed in a suitable solution and determined spectrophotometrically as indophenol blue.[2–4] The success of this thermal method depends on two factors. Firstly, there must be no reaction at 500 °C between the mobile nitrogen and a metal in the steel, which will result in the precipitation of more stable nitride. Such a reaction would lead to a low result for mobile nitrogen. It has been established that such a reaction does not occur between mobile nitrogen and aluminium, silicon or titanium at 500 °C, hence, such an interfering reaction will not occur with most commercial steels. The interfering reaction occurs only with certain special steels, which contain appreciable concentrations of elemental vanadium and niobium.[2] Secondly, it is important that no stable nitrides should dissociate at 500 °C as this would give rise to high results for mobile nitrogen. It appears that this is an interfering effect only for steels that contain appreciable concentrations of chromium nitride,[2] and carbon and low-alloy steels of this type are rarely produced. Therefore, it is generally agreed that the thermal method, using hydrogen at 500 °C, is reliable for the determination of mobile nitrogen in most commercial carbon and low-alloy steels. Actually, the optimum temperature for this extraction method for mobile nitrogen may not be 500° C for all types of steels, but this information can be acquired only by more extensive use of the technique.

The thermal method using hydrogen, coupled with an indophenol blue spectrophotometric finish, has been used successfully in our laboratory for some time. However, a spectro-

photometric determination of the ammonia that is evolved has the disadvantage that one cannot be certain that all of the mobile nitrogen from a particular alloy sample has been converted into ammonia at 500 °C within a particular period of time, unless multiple runs with increasing collection times are undertaken. The collection time for ammonia depends on the flow-rate of the hydrogen and on the dimensions of the steel millings. Millings that have at least one dimension less than 0·5 mm are usually used; also, collection times of the order of 1 h are often used.

Clearly, it would be advantageous to have available a simple method for continuously recording the amount of mobile nitrogen that has been extracted as ammonia during a run and to know beyond doubt when all of the mobile nitrogen has been extracted. Such a method is described in this paper. To this end a special absorption cell for ammonia, incorporating an ammonium ion-selective electrode in a triethanolamine - triethanolammonium ion buffer solution, has been constructed. The potential difference between this electrode and a mercury - mercury(I) sulphate reference electrode is passed to a digital voltmeter and continuously recorded on a potentiometric recorder. The point at which all of the mobile nitrogen has been collected can be seen at a glance and the mobile nitrogen content of the steel can then be determined immediately by reference to a suitable calibration graph.

Because it was also our intention to compare the quality of the ion-selective electrode results for mobile nitrogen with those obtained by use of colorimetry, the 10 steel samples analysed by the proposed method were first analysed by using the spectrophotometric indophenol blue method.[2–4] In order to obtain useful values for the precision of the methods, six samples of each steel were analysed by use of each method.

Experimental

Apparatus

The apparatus for the release from a 1-g sample of steel of mobile nitrogen as ammonia and its collection and determination was straightforward in design and is shown in Fig. 1.

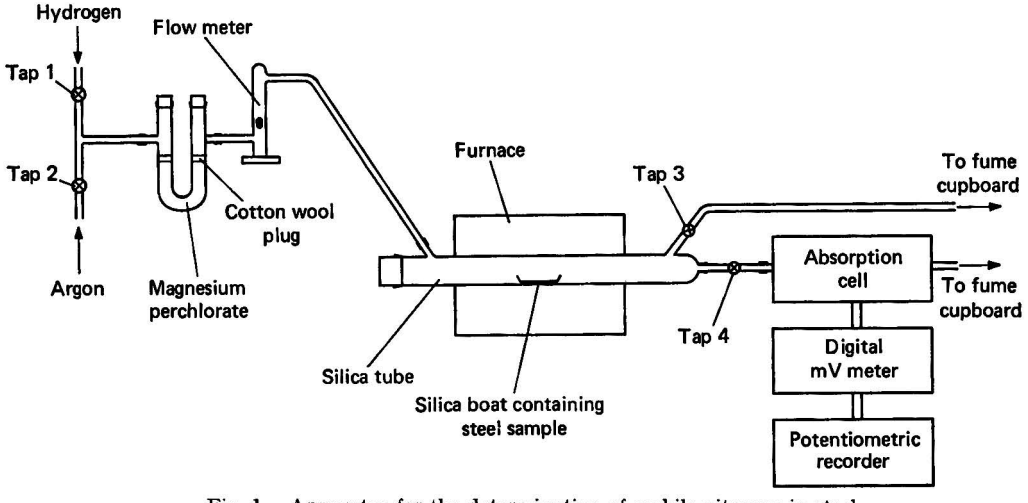

Fig. 1. Apparatus for the determination of mobile nitrogen in steel.

The various components were as follows.

Flow meter. This was a Meterate, Type RS2, fitted with a hydrogen tube (Glass Precision Engineering Ltd., Hemel Hempstead).

Resistance heated tube furnace (maximum temperature 1000 °C). This was made by the Amalgams Co. Ltd., Sheffield, and controlled by a Pye Ether Mini temperature controller. The furnace contained a silica tube of 40 mm internal diameter with a hot zone approximately 150 mm in length.

Silica boats. These boats had internal dimensions of 100 × 17 × 7 mm and were formed from silica sheet 2·5 mm thick.

Absorption cell. This contained a mercury - mercury(I) sulphate reference electrode (see Fig. 2).

Ammonium - potassium ion-selective electrode. EIL, Model 1057 200.

Digital millivoltmeter. EIL, Model 7060.

Potentiometric recorder. Oxford, 3000 series, single pen.

Constant-temperature bath, thermostatically controlled at 25 °C. For immersion of the absorption cell.

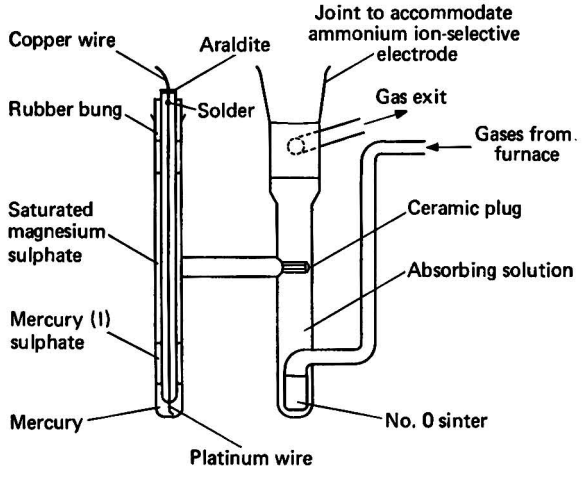

Fig. 2. Absorption cell for the ammonia produced by reaction of hydrogen with mobile nitrogen from a steel sample.

Reagents

Acetone. Redistilled analytical-reagent grade.

Hydrogen. Air Products Ltd., high-purity grade, 99·99 per cent.

Argon. Air Products Ltd., ultra-high-purity grade, 99·999 per cent.

Triethanolamine. Fisons SLR grade.

Hydrochloric acid, 1·000 M. This was prepared from ConvoL solution, Hopkin and Williams Ltd.

Ammonium ion free water. This was prepared by passing distilled water through a column of Amberlite IR-120 ion-exchange resin (H^+ form) and was used throughout this work.

Magnesium perchlorate. Fisons LR grade.

Ammonium chloride solution A. Dissolve 3·821 g of analytical reagent grade ammonium chloride (dried at 140 °C) in ammonium ion free water and dilute to 1 l in a calibrated flask with the same solvent.

1 ml of solution ≡ 1 mg of nitrogen.

Ammonium chloride solution B. Dilute 10 ml of solution A to 100 ml with ammonium ion free water.

1 ml of solution ≡ 100 μg of nitrogen.

Ammonium chloride solution C. Dilute 10 ml of solution B to 100 ml with ammonium ion free water.

1 ml of solution ≡ 10 μg of nitrogen.

Solution for the Absorption of Ammonia

To respond to the ammonium ion-selective electrode the ammonia must be fixed as ammonium ion. Triethanolamine and its conjugate acid form a suitable buffer solution for the absorption of ammonia because the pK_a value for triethanolammonium ion at 25 °C is 7·76. In theory, a buffer solution of triethanolamine and triethanolammonium ion in a concentration ratio of 1:10 should have a pH of 6·76 and in such a solution the ratio of

ammonium ion to ammonia resulting from the absorption of ammonia should be 309:1, indicating that the fixing of ammonia as ammonium ion is virtually complete.

Commercial triethanolamine contains some diethanolamine and it was therefore necessary to determine the mass of triethanolamine that was equivalent to 1 mol of hydrogen ion. This was determined by titrating potentiometrically a suitable mass of the triethanolamine with 0·1000 M hydrochloric acid. One mole of hydrogen ion was found to be equivalent to 147·7 g of the commercial base.

Preparation of the buffer solution

One litre of 1 M hydrochloric acid was added, with agitation, to 162·5 g of commercial triethanolamine (1·1 mol) dissolved in approximately 800 ml of water. The solution was then diluted to 2 l. The pH of this BH^+ - B buffer solution (10 + 1) was measured as 6·88 at 25 °C.

Construction of a Suitable Calibration Graph

A graph of cell potential *versus* the logarithm of the concentration of ammonium ion took the form of a straight line down to 10^{-4} M with a slope of 54 mV per unit of $\log[NH_4^+]$. At lower concentrations the line curved increasingly towards the log concentration axis, but the electrode responded satisfactorily to changes in ammonium-ion concentration down to 7×10^{-6} M, which is the concentration of ammonium ion produced when the ammonia equivalent to 0·0001 per cent. of mobile nitrogen in 1 g of steel is absorbed in 10 ml of buffer solution.

A calibration graph of cell potential *versus* concentration of nitrogen as ammonium ion (0·5–8 μg ml^{-1} of nitrogen) was constructed after measuring the potential of the ion-selective electrode *versus* the reference electrode for seven solutions of ammonium ion in the buffer solution; these solutions were prepared as follows. To 50 ml of buffer solution in each of seven 100-ml calibrated flasks add, in turn, 5 ml of ammonium chloride solution C, and 1, 2, 3, 4, 6 and 8 ml of ammonium chloride solution B and dilute each solution with ammonium ion free water to 100 ml.

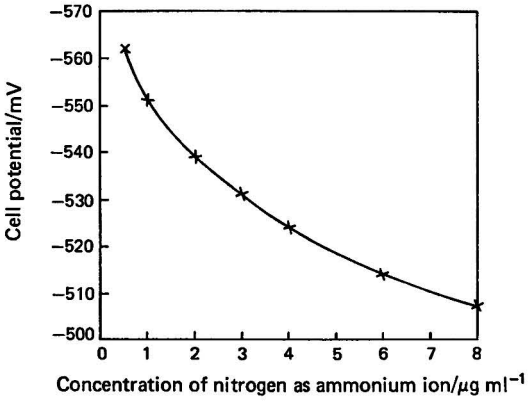

Fig. 3. A typical calibration graph for the determination of nitrogen as ammonium ion collected from steel samples.

The ammonium ion-selective electrode was conditioned before use by standing it in the most dilute calibration solution (0·5 μg ml^{-1} of nitrogen) for 2 d. The solutions were placed in the absorption cell in turn, in order from the most dilute to the most concentrated, and the cell potential was measured with each solution. Several minutes were allowed for the electrode to attain a steady potential, the electrode being agitated during this time. The electrode was washed only with the next solution between readings and not with distilled water. A typical calibration graph is shown in Fig. 3; calibration was carried out every 72 h. The changes in potential of the ammonium ion-selective electrode, when used with the cali-

bration solutions, from one calibration to the next were never in excess of and usually less than 2 mV. When not in use the electrode was stored in the most dilute calibration solution.

Method for the Determination of Mobile Nitrogen in Steel Using the Ion-selective Electrode

With argon flowing through the furnace and the by-pass tube at a rate of 300 ml min^{-1}, turn on the furnace and allow the temperature to become steady at 500 °C. Wash the absorption compartment of the cell with water, followed by acetone, these solvents being removed by means of a hypodermic needle connected to a suction pump. Close tap 3 and open tap 4 so that hot argon passes through the sinter and completely dries the absorption compartment (Note 1). Then close tap 4 and open tap 3 so that the argon by-passes the cell.

Increase the flow-rate of argon to approximately 1·5 l min^{-1} and remove the rubber bung at the end of the silica tube. Place the silica boat containing exactly 1 g of steel into the cool end of the furnace tube nearest the flow meter and replace the bung. Next, purge the furnace tube with argon for approximately 3 min (Notes 2 and 3). Reduce the flow-rate of argon to 300 ml min^{-1} and switch the flow of argon through the absorption cell.

Pipette 10 ml of the buffer solution containing ammonium ion equivalent to 5 μg ml^{-1} of nitrogen into the absorption compartment of the cell and insert the ion-selective electrode. Allow the argon to flow through the solution for 5 min and switch the flow of gas to the by-pass tube. Then increase the flow-rate of argon to 1·5 l min^{-1} and push the boat to the centre of the furnace tube. Continue the passage of argon for 2 min and then switch to a stream of hydrogen at a flow-rate of 140 ml min^{-1}. Immediately switch the flow of gas to the absorption cell and continue to pass hydrogen through the cell until the electrode potential has stabilised, showing that no more ammonia is being released from the steel. For most steels this is a period of 120 min. Note the cell potential on the digital voltmeter and read off the concentration of nitrogen in the absorption cell from the calibration graph; then switch back to an argon stream. Determine the blank value for an empty silica boat after passing hydrogen through the apparatus for 120 min.

NOTES—

1. It is important that the inlet arm to the absorption cell should be completely dry while the ammonia is being collected, otherwise some ammonia is absorbed in solution on the sides of the inlet arm before the sinter and low results are obtained.
2. Use steel millings with at least one dimension less than 0·5 mm.
3. For samples containing more than 0·0070 per cent. of mobile nitrogen use 0·5 g of steel.

Calculation of the Concentration of Mobile Nitrogen in the Steel

The passage of hydrogen through the absorption cell for 120 min caused the volume of the solution to diminish from 10·0 to 9·7 ml. The volume change is most easily determined by adding the appropriate buffer solution to the absorption cell from a microburette until the volume is restored to its original value, as shown by a mark on the outside of the cell. During this operation the cell is removed from the bath, tap 4 being open.

For an empty tube:
Initial cell potential $\equiv$ 0·5 μg ml^{-1} of nitrogen = 5 μg of nitrogen for 10 ml of solution
Final cell potential $\equiv x$ μg ml^{-1} of nitrogen = $x \times 9{\cdot}7$ μg of nitrogen for 9·7 ml of solution
Hence, nitrogen as ammonia from the hydrogen (the blank) = $[(x \times 9{\cdot}7) - 5]$ μg

For the steel sample:
Initial cell potential $\equiv$ 5 μg of nitrogen for 10 ml of solution
Final cell potential $\equiv y$ μg ml^{-1} of nitrogen = $y \times 9{\cdot}7$ μg of nitrogen for 9·7 ml of solution
Hence mobile nitrogen from the steel + blank = $[(y \times 9{\cdot}7) - 5]$ μg
Thus mobile nitrogen from the steel = $[(y - x) \times 9{\cdot}7]$ μg

For a 1-g sample the concentration of nitrogen in the steel = $[(y - x) \times 9{\cdot}7] \times 10^{-4}$ per cent.

Method for the Spectrophotometric Determination of Mobile Nitrogen[2–4]

The equipment was identical with that for the ion-selective electrode method except that the ammonia in the stream of hydrogen from the furnace tube was absorbed in 50 ml of 0·001 M hydrochloric acid after passing through a larger No. 0 sinter. A collection time of 70 min was generally employed, with a flow-rate of 220 ml min^{-1}.

Results

Compositions of the Steels

The compositions of the steels analysed by both the spectrophotometric and ion-selective electrode methods are shown in Table I.

TABLE I

COMPOSITIONS OF THE STEELS

Alloy	Concentrations of elements in the alloy, per cent. C	Si	Mn	Ni	Cr	Al	Mo	Ti	Cu	Total N
A	0·31	0·67	0·87	0·04	0·03	0·054	—	—	0·07	0·0108
C	0·30	0·67	0·87	0·04	0·03	0·15	—	—	0·07	0·0092
D	0·29	0·65	0·86	0·04	0·03	0·066	—	—	0·07	0·0122
12N	0·16	0·12	1·17	—	—	—	—	0·024	—	0·0087
13N	0·15	0·17	0·97	—	—	—	—	0·058	—	0·0220
14N	0·15	0·25	1·00	—	—	—	—	0·099	—	0·0228
7	0·33	0·40	1·48	—	—	—	0·33	—	—	0·012
B3275 (A) and (B)	0·28	1·23	0·61	0·04	0·03	—	0·32	—	—	0·012
P74	0·07	1·56	1·11	21·4	15·0	—	0·05	—	—	0·0169

Analysis of the Steels by Using the Ion-selective Electrode Method

Results for the analysis of the steels by this method are shown in Table II and are also compared with the results obtained by the spectrophotometric procedure. The blank corresponded to 0·5 μg or less of nitrogen in 9·7 ml of solution. A typical recording of cell potential *versus* time for a steel is shown in Fig. 4. By using the calibration graph, these cell potentials were converted to concentrations of nitrogen as ammonium ion and a graph of concentration of nitrogen *versus* time is also shown in Fig. 4.

TABLE II

RESULTS FOR THE DETERMINATION OF MOBILE NITROGEN IN STEEL SAMPLES USING THE ION-SELECTIVE ELECTRODE AND A COMPARISON OF THE RESULTS WITH THOSE OBTAINED BY THE SPECTROPHOTOMETRIC PROCEDURE

Steel	Results for the determination of mobile nitrogen using the ion-selective electrode, per cent. × 10^4*	Average result using the ion-selective electrode, per cent. × 10^4	Standard deviation using the ion-selective electrode, per cent. × 10^4	Average result using the spectrophotometric method, per cent. × 10^4	Standard deviation using the spectrophotometric method, per cent. × 10^4
A	5·5, 3·5, 6·5, 5·5, 5·5, 6·5	5·5	1	6	2
C	6·5, 9·5, 6·5, 6, 8·5, 8·5	7·5	1·5	9	2
D	4·5, 7·5, 5, 5·5, 6, 6	6	1	6	3
12N	61, 63·5, 63·5, 65·5, 61·5, 65·5	63·5	2	64	7
13N	106, 109, 106, 109, 109, 109	108	1·5	106†	5†
14N	46·5, 44·5, 43, 49, 41, 45	45	3	45	3
7	32·5, 31·5, 31, 30·5, 31, 32·5	31·5	1	28	3
B3275 (A) ‡	7·5, 5·5, 6, 9·5, 9, 8·5	7·5	1·5	8	2
B3275 (B)	31, 31·5, 35·5, 35·5, 36, 37	34·5	2·5	36	6
P74	4, 4·5, 6, 5·5, 5, 6	5	1	7	3

* Collection time 120 min for all samples.
† Ammonia collected for 120 min.
‡ Heat treated and quenched form of B3275 (B).

For most steels the rate of release of ammonia was greatest after the passage of hydrogen for 15 min in the ion-selective electrode method, but ammonia continued to be released at a diminishing rate up to 2 h after switching from argon to hydrogen. A typical graph of the rate of accumulation of nitrogen as ammonium ion *versus* time is shown in Fig. 5.

Discussion

The results shown in Table II are considered to be very satisfactory, excellent agreement between the two methods being achieved. With the spectrophotometric procedure, steel 13N

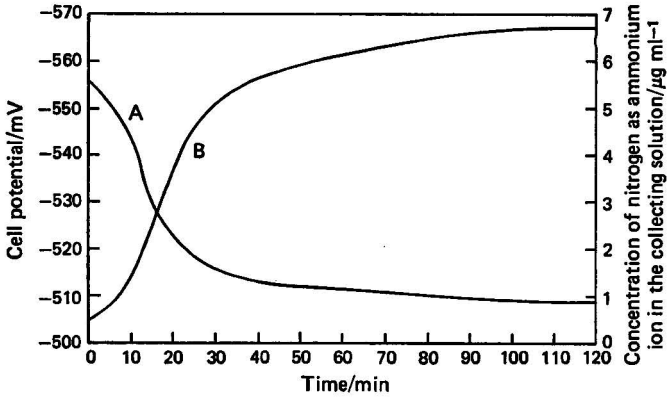

Fig. 4. A, A recording of cell potential *versus* time for steel 12N. B, A graph of nitrogen concentration as ammonium ion in the collecting solution *versus* time for steel 12N.

appeared to contain only 0·0098 per cent. of mobile nitrogen, but this was raised to 0·0106 per cent. when the collection period was increased from 70 to 120 min. This result illustrates the drawbacks of the spectrophotometric procedure with a fixed collection time. Different collection periods arose when using the two procedures because of the different sizes of the No. 0 sinters used in the absorbing solutions. A lower flow-rate inevitably leads to a longer collection period. It is evident from Table II that the precision of the ion-selective electrode method is superior to that of the spectrophotometric method, but its main advantage lies in the fact that the completion of the collection of ammonia for any steel sample is at once obvious to the operator. The use of a potentiometric recorder coupled to a digital voltmeter is not essential but it is a distinct advantage because the amount of ammonia collected is automatically recorded and, while this is occurring, the operator can be engaged in other work.

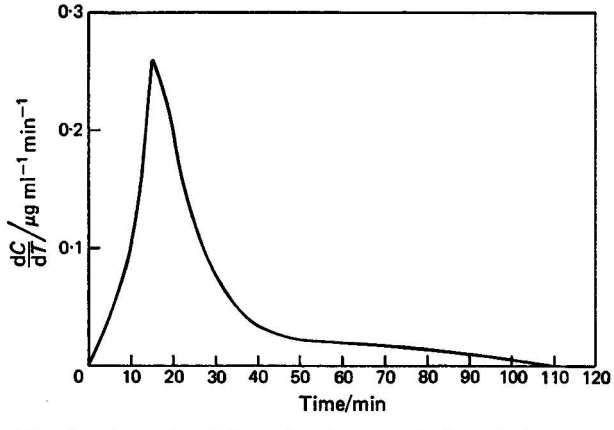

Fig. 5. A graph of the rate of accumulation of nitrogen as ammonium ion in the collecting solution *versus* time for steel 12N. (*C* is the concentration of nitrogen and *T* the time).

The response of the EIL, Model 1057 200, ion-selective electrode to changes in ammonium-ion concentration from more to less concentrated solutions was rather sluggish. The potential of the ion-selective electrode *versus* the reference electrode changed rapidly over a period of a few minutes, and then tended to drift to more negative values very slowly when the electrode was placed in the most dilute standard solution (0·5 μg ml^{-1} of nitrogen) after being in a more concentrated ammonium-ion solution. For the first run on a particular

day the cell potential stabilised quickly at the start of the run because the ion-selective electrode had been standing overnight in the most dilute calibration solution, but for the second and later runs it was inconvenient to wait until the starting potential had stabilised completely before commencing the collection of ammonia. The starting potentials were often 1–2 mV more positive than the corresponding potential on the calibration graph. This was of no consequence as the cell potential that was required for the calculation of mobile nitrogen in a steel was that measured after the passage of hydrogen for 2 h, and a steady potential corresponding to the concentration of ammonium ion in the absorption cell was always achieved under these conditions. It has been suggested that a suitable poly(vinyl chloride) membrane electrode for the ammonium ion would respond more rapidly than the glass membrane electrode to changes in the ammonium-ion concentration, but the EIL 1057 200 glass membrane electrode can be used almost indefinitely and its rate of response is sufficiently rapid for the work described in this study.

All of the steels except P74 were low-alloy steels containing only trace amounts, if any, of vanadium and niobium. Therefore, the results obtained for mobile nitrogen from these nine steels should be reliable. Alloy P74 is a high-alloy steel and might possibly contain some chromium nitride, although silicon forms a more stable nitride than does chromium.[5] However, if the alloy does contain chromium nitride there is little evidence for its breakdown at 500 °C because it can be seen from Table II that its mobile nitrogen content, 0·0005 per cent., is very low, although the total nitrogen content is 0·0169 per cent.

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References

1. Scholes, P. H., and White, G., *Steel Times A. Rev. Steel Ind.*, 1970, 172.
2. Fisher, R., and White, G., Advanced Process Laboratory, British Steel Corporation, Research Report CAPL/SM/G/51/73.
3. Jenkins, R. H., *Open Rep. Br. Iron and Steel Res. Ass.*, MG/CC/520/72.
4. Hill, R., and Swinburn, D. G., Steel Founders' Society of America Project No. 88, Restricted Report No. 4, Steel Founders' Society of America, New York, 1972.
5 Pearson, J., and Ende, U. J. C., *J. Iron Steel Inst.*, 1953, **175**, 53.

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The Determination of Substituted Phenylurea Herbicides and Their Impurities in Technical and Formulated Products by Use of Liquid Chromatography

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The application of liquid chromatography to the identification and determination of the active ingredient and the impurities in phenylurea herbicides commonly employed in agriculture is described. Technical materials are dissolved in dichloromethane and chromatographed on microparticulate silica with dichloromethane or dichloromethane - methanol as eluting agent, or on microparticulate silica bonded with octadecyltrichlorosilane with methanol - water as eluting agent. An initial extraction procedure is required for dispersible powders. Detection was by means of ultraviolet absorbance.

Substituted phenylurea compounds (urons) are widely used in agriculture as selective herbicides for the pre- or post-emergence control of various weeds. Technical materials and dispersible powders are usually analysed by means of acid or alkali hydrolysis with titration of the liberated aliphatic amine[1–3] or a colorimetric determination of the aromatic amine formed.[4] Methods based on hydrolysis, however, lack specificity for individual urons, as impurities which may be present will be included in the results for the assay. Gas - liquid chromatography[5,6] can be used but suffers from the disadvantage that carefully controlled conditions are required in order to prevent thermal decomposition of the phenylurea, either on the column or during injection. A need therefore exists for a rapid and specific procedure for the determination of these compounds and their impurities in technical and formulated products. Methods have been developed that involve liquid chromatography, a technique first applied to analysis for some urons by Kirkland,[7] and these methods do not have the shortcomings of the procedures mentioned above. The urons examined are shown in Table I.

Experimental

Apparatus and Reagents

All reagents were of analytical-reagent grade unless otherwise specified.

The equipment used for liquid chromatography was of modular construction.

Solvent delivery. A Waters Associates, Model 6000, constant-volume solvent delivery system was used.

Sample injection. A Varian Associates stop-flow injector was used throughout this work. For maximum resolution samples were injected with a standard 10-μl syringe on to a stainless-steel fine-mesh gauze fitted on top of the column packing. In order to prevent tailing of peaks, a needle guide was incorporated in the injector so that samples were introduced on to the centre of the column. On-column injection was not employed as it was found that the top part of the column gradually became disturbed, which resulted in a dramatic reduction in efficiency.

Silica column. A slurry of LiChrosorb SI 60 5-μm silica packing (E. Merck, Darmstadt) in 2,2,4-trimethylpentane saturated with tetrachloroethylene was prepared. By using pressures of 5000–6000 lb in^{-2} the slurry was forced with 2,2,4-trimethylpentane into a 150 $\times$ 4·6 mm i.d. stainless-steel column fitted with a low dead-volume connector containing a frit of pore size 2 μm. The packed column required a pressure of 600 lb in^{-2} for a flow-rate of dichloromethane of 1 ml min^{-1}. The column was maintained at 30 °C by means of a water-jacket.

C_{18} bonded silica column. This column packing material was prepared in the laboratory by using the following procedure.

LiChrosorb SI 60 (5 g), dried at 120–140 °C for 2 h, was placed in a 100-ml centrifuge tube together with 50 ml of light petroleum (boiling range 60–80 °C, sodium-dried) and 20 ml of octadecyltrichlorosilane. The mixture was then shaken and placed in an ultrasonic bath for 30 min with shaking at intervals. The mixture was centrifuged, the light petroleum discarded and the packing treated with a further 50 ml of light petroleum and 20 ml of trimethylchlorosilane to react with any remaining non-bonded surface-active sites on the silica. The packing, after removal of excess of reaction mixture by centrifuging, was then washed with three 50-ml portions of light petroleum, one 50-ml portion of propan-2-ol and two 50-ml portions of methanol. All washings were removed after centrifuging.

The bonded material was then packed into a 250 × 4·6 mm i.d. stainless-steel column fitted with a low dead volume connector containing a frit of pore size 2 μm, using a balanced-density slurry in chloroform - bromoform and pressures of 5000–6000 lb in^{-2}. The packed column required a pressure of 2000 lb in^{-2} for a flow-rate of 1 ml min^{-1} for water containing 60 per cent. of methanol. The column was maintained at 30° C by means of a water-jacket.

Solvents. For chromatography on the silica column dichloromethane (containing 0·1 per cent. of methanol as stabiliser) was used as the eluting agent. For the determination of certain urons small amounts of methanol were added to the dichloromethane in order to increase the polarity. Mixtures of methanol (Spectro Grade, Eastman) and water, which were warmed and stirred continuously in order to remove air bubbles, were used with the C_{18} bonded packing material.

Detector. A variable wavelength ultraviolet detector (Cecil CE 212) fitted with a 10-μl cell (1-cm light path) was employed. With methanol - water and dichloromethane as eluting agents, determination of the urons plus their impurities was carried out at 240 and 245 nm, respectively. A wavelength of 254 nm can also be used but measurement at this wavelength is not as sensitive. The detector output was connected to a 10-mV input chart recorder.

Peak measurement. A digital integrator (Autolab 6300) was used to measure peak areas and a transparent bevelled rule to measure peak heights.

It is important that sample solutions that are kept for more than 2 d before examination should be stored in the dark in order to prevent photodecomposition.

Methods

Identity Test for Phenylurea Herbicides

For positive identification, comparison of retention of the sample with that of a reference standard on at least two types of liquid-chromatography packing is recommended. Use of a 5-μm silica column and a C_{18} bonded 5-μm silica column meets this requirement.

Normal phase separation on a silica column

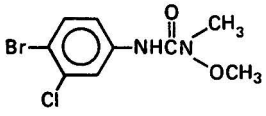
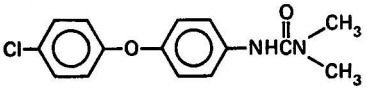
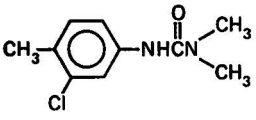
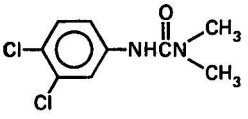
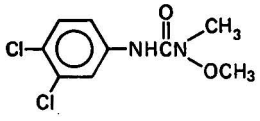
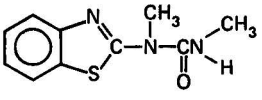
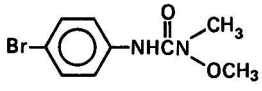
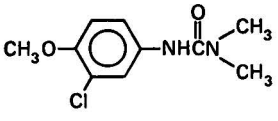
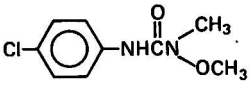
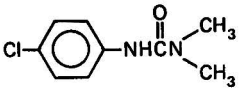
Prepare solutions of the technical uron sample and the reference standard (about 1–5 mg of each) in 10 ml of dichloromethane. For dispersible powders extract into 10 ml of dichloromethane about 1–5 mg of the uron active ingredient from a 5-ml slurry of the sample in water. By reference to Table I select a dichloromethane - methanol mixture of such a composition that elution of the uron from the column will occur in a reasonable time. Using a flow-rate of 0·5–1·0 ml min^{-1} inject 2 μl of both sample and standard solutions, and set the detector sensitivity so that peak heights of 60–80 per cent. full scale are obtained. Check that the sample and standard are eluted with the same retention time. Alternatively, for unknown urons, check the retention time of the sample against those obtained for a mixture of standard urons with dichloromethane as the eluting agent (Fig. 1).

Reverse-phase separation on a C_{18} bonded silica column

Prepare solutions of the technical uron sample and the reference standard (about 1–5 mg each) in 10 ml of methanol. For dispersible powders proceed initially as described for the silica column but evaporate the dichloromethane extract to dryness and dissolve the uron residue in 10 ml of methanol. By reference to Table I select a methanol - water mixture of such a composition that elution of the uron from the column will occur in a reasonable time. Using a flow-rate of 0·5–1·0 ml min^{-1}, inject 2 μl of both sample and standard solutions, and set the detector sensitivity so that peak heights of 60–80 per cent. full scale are obtained. Check that the sample and standard are eluted with the same retention time. Alternatively,

TABLE I

SUITABLE ELUTING AGENTS FOR THE LIQUID-CHROMATOGRAPHIC DETERMINATION OF URONS

Uron	Structure	Column: Silica	Column: C_{18} bonded silica
Chlorbromuron ..		Dichloromethane	65% methanol in water
Chloroxuron		1% methanol in dichloromethane	70% methanol in water
Chlortoluron		1% methanol in dichloromethane	65% methanol in water
Diuron		0·5% methanol in dichloromethane	65% methanol in water
Linuron		Dichloromethane	65% methanol in water
Methabenzthiazuron		0·5% methanol in dichloromethane	65% methanol in water
Metobromuron ..		Dichloromethane	60% methanol in water
Metoxuron		1% methanol in dichloromethane	60% methanol in water
Monolinuron		Dichloromethane	60% methanol in water
Monuron		1% methanol in dichloromethane	60% methanol in water

for unknown urons, check the retention time of the sample against those obtained for a mixture of standard urons with methanol - water as the eluting agent (Fig. 2).

Determination of the Content of Active Ingredient

The following procedure, which involves the use of an internal standard, is suitable for the determination, using a silica column, of monuron, diuron and chlortoluron in technical materials and formulated products. The general principles can be applied to analysis for other urons. Prepare a sufficient amount of the eluting agent (dichloromethane containing 0·6 per cent. of methanol) for the analysis.

Technical materials

Accurately weigh 0·25 g of uron sample and 0·30 g of internal standard (acetanilide for monuron and chlortoluron and 4′-chloroacetanilide for diuron) into a 100-ml calibrated flask. Dissolve the contents of the flask in dichloromethane and dilute to 100 ml. Repeat with a reference standard uron of known content of active ingredient. Using a flow-rate of 1 ml min^{-1} for the eluting agent and a column temperature of 30 °C inject separately several 1-μl portions of the uron sample and standard solutions on to the silica column, adjusting the sensitivity of the detector so that peak heights of approximately 80 per cent. full scale are obtained on the recorder. Calculate the content of active ingredient of the sample by comparison of the peak heights or peak areas of the uron and internal standard, using the following equation:

$$\text{Active ingredient, per cent.} = \frac{A_1 \times I_2 \times W_2 \times 100}{A_2 \times I_1 \times W_1 \times P}$$

where A_1 and A_2 are the mean peak areas (or peak heights) for the uron sample and the standard uron, respectively; I_1 and I_2 are the mean peak areas (or peak heights) for the internal standard in the sample and standard solution, respectively; W_1 is the mass of uron sample taken; W_2 is the mass of standard uron taken; and P is the percentage content of active ingredient of the standard uron.

Dispersible powders

Accurately weigh enough of the dispersible powder to contain 0·25 g of active ingredient into a 500-ml separating funnel. Add 50 ml of distilled water and shake to disperse the powder. Extract with three 100-ml portions of dichloromethane, collecting the dichloromethane layer in a round-bottomed flask. Evaporate to dryness by using a rotary evaporator (see Note). Transfer the residue quantitatively into a 100-ml calibrated flask by rinsing with three 10-ml portions of dichloromethane. Accurately add 0·30 g of internal standard and proceed as for technical materials.

NOTE—
Complete removal of any remaining traces of water is advised in order to prevent changes in the adsorption characteristics of the column.

Determination of Impurities

Accurately weigh 0·25 g of uron into a 100-ml calibrated flask and dilute to volume with dichloromethane. Inject 2 μl of the solution on to the silica column and examine the impurities present by eluting the sample with the eluting agent suggested in Table I. Set the detector sensitivity so that the impurities are of sufficient peak height for accurate measurement. Identify the impurities present by comparison of their retention times with those of known compounds eluted under similar conditions. Unknown impurities can be identified by means of mass spectrometry after collection of the peak fraction eluted from the column following injection of 100 μl of the solution. Determine the impurities by constructing a calibration graph with standard material. Should difficulty be experienced in dissolving certain impurities, *e.g.*, substituted diphenylureas, in dichloromethane, use 1,4-dioxan to effect dissolution, warming if necessary, and dilute with dichloromethane to give a ratio of 1,4-dioxan to dichloromethane of 1:9 prior to injection.

Results and Discussion

Identity Test

Figs. 1 and 2 show the separation of urons on 5-μm silica and C_{18} bonded 5-μm silica. A difference in elution order is given by these two columns. The separation mode of urons

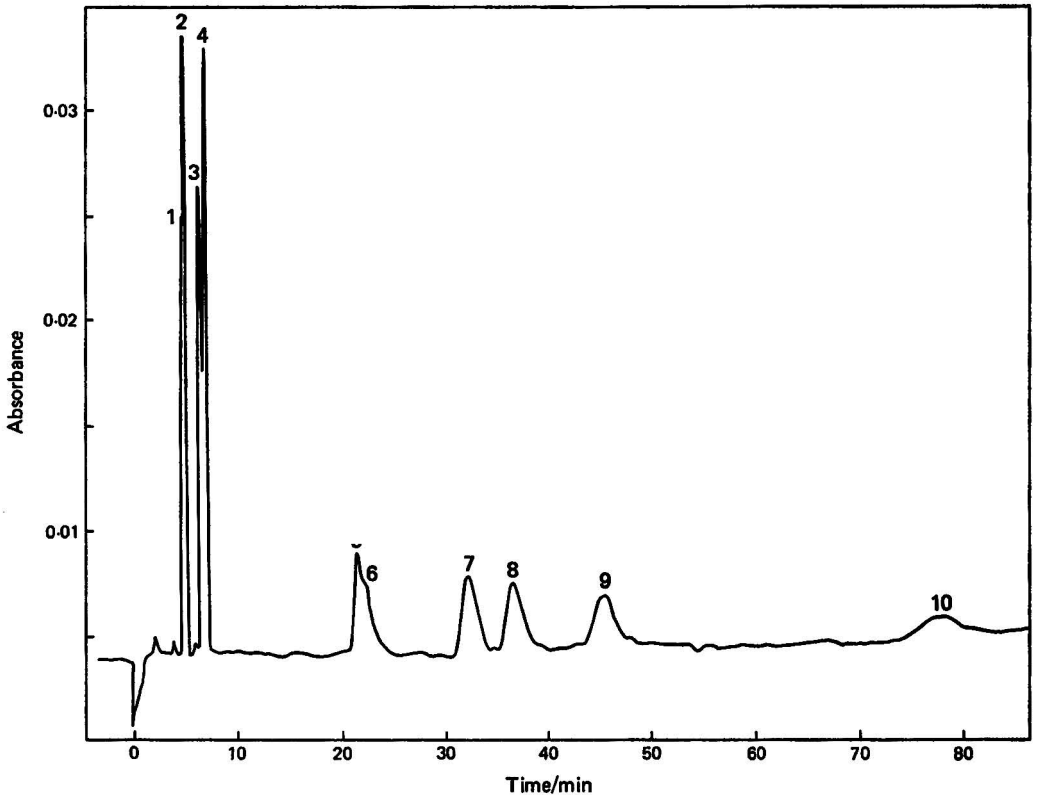


Fig. 1. Separation of uron herbicides on a microparticulate (5 μm) silica column: 1, chlorbromuron; 2, linuron; 3, monolinuron; 4, metobromuron; 5, methabenzthiazuron; 6, diuron; 7, chlortoluron; 8, monuron; 9, chloroxuron; and 10, metoxuron. Mobile phase, dichloromethane at a flow-rate of 1·2 ml min^{-1}.

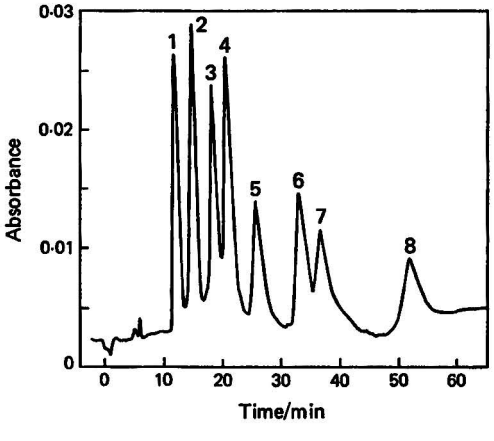


Fig. 2. Separation of uron herbicides on a C_{18} bonded microparticulate (5-μm) silica column: 1, metoxuron; 2, monuron; 3, monolinuron; 4, metobromuron; 5, diuron; 6, linuron; 7, chlorbromuron; and 8, chloroxuron. Mobile phase, methanol - water (3 + 2) at a flow-rate of 0·5 ml min^{-1}.

on the bonded packing is primarily partition whereas on the silica, separation depends on the extent of adsorption of the individual urons on the active sites of the packing. As a result, certain urons, *e.g.*, chlorbromuron and chloroxuron, have similar retention times on the bonded packing but widely differing times on silica. These two columns can therefore be used for confirmation of the identity of urons. In Fig. 1, better resolution of the earlier peaks can be achieved by reducing the flow-rate or by decreasing the polarity of the eluting agent. The retention time of the later peaks will, however, be increased. Alternatively, a gradient elution separation technique could be used.

Urons were also separated on a column packed with 5-μm silica bonded with 3-(trifluoromethyltetrafluoroethoxy)propyltrichlorosilane. Using water containing 40 per cent. of methanol as eluting agent, the elution order of the urons on this polar column was the same as on the less polar C_{18} bonded silica. However, the resolution of the urons was not as good.

Quantitative Analysis

For the determination of the content of active ingredient a procedure involving the use of an internal standard was adopted in order to overcome any dilution or injection errors. The analysis of technical monuron and diuron materials and dispersible powders has been studied in depth. The silica column was used rather than the C_{18} bonded silica column so that any substituted diphenylureas present as impurities could be determined under the same conditions. For monuron and diuron, acetanilide and 4′-chloroacetanilide, respectively, were selected as internal standards, being structurally related to and eluted closely after the uron but not having the same retention time as any impurity (Fig. 3). Masses taken were such that the peak heights of the internal standard and the uron were approximately the same. Relative retention times of certain urons and acetanilides are shown in Table II. For repeat injections of solutions of the uron and internal standard, the coefficients of variation of the

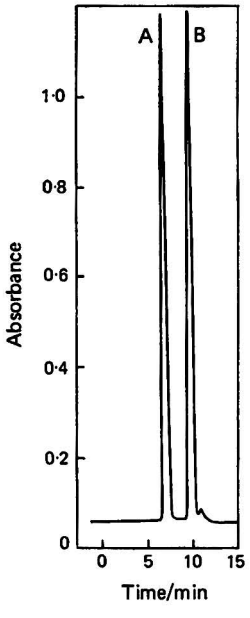


Fig. 3. Separation of uron from internal standard in the quantitative determination of diuron using a 5-μm silica column: A, diuron; B, 4′-chloroacetanilide. Mobile phase, dichloromethane containing 0·6 per cent. of methanol, at a flow-rate of 1 ml min^{-1}.

peak-height and peak-area ratios were 0·38 and 0·39 per cent., respectively, for monuron and acetanilide and 0·40 and 0·54 per cent., respectively, for diuron and 4′-chloroacetanilide. A small gradual increase in retention time was observed over a large number of injections. However, the relative retention times of the uron and the internal standard remained constant and thus the over-all precision of the method was unaffected.

TABLE II

RELATIVE RETENTION OF SOME URONS AND ACETANILIDES ON SILICA

Eluting agent: 0·6% methanol in dichloromethane at a flow-rate of 1 ml min^{-1}.

Uron	Relative retention	Acetanilide	Relative retention
Linuron	1·0	3′,4′-Dichloroacetanilide	2·7
Diuron	2·3	4′-Chloroacetanilide	3·2
Chlortoluron	2·8	Acetanilide	3·6
Monuron	3·1		
Metoxuron	4·1		

Various technical monuron and diuron materials and dispersible powders were analysed, using certified samples of urons (monuron, 99·92 per cent.; diuron, 99·90 per cent.) as reference primary standards. For formulated products containing less than 90 per cent. of active ingredient it was found necessary to take a mass of sample containing an amount of active ingredient comparable with that in the uron standard solution. Otherwise correction factors have to be applied in order to compensate for an observed non-linearity of the uron to internal standard ratio at low concentrations.

The content of active ingredient of the samples was also determined by the CIPAC acid hydrolysis procedure in order to check the accuracy of the analysis by use of liquid chromatography (Table III). Uron samples were partitioned between 4 N hydrochloric acid and chloroform in order to remove any basic impurities or wetting agents, etc., and the residue, after evaporation of the chloroform, was hydrolysed by refluxing with 24 N sulphuric acid. After making the solution alkaline, the liberated dimethylamine was steam distilled, absorbed in excess of acid and back-titrated with standard sodium hydroxide solution. The results obtained by liquid chromatography were slightly lower than those obtained by hydrolysis. In the instance of monuron, sample 1, this difference can be accounted for by the presence of 0·34 per cent. of diuron. There would appear to be little significant difference between contents of active ingredient calculated from peak-height ratios or from integrated peak-area ratios. The determination of other urons by a similar procedure should also be possible provided that suitable internal standards are selected. When the determination of impurities is of secondary importance a C_{18} bonded packing can be substituted for the

TABLE III

COMPARISON OF RESULTS OBTAINED WITH LIQUID CHROMATOGRAPHY AND ACID HYDROLYSIS FOR THE ACTIVE INGREDIENT CONTENT OF MONURON AND DIURON

	Active ingredient, per cent., obtained by—		
		Liquid chromatography and calculated from—	
Sample	acid hydrolysis	integrated peak-area ratio	peak-height ratio
Technical monuron (sample 1)	97·9	97·8	97·4
	98·2	97·7	97·2
		97·8	97·4
Technical monuron (sample 2)	98·0	97·8	97·9
	97·9		
Technical diuron	98·5	98·3	98·2
		98·0	98·2
		98·0	98·3
Diuron dispersible powder	79·0	78·9	78·6
	79·3	79·1	78·6

silica column. Monuron, for example, has been determined on a Corasil C_{18} column using diallyl phthalate as internal standard.

Determination of Impurities

The nature and extent of impurities present in monuron, diuron, linuron, metoxuron and chlortoluron have been investigated. The relative retentions of some possible impurities together with the percentage amounts of those identified in technical samples are given in Table IV. Typical chromatograms are shown in Figs. 4 and 5. Major impurities found were substituted diphenylureas formed from the reaction of excess of isocyanate (used in the manufacture of urons) with water. In general, these compounds have poor solubility in methanol and other polar solvents, which makes their determination on reverse-phase bonded packings difficult or impossible. For this reason the 5-μm silica column only was used for the determination of impurities.

TABLE IV

IMPURITIES IN URONS

Some possible impurities	Relative retention	Impurities in technical samples, per cent. A	B	C
Linuron	1·00*			
3,4-Dichloroaniline	0·41	—	—	—
Methyl 3,4-dichlorophenylcarbamate	0·48	4·8	0·05	3·4
1,3-Bis(3,4-dichlorophenyl)urea	1·31	1·5	2·7	1·5
Monolinuron	1·66	0·1	0·1	0·4
Diuron	1·00*			
3,4-Dichloroaniline	0·06	—	—	
1,3-Bis(3,4-dichlorophenyl)urea	0·21	0·35	0·40	
Monuron	1·00†			
4-Chloroaniline	0·20	—		
1,3-Bis(4-chlorophenyl)urea	0·38	0·78		
Diuron	0·75	0·34		
Chlortoluron	1·00†			
3-Chloro-4-methylaniline	0·20	—		
1,3-Bis(3-chloro-3-methylphenyl)urea	0·29	0·10		
3-(4-Methylphenyl)-1,1-dimethylurea	1·54	0·40		
3-(3-Chloro-4-methylphenyl)-1-methylurea	3·57	—		
Metoxuron	1·00†			
3-Chloro-4-methoxyaniline	0·24	—		
1,3-Bis(3-chloro-4-methoxyphenyl)urea	0·48	0·47		
Diuron	0·57	0·35		
3-(4-Methoxyphenyl)-1,1-dimethylurea	1·66	0·77		
3-(3-Chloro-4-methoxyphenyl)-1-methylurea	3·46	—		

* Silica column (5 μm) with dichloromethane as eluting agent at a flow-rate of 0·5 ml min^{-1}.
† Silica column (5 μm) with 1 per cent. methanol in dichloromethane as eluting agent at a flow-rate of 0·5 ml min^{-1}.

All of the uron samples examined dissolved completely in dichloromethane. In preparing calibration graphs with which to determine impurities, it was noted that the rate of dissolution of certain compounds in dichloromethane was very slow. Impurity standards were therefore dissolved in 1,4-dioxan, by warming if required, and then diluted with dichloromethane to give a 1:9 ratio of 1,4-dioxan to dichloromethane. No differences were observed in the retention times for impurities dissolved in this way and for impurities partly dissolved in dichloromethane. No difference in the level of impurity was found whether the uron was dissolved in dichloromethane or in 1,4-dioxan - dichloromethane (1 + 9). The calibration graphs for the impurities were linear.

The presence of methyl 3,4-dichlorophenylcarbamate in samples of linuron was verified by collecting the peak fraction following elution from the detector and analysing it by means of mass spectrometry (Fig. 6). A parent ion, *m/e* 218·9854, corresponding to $C_8H_7NO_2Cl_2$ confirmed the identity of the impurity. The 1,3-bis(3,4-dichlorophenyl)urea present in diuron pyrolysed during mass spectrometry to give parent ions corresponding to 3,4-dichloroaniline and 3,4-dichlorophenyl isocyanate, and was thus confirmed. Checks were made for

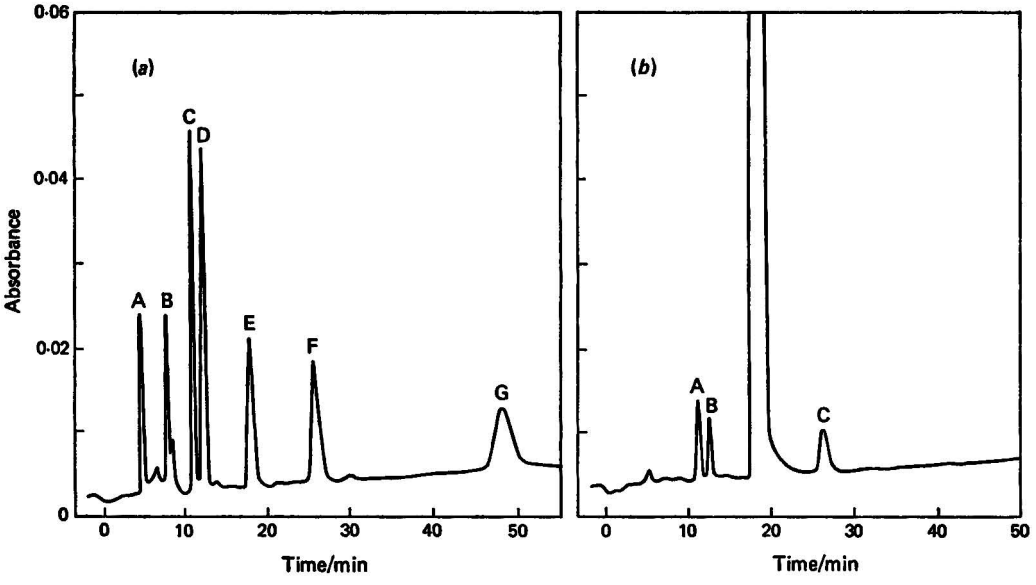


Fig. 4. Impurities in technical metoxuron. (*a*), Some possible impurities: A, unreacted 3-chloro-4-methoxyphenyl isocyanate; B, 3-chloro-4-methoxyaniline; C, 1,3-bis(3-chloro-4-methoxyphenyl)urea; D, diuron; E, metoxuron; F, 3-(4-methoxyphenyl)-1,1-dimethylurea; G, 3-(3-chloro-4-methoxyphenyl)-1-methylurea. (*b*), Technical sample: A, 1,3-bis(3-chloro-4-methoxyphenyl)urea, 0·47 per cent.; B, diuron, 0·35 per cent.; C, 3-(4-methoxyphenyl)-1,1-dimethylurea, 0·77 per cent. Column, 5-μm silica. Mobile phase, dichloromethane containing 1 per cent. of methanol, at a flow-rate of 0·5 ml min^{-1}.

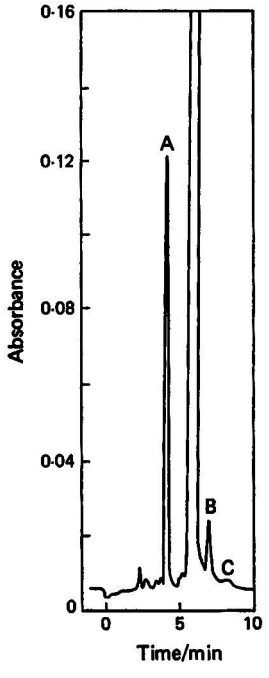


Fig. 5. Technical sample of linuron: A, methyl 3,4-dichlorophenylcarbamate, 4·8 per cent.; B, 1,3-bis(3,4-dichlorophenyl)urea, 1·5 per cent.; C, monolinuron, 0·1 per cent. Column, 5-μm silica. Mobile phase, dichloromethane at a flow-rate of 0·5 ml min^{-1}.

the presence of any free isocyanate in the urons by comparing chromatograms of urons dissolved in methanol-free dichloromethane (*i.e.*, methanol stabiliser removed) with chromatograms of urons dissolved in dichloromethane - propan-2-ol (20 + 1). No changes in the chromatograms owing to reaction between isocyanates and propan-2-ol were observed and hence the absence of free isocyanate was inferred.

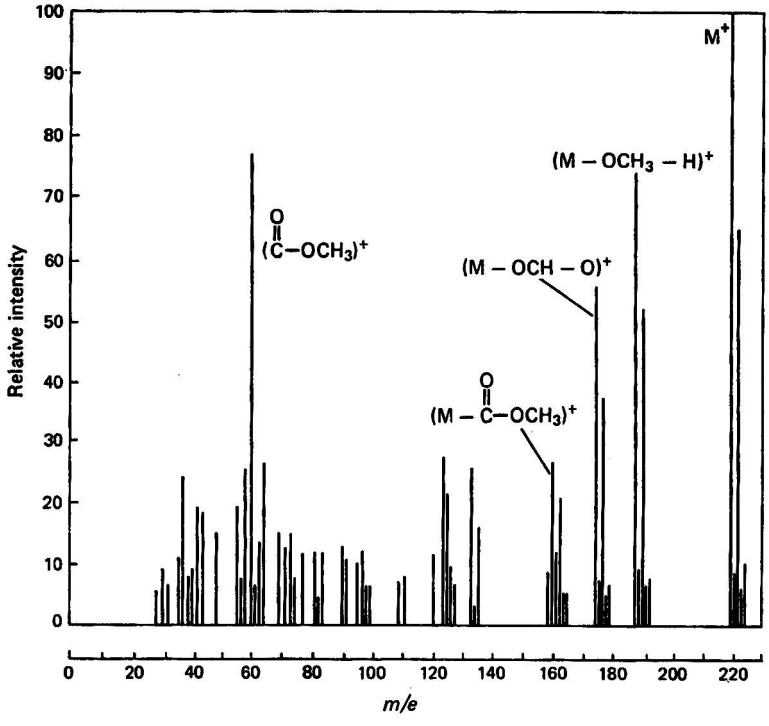
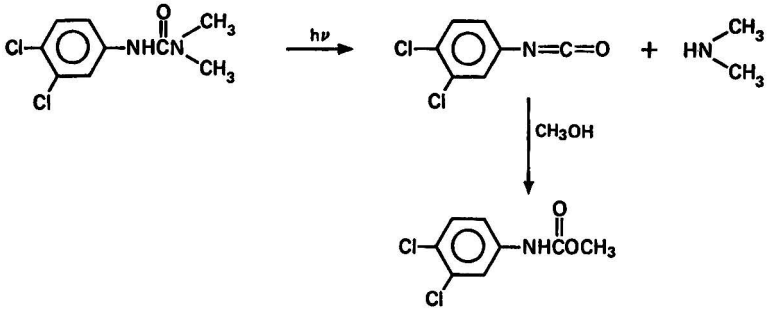


Fig. 6. Mass spectrum of methyl 3,4-dichlorophenylcarbamate (an impurity in linuron).

During work on the determination of impurities it was noted that peaks were appearing in the chromatograms of uron solutions that had been standing in sunlight, indicating that photochemical breakdown had occurred. For example, with diuron, the methyl 3,4-dichlorophenylcarbamate slowly appeared in the chromatogram. This is explained by:



the methanol being present as stabiliser in the solvent. It is therefore important that impurities should be determined in freshly prepared solutions. The large amounts of methyl 3,4-dichlorophenylcarbamate found in linuron did not arise from photochemical breakdown

of linuron on standing in solution. Its formation may arise either during manufacture, from side reactions between 3,4-dichlorophenyl isocyanate and *NO*-dimethylhydroxylamine involving the methoxy radical, or by photochemical breakdown of the solid.

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References

1. Yuen, S. H., and Milosevic, B., *Analyst*, 1969, **94**, 820.
2. Yuen, S. H., and Palmer, J. M. C., *Analyst*, 1972, **97**, 921.
3. Lowen, W. K., Bleidner, W. E., Kirkland, J. J., and Pease, H. L., *in* Zweig, G., *Editor*, "Analytical Methods for Pesticides, Plant Growth Regulators and Food Additives, Volume IV, Herbicides," Academic Press, New York, 1964, p. 157.
4. Yuen, S. H., *Analyst*, 1970, **95**, 408.
5. Katz, S. E., and Strusz, R. F., *J. Agric. Fd Chem.*, 1969, **17**, 1409.
6. Buser, H., and Grolimund, K., *J. Ass. Off. Analyt. Chem.*, 1974, **57**, 1294.
7. Kirkland, J. J., *J. Chromat. Sci.*, 1969, **7**, 7.

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An Improved Column-chromatographic Quantitative Isolation of Diosgenin and Yamogenin from Plant Crude Extracts Prior to Their Determination by Infrared Spectrophotometry

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A previously described routine procedure involving the use of a silica gel column in determining diosgenin and yamogenin has been improved by using water-containing solvents. The advantages are that there is less variation between duplicate results, that each column can be used at least five times and that component bands are eluted in predictable volumes of solvents. An apparatus and solvent sequence is described that allows twelve columns to be developed simultaneously.

The method has been successfully applied to crude extracts from *Dioscorea deltoidea* tuber and to oily crude extracts from the seeds of *Trigonella foenum-graecum* (fenugreek) and *Balanites aegyptiaca*. The over-all error of the procedure, including sampling, extraction and infrared spectrophotometric determination for duplicate analyses of 2·5-g samples of the fenugreek seed used, expressed as a 95 per cent. confidence interval of the mean sapogenin value, was 1·04 ± 0·025 per cent. for diosgenin plus yamogenin, 0·64 ± 0·019 per cent. for diosgenin and 0·40 ± 0·023 per cent. for yamogenin.

As the method does not permit the separation of tigogenin from diosgenin nor that of neotigogenin from yamogenin, the results indicate maximum yields for diosgenin and yamogenin in fenugreek seed. The results exclude sterols, steryl esters, dihydroxysapogenins and spirostadienes.

Plants that contain diosgenin, (25*R*)-spirost-5-en-3β-ol, also contain yamogenin, the (25*S*) epimer. The proportions of the epimers present vary with the plant species and also often within different morphological parts of the same plant.[1] The epimers can be determined individually in the presence of each other, in any proportion, by infrared spectrophotometry,[2] but in order to obtain accurate results the diosgenin - yamogenin mixture must be pure. The required degree of purity was achieved by column chromatography[3] of the plant crude extract. With other methods for the determination of diosgenin in plant extracts using gas - liquid chromatography[4,5] and thin-layer chromatography[6] it is not possible to distinguish between diosgenin, yamogenin and their 5α- or 5β-saturated compounds (tigogenin, neotigogenin, smilagenin and sarsasapogenin). Our improved method enables diosgenin plus tigogenin and yamogenin plus neotigogenin to be determined.

The study of *Trigonella foenum-graecum* Linn. (fenugreek) seed as a commercial source of diosgenin and yamogenin required that both epimers be accurately determined; the yamogenin usually accounts for 40 per cent. of the total diosgenin - yamogenin content. A breeding programme for seed with high sapogenin, protein and fixed oil contents required a method that is suitable for a large number of determinations. In the previous method[3] the columns were used only once. The improved method, however, enables them to be used at least five times. Yamogenin is more soluble than diosgenin in, for example, oil-containing liquors, and the method is invaluable for determining the amounts of steroid in mother-liquors and other fractions from the pilot treatment of plant material. The improved procedure can also be used for the simultaneous isolation of the free sterols and dihydroxysapogenins that occur in fenugreek seed.

Experimental

Apparatus and Materials

These were as previously reported.[3]

Chromatographic columns. Whatman precision chromatographic columns (20 × 1 cm).

Design of the Column Apparatus

Twelve columns were mounted close together on a vertical board. Solvent-proof connections between PTFE tubing and glass tubing were made by making PTFE connectors of precise dimensions, such that the outside diameter of the connector was slightly larger than the internal diameter of the glass tubing and that the internal diameter of the central bore of the connector was slightly less than the outside diameter of the PTFE tubing. Above each column, a 3-way tap was fitted which led to a specimen tube and to a solvent reservoir of 2-l capacity. The specimen tube was used to siphon the plant crude extract into the column. The outlet of the solvent reservoir was a PTFE stopper carrying twelve PTFE tubes, one to each column. Below each column was a PTFE-tube S-bend with a tap fitted in the middle of the S-bend, which prevented air in the tap from reaching the adsorbent in the column.

Column Procedure

Two sets of the solvent mixtures hexane - ethyl acetate (9 + 1), (3 + 1) and (2 + 3), one set dry and the other set saturated with water, were prepared; 4 volumes of each dry mixture were mixed with 1 volume of the corresponding wet mixture to give three wet-solvent mixtures, which mixtures were used in the following steps of the procedure. Silica gel for adsorption, activity II, 6 g per Whatman column (20 × 1 cm), was packed in hexane - ethyl acetate (9 + 1). Crude sapogenin extracts were prepared and added to the columns as before.[3]

At a flow-rate of 1 ml min^{-1} the sequence of hexane - ethyl acetate mixtures used for the elutions and the fractions collected was: 9 + 1 mixture, 40 ml containing fixed oil, steryl esters and spirostadienes, then 45 ml containing free sterols, followed by three 5-ml fractions for a thin-layer chromatographic check; 3 + 1 mixture, 40 ml containing diosgenin and yamogenin (plus tigogenin and neotigogenin when present), again followed by three 5-ml fractions for a thin-layer chromatographic check; and 2 + 3 mixture, 20 ml containing trace compounds, then 30 ml containing dihydroxysapogenins (such as gitogenin). Finally, ethyl acetate was used and a 25-ml fraction collected that contained column residues. For the regeneration of the column, 10, 10 and 25 ml of the 2 + 3, 3 + 1 and 9 + 1 mixtures, respectively, were used; the column can then be re-used.

Results and Discussion

From the aspect of column life in a routine procedure, the effect of the moisture content of the solvent on the adsorbent activity was studied by collecting 5-ml fractions for thin-layer chromatographic analysis. When solvent mixtures containing 10 per cent. V/V of water-saturated solvents were repeatedly used, the band widths of components became wider and retention volumes increased. This effect was even more pronounced when dry solvents were repeatedly used. A mixture containing 20 per cent. V/V of water-saturated solvents gave exactly reproducible separations, with no change in band widths or retention volumes for free sterols, for diosgenin - yamogenin and only slight variation for the gitogenin isolated, probably owing to minor variations in the flow-rate. The presence of water in the solvents did not influence the amount of the diosgenin - yamogenin fraction collected. Recovery was found to be 97 to 104 per cent., as previously reported.[3]

The reproducibility of the procedure was tested by isolating the diosgenin plus yamogenin (and their accompanying trace amounts of tigogenin and neotigogenin, see below) from a given fenugreek crude extract using twelve columns. Then, by re-using four of these columns, the isolation from the same crude extract was repeated four times on each column. Analysis of variance on the infrared spectrophotometric results showed that the results from the twelve columns used once, and those from the four columns used five times, were from the same population, giving an experimental F value of 1·6 compared with a tabulated F value of 2·82 at $P = 0·05$.

The over-all error of the procedure, including sampling, extraction and infrared spectrophotometric analysis, was tested by analysing twelve 2·5-g samples of the fenugreek seed, and the confidence intervals (t at $P = 0·05$) were calculated for duplicate results. This gave a value for diosgenin plus yamogenin of 1·04 ± 0·025 per cent., diosgenin 0·64 ± 0·019 per cent. and yamogenin 0·40 ± 0·023 per cent. This procedure represents a marked improvement over the original procedure,[3] as shown by a comparison of their respective over-all percentage ranges of error (results obtained by the original procedure are given in

parentheses): diosgenin plus yamogenin, ±2·4 per cent. (±4·4 per cent.), diosgenin ±3·0 per cent. (±3·5 per cent.) and yamogenin ±5·9 per cent. (±10·6 per cent.).

The method has been found to be satisfactory for column loadings of up to 75 mg of diosgenin plus yamogenin in the presence of up to 600 mg of fixed oil, which is approximately three times the amount of oil present in a 2·5-g sample of commercial Moroccan fenugreek seed.

It has recently become possible to separate the four sapogenins diosgenin, tigogenin, yamogenin and neotigogenin by use of argentation thin-layer chromatography.[7] The sapogenin extracts purified by column chromatography were examined by this method and the results assessed visually against a range of standard solutions. (Densitometric scanning of the plates with a Joyce-Loebl Chromoscan was unsuccessful because of the colour of the spots.) In fenugreek seed, about 10 per cent. of the diosgenin plus yamogenin content was found to be due to tigogenin and neotigogenin, each contributing about 5 per cent. to the spectrophotometric result.

The suitability of the method for the analysis of other plant extracts that had different contents of sterol, diosgenin and fixed oil was tested on crude extracts of *Dioscorea deltoidea* root, which afforded a non-oily sapogenin extract, and fruits of *Balanites aegyptiaca*, a material with seed containing up to 50 per cent. of fixed oil.[8] The sequence of solvents used and the fractions collected for fenugreek seed were found to be satisfactory for these different plant samples. The roots of *D. deltoidea*, and the fruit wall and seed of *B. aegyptiaca* did not contain any tigogenin or neotigogenin.

The error introduced into the infrared spectrophotometric assay by omitting the column procedure and analysing the crude extract directly was studied. In each instance the result obtained with the crude extract is given before that obtained with the extract purified by column chromatography. For *Balanites aegyptiaca* seed, previously defatted so as to remove 44 per cent. of the seed mass, a result of 2 per cent. was obtained for diosgenin plus yamogenin with the proportions 74:26 instead of 1 per cent. with the proportions 92:8. *Trigonella foenum-graecum* seed containing 8 per cent. of fixed oil gave 1·5 per cent. of diosgenin plus yamogenin with the proportions of 50:50 compared with 1·0 per cent. and 58:42 using the column procedure. *Dioscorea deltoidea* root, containing less than 1 per cent. of fixed oil, gave 5·3 per cent. of diosgenin plus yamogenin with the proportions 99:1 compared with 4·8 per cent. and proportions of 99:1. The fruit wall of *B. aegyptiaca*, which does not contain any fixed oil, gave 1·2 per cent. of diosgenin plus yamogenin, the proportions being 48:52, compared with 1·1 per cent. and the same proportions.

The results obtained show that in the presence of the fixed oil component, not only is the isolated diosgenin - yamogenin value greatly exaggerated, but that the proportions calculated as diosgenin or yamogenin are incorrect. These effects are due to greater interference taking place at 920 cm^{-1}, which increases the apparent yamogenin value, as previously reported.[2]

The improved method could also be applied to the determination of individual amounts of other pairs of (25*R*)- and (25*S*)-spirostan-3β-ols, which may be present in any proportion, for example, smilagenin and sarsasapogenin, and gitogenin [(25*R*)-5α-spirostan-2α,3β-diol] and neogitogenin. The method does not enable the individual amounts of monohydroxy (25*R*)-spirostan-3β-ols (*e.g.*, diosgenin, tigogenin and smilagenin) to be determined in a mixture of them in the presence of their (25*S*)-epimers, but the authors are unaware of the existence of any method that is capable of permitting such a determination.

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References

1. Hardman, R., and Sofowora, E. A., *Phytochemistry*, 1970, **9**, 645.
2. Jefferies, T. M., and Hardman, R., *Planta Med.*, 1972, **22**, 78.
3. Hardman, R., and Jefferies, T. M., *Analyst*, 1972, **97**, 437.
4. Cooke, B. K., *Analyst*, 1970, **95**, 95.
5. Bohannon, M. B., Hagemann, J. W., and Earle, F. R., *Phytochemistry*, 1974, **13**, 1513.
6. Brain, K. R., and Hardman, R., *J. Chromat.*, 1968, **38**, 355.
7. Dawidar, A. M., Saleh, A. A., and Elmotei, S. L., *Planta Med.*, 1974, **24**, 367.
8. Hardman, R., and Sofowora, E. A., *Econ. Bot.*, 1972, **26**, 169.

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Rapid Sample Dissolution and Determination of Total Iron in Iron Ore, Sinter, Concentrates and Agglomerates

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A method is described for rapid and complete dissolution of iron ores with a wide range of composition in order to determine total iron. The sample is fused with a mixed flux of sodium carbonate and sodium peroxide in a vitreous carbon crucible and the melt is dissolved in hydrochloric acid. Iron is then determined by redox titration with dichromate. The wide range of composition of the samples for which the method can be used, as exemplified by results obtained for ISO, BCS and NBS reference standards, demonstrates its universal applicability. The method is rapid, free from tedious and time-consuming manipulations, suitable for routine control and yields results comparable with those obtained by the referee method.

Redox titration is a standard method for the determination of iron in iron ore, sinter, concentrates or agglomerates. The complexometric determination of iron as iron(III), using EDTA, salicylic acid as a metallochromic indicator and acetate buffer at pH 2, has also been used. Prior reduction to the iron(II) state is not necessary with the complexometric method but the end-point with EDTA is not as sharp as it is with the diphenylamine indicator in the redox titration with dichromate. Therefore, the use of EDTA is not so attractive for referee analysis.

It is imperative to ensure complete sample dissolution prior to determining the iron. The ASTM[1] and the ISO methods use two alternative dissolution techniques, each of which is tedious and time consuming. The development of a rapid, effective method is described below.

Experimental

Blast-furnace slag can be completely dissolved[2] after sintering the sample with sodium peroxide at 380 °C for 20 min in a platinum crucible in a muffle furnace. However, this sintering technique was not successful for rendering soluble sinter or iron ore, even after increasing the sintering time to 1 h. Grinding the sample down to 250 mesh and increasing the ratio of peroxide to sample still left some residue undissolved.

Kilsby[3] employed a mixed flux of sodium carbonate - boric acid (5 + 1) for fusing the iron ore or sinter in a platinum crucible at 900 °C for 20 min in a muffle furnace. This approach was tried but proved unsuccessful as some sample remained undissolved. Increasing the fusion temperature from 900 to 1100 °C and the fusion time from 20 to 30 min was of no avail. Additionally, the amount of flux was increased and a blast Meker burner was used, but still there was no improvement in dissolution.

In the past we had attempted to use the vitreous carbon crucible for sintering at 380 °C with sodium peroxide and for direct fusion with a Meker burner. Sintering was not adequate for decomposing the sinter and fusion eroded the crucible considerably. Sodium carbonate is incorporated in some fluxes (using an iron or nickel crucible) in order to prevent violent explosive reaction when decomposing some steelmaking reagents such as Calsibar and ferro-alloys, and it was thought worthwhile to mix sodium carbonate with sodium peroxide for use in the fusion of sinter samples in a vitreous carbon crucible. This modification helped to render the sample completely soluble in about 2 min. After acidifying the melt a clear solution free from carbon specks and with no contaminants was obtained.

Apparatus

Vitreous carbon crucible. A 20-ml capacity, Grade V-25, crucible obtainable from Le Carbonne Larraine, Paris.

Reagents

All reagents are of analytical-reagent grade. Distilled and de-ionised water is used throughout.

Sodium carbonate, anhydrous.

Sodium peroxide, powdered.

Standard potassium dichromate solution, 0·1 N.

Tin(II) chloride solution. Dissolve 37·5 g of tin(II) chloride dihydrate in 75 ml of hydrochloric acid and dilute to 250 ml with water.

Mercury(II) chloride, saturated solution.

Barium diphenylaminesulphonate indicator solution, 0·3 per cent. m/V. Dissolve 0·3 g of reagent in 100 ml of water. Store in an amber-coloured glass-stoppered dropping bottle. This solution should be freshly prepared every 2 weeks.

Mixed acid solution. To about 600 ml of water cautiously add, with stirring, 150 ml of sulphuric acid and 150 ml of orthophosphoric acid. Cool the solution and dilute to 1 l with water.

Procedure

Transfer 0·50 g of sodium carbonate into a dry vitreous carbon crucible. Add 0·3000 g of accurately weighed sample to the crucible, followed by 2 g of sodium peroxide. Mix the contents of the crucible with a dry stainless-steel spatula and fuse over a Meker burner (low heat), swirling the crucible until the melt is cherry red and clear. Remove the crucible from the heat and swirl it until the melt solidifies on the crucible wall. Allow the crucible to cool in air for 1–2 min and place it in a dry 250-ml beaker. Introduce about 10 ml of water into the crucible, while covering the beaker with a watch-glass. After effervescence has ceased, empty the crucible contents into the beaker and wash the crucible with 10–15 ml of water. Introduce 30 ml of hydrochloric acid - water (1 + 1) via the crucible into the beaker and rinse the crucible with water. Boil the solution in the beaker for 3–5 min. Wash the sides of the beaker with hydrochloric acid - water (1 + 1) and continue boiling for about 30 s.

Reduce the iron(III) by means of dropwise addition of tin(II) chloride (until the solution is colourless) and then add 1 drop in excess. Allow to cool. Add rapidly 10 ml of the saturated solution of mercury(II) chloride and allow to stand for 3 min. Transfer the solution to a 400-ml beaker. Add 30 ml of mixed acid solution and 5–6 drops of barium diphenylaminesulphonate indicator solution. Dilute to about 175 ml with water. Titrate immediately with standard potassium dichromate solution to a permanent purple end-point. The end-point is discernible within 0·02 ml.

$$\text{Iron, per cent.} = \frac{5{\cdot}585 \times T \times N}{M}$$

where T ml is the titre, N is the normality of the potassium dichromate solution and M g is the sample mass.

Results and Discussion

The redox titration of iron(II) solution with dichromate solution, including factors such as hydrogen ion concentration, the role of orthophosphoric acid in forming a colourless heteropoly complex with iron(III) and the suitability of indicators with respect to the redox potential of the system $Cr_2O_7^{2-}$ - Cr^{3+} and Fe^{3+} - Fe^{2+} has been well documented.[4]

As indicated earlier, the fusion of the iron ore or sinter sample in a vitreous carbon crucible with a mixed flux of sodium carbonate and sodium peroxide results in the sample being rendered completely soluble. The order of addition of the sodium carbonate, sample and sodium peroxide, and the mixing (see under Procedure) are essential for sample dissolution and crucible life. In our earlier studies we have established that 2 g of sodium peroxide is the optimum amount. The optimum amount of sodium carbonate, with 2 g of sodium peroxide, is 0·5 g under the conditions of the procedure and for maximum crucible life. It is pertinent to say that any sample speck (unmixed with flux) may result in hot spots and damage to the crucible. The crucible should be swirled while gently heating over a Meker burner until a semi-viscous melt appears (after 30–50 s). The heating is then continued until the melt is cherry red and clear. After complete extraction of the melt and rinsing of the crucible, the

crucible should be wiped dry on the outside (including the base) and then dried completely on a clean hot-plate for 2–3 min. The crucible, after cooling, is ready for the next fusion. We have been able to carry out 16–18 fusions with a single crucible.

TABLE I

COMPARISON OF RESULTS

Ore sample	Iron content, per cent. ISO or certified value	Found	Mean
Sweden-2	64·84	64·83, 64·86	$64·84_5$
Sweden-7	61·65	61·61, 61·56	$61·58_5$
Sinter, British BCS 303	35·93	35·86, 35·81	$35·83_5$
Canadian	65·22	65·15, 65·14	65·15
Minette	31·82	31·74, 31·76	31·75
Philippine iron sand	60·57	60·63, 60·53	60·58
Krivoy rog	47·32	47·37, 47·26	$47·31_5$
Marcona	62·66	62·59, 62·54	$62·56_5$
Nimba BCS 175/2	66·1	66·09, 65·97	66·03
Sibley NBS 27e	66·58	66·61, 66·58	$66·59_5$

Table I demonstrates that results obtained using the dissolution procedure described are in acceptably close agreement with values obtained by referee methods.[1] The first eight materials listed (seven ores and one sinter) were the subject of international round-robin testing by ISO using the standard ISO method, resulting in the assigned values shown. The last two materials are standard reference ores. The range of compositions to which the dissolution method is applicable is demonstrated by the composition of the materials shown in Table II.

TABLE II

PERCENTAGE COMPOSITION OF IRON ORE SAMPLES

Ore sample	Fe	SiO_2	CaO	MgO	Al_2O_3	TiO_2	P	S	Mn	As	V	F
Sweden-2	64·8	8	0·7	0·5	0·5	0·05	0·01	0·01	0·05	0·005	0·002	0·01
Sweden-7	61·6	4	6	1	0·7	0·2	1·5	0·05	0·1		0·2	0·2
Sinter, British BCS 303	35·9	17	20	2	7	0·3	0·5	0·2	1			
Canadian	65·2	5	0·5	0·4	0·4	0·05	0·01	0·01	0·2	0·05	0·001	
Minette	31·8	9	16	2	4	0·2	0·7	0·1	0·2	0·02		
Philippine iron sand	60·6	2	0·7	2	3	6	0·1	0·01	0·6	0·003	0·3	0·01
Krivoy rog	47·3	28	0·9	0·2	1·1	0·04	0·05	0·03	0·03	0·002	0·003	
Marcona	62·7	5·4	1·4	1·9	0·8	0·06	0·04	1·2	0·03			
Nimba BCS 175/2	66·1	2·58	0·08	0·03	1·08	$0·09_5$	0·047	0·007	0·11			
Sibley NBS 27e	66·6	3·65					0·042					

The method is rapid, free from tedious and time-consuming manipulations and is therefore suitable for use in routine control. Two samples can be analysed within 30 min of receipt.

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References

1. "1974 Annual Book of ASTM Standards," Part 12, American Society for Testing and Materials, Philadelphia, 1974.
2. Bhargava, O. P., Donovan, J. F., and Hines, W. G., Paper presented at the 25th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March 1974.
3. Kilsby, P. E., "Proceedings of the Technicon International Congress, 1970," Technicon Controls Inc., Chauncey, New York, 1970.
4. Kolthoff, I. M., and Belcher, R., *Editors*, "Volumetric Analysis Volume III," Interscience Publishers, New York and London, 1957.

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Spectrophotometric Determination of Free Chlorine in Air

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A spectrophotometric method that is suitable for the micro-determination of free chlorine in ambient air is described. When free chlorine is absorbed in an alkaline solution of 4-nitroaniline, an orange - brown colour develops, with a molar absorptivity (ϵ) of 19 000 at 485 nm. The method is suitable for the determination of chlorine in the range from a few parts per hundred million to about 20 p.p.m.

Ozone, ammonia and sulphur reducing gases interfere with the reaction, but these interferences can be reduced. Features of the method include high sensitivity, stability of the reagents and coloured reaction product, high collection efficiency, relative specificity to chlorine, reproducibility, simplicity and convenience.

The most widely used colorimetric methods for determining free chlorine in air are those involving the use of *o*-tolidine (acidic),[1] potassium iodide,[2] methyl orange[3] and dimethylnaphthidine[4]; these methods as well as other procedures for determining residual chlorine in water analysis have been reviewed and criticised by Marks,[5] Nicolson,[6] Zabicky and Ehrlich-Rogozinski[7] and Pilipenko and Gakal.[8]

In practice, some difficulties are encountered when these colorimetric methods are used. They include: fading of colour (*o*-tolidine); relatively inconvenient procedures (methyl orange, *o*-tolidine and dimethylnaphthidine); and the results obtained are influenced by the rate of sampling and lack of reproducibility (methyl orange). Moreover, interference from oxidising agents such as nitrogen dioxide, hydrogen peroxide, ozone, chlorates and iron(III) compounds, as well as reducing agents, such as sulphur dioxide, hydrogen sulphide and thiols, occurs in all of the above methods.

A chromic acid scrubber[9] can be used to remove most of these interferences. Such a scrubber was originally intended for absorbing sulphur dioxide but it was found that it also eliminated other sulphur reducing gases, as well as ammonia and hydrogen peroxide. However, as chromic acid is itself an oxidant, its use is limited in the colorimetric analytical procedures cited above because it gives rise to the formation of nitrogen dioxide from nitric oxide. In a newly developed method described in this paper, nitrogen dioxide does not interfere, hence the chromic acid scrubber can be used to greater advantage.

The proposed simple, rapid and relatively specific spectrophotometric method is based on the reaction between free chlorine and 4-nitroaniline in alkaline solution. A stable coloured product is obtained, without experiencing most of the difficulties encountered in the other methods.

The method has high sensitivity and gives good reproducibility in comparison with other colorimetric methods; the analytical procedure is insensitive to some interfering oxidising gases and less sensitive to others.

Experimental

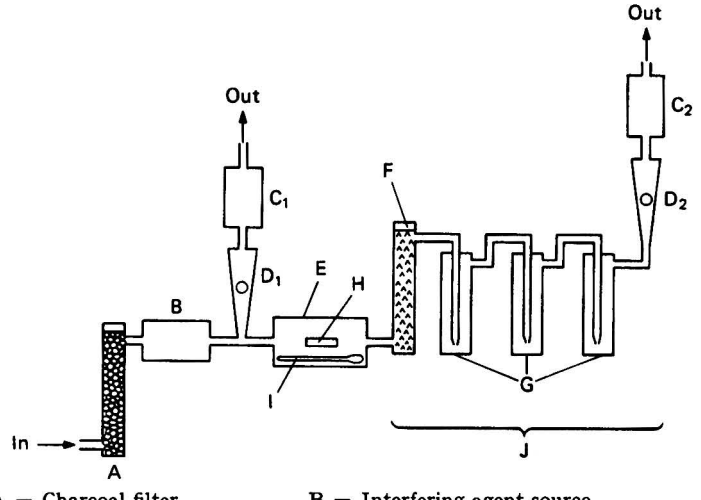
Apparatus

A Coleman Junior II, Model 6/20, spectrophotometer, with circular cells of 1·7-cm optical path length, was used for light absorption measurements.

A sampling train for sampling the atmosphere, consisting of three midget impingers (Gelman Instrumentation Co.), the third impinger serving as a trap, a flow meter and a suction pump, was used. In order to eliminate the interference of the sulphur reducing gases, ammonia and hydrogen peroxide, a scrubber consisting of chromic acid impregnated paper[9] was incorporated upstream from the first impinger. This scrubber was prepared as follows: 40 ml of an aqueous solution containing 6·5 g of chromium(VI) oxide and 1·8 ml of concentrated sulphuric

acid were added, dropwise, uniformly over a 1000-cm² area of flash-fired glass-fibre paper, and the paper was dried in an oven at 80–90 °C for 1 h followed by storage in a tightly capped container. The paper was cut into 6 × 12-mm strips, each folded once into a V shape, packed into a 200-ml tube and conditioned by drawing air that had been dried over silica gel through the tube overnight. The absorber is active for at least 1 month. When it becomes visibly wet from sampling humid air, it must be dried in dry air before further use. Electrical heating of the sampled air within the scrubber to 50 °C is particularly recommended.

A gas dilution system (Fig. 1) in a thermostatically controlled environment was used to measure the collection efficiency and interference effects. For the former purpose a chlorine permeation tube and a thermometer were placed in a glass housing tube, one end of which was connected to a charcoal filter and the other inserted into the sampling train described above, and for the latter purpose a source of interference (populated with appropriate permeation tubes), a flow meter and a suction pump were installed between the charcoal filter and the housing tube. A calibrated ozone generator was used as a source for the study of interference from ozone.



A = Charcoal filter
C_1, C_2 = Suction pumps
E = Housing tube
G = Midget impingers
I = Thermometer
B = Interfering agent source
D_1, D_2 = Flow meters
F = Chromic acid scrubber (optional)
H = Chlorine permeation tube
J = Atmospheric sampling system

Fig. 1. Dilution system for dynamic gas measurements.

Reagents

Analytical-reagent grade chemicals were used. De-ionised water was redistilled over potassium permanganate. No significant changes were observed when de-ionised water was used instead of double-distilled water.

Absorbing reagent. A stock solution of 4-nitroaniline was prepared by dissolving 0·4 g of the reagent (Merck) in 1 l of water. The solution was then diluted with an equal volume of an 8 g l^{-1} solution of potassium hydroxide ($KOH.\frac{1}{2}H_2O$). This stock solution was kept in a dark bottle and remained stable for several weeks.

On the day of sampling, 2 g of barbitone sodium were added to 1 l of the stock solution.

Procedure

Air was bubbled through the absorbing solution in the first two impingers (20 ml of absorbing reagent in each impinger) at a rate of 0·5–2 l min^{-1}. The sampling volume was adjusted so as to give a chlorine concentration of 0·2–50 μg ml^{-1} in the absorbing solution. After an interval of 3 min, the absorbance of the sample was measured spectrophotometrically at 485 nm, using unexposed absorbing reagent as a blank, and the readings obtained were

compared with a calibration graph. Samples that produced readings which corresponded to the non-linear portion of the graph were diluted with absorbing reagent (see Results and Discussion and Table I).

The collection efficiency was measured by bubbling air samples containing 0·02–2·0 p.p.m. *V/V* of chlorine into the sampling system; and the effect of interfering gases was studied by introducing various concentrations of such gases into the stream of chlorinated air, with and without the use of the chromic acid scrubber. The temperature of the whole system was controlled to within ±0·5 °C of the required temperature in each series of experiments.

Calibration Graph

Freshly prepared chlorine was bubbled through an ice-cold 3 N potassium hydroxide solution contained in a dark bottle and the chlorine concentration in the resulting solution was determined by iodimetric titration. Dilute solutions containing 25 and 100 μg ml^{-1} of chlorine were prepared from this solution, small volumes of which containing 1–27 μg of chlorine were added to 9 ml of the absorbing reagent and then made up to 10 ml with the reagent.

Calculation

The chlorine content in the air was calculated from the following equation:

$$\text{Chlorine, p.p.m.} = \frac{\text{Chlorine found } (\mu g)}{\text{Number of litres of air sampled}} \times \frac{24{\cdot}45}{71} \text{ (25 °C, 760 torr)}$$

For different temperatures and atmospheric pressures, appropriate corrections for the volume of the air should be made.

Results and Discussion

Spectral Characteristics

The absorption spectrum of the coloured solution at pH 12·8 is shown in Fig. 2, maximum absorption of the coloured product occurring at 485 nm. As shown in the calibration graph (Fig. 3), Beer's law is obeyed in the chlorine concentration range 0·1–1·3 μg ml^{-1}.

The coloured product developed in solutions containing initially up to 50 μg ml^{-1} of chlorine can be diluted with the absorbing reagent so as to fall within the linear range; in this event the absorbance of the samples still follows strictly the calibration graph (Table I).

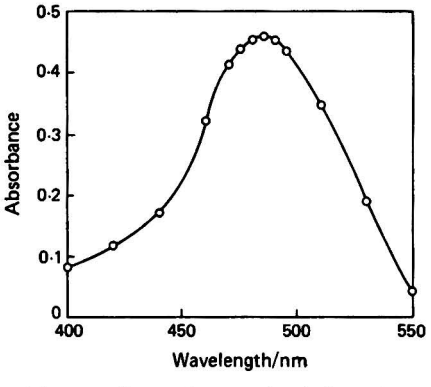


Fig. 2. Absorption graph of the coloured product at pH 12·8 (concentration of chlorine, 1 μg ml^{-1}).

Effect of pH

The dependence of the absorbance on pH is illustrated in Fig. 4 and it can be seen that the relationship is approximately constant in the pH range 11·2–13·6. Once the reaction is complete, the solution can be acidified and brought back to the original pH without change in the initial absorbance.

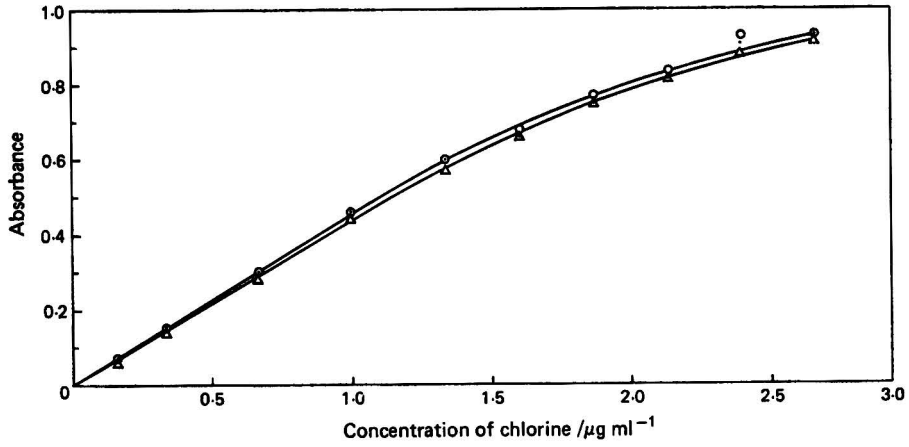


Fig. 3. Calibration graph for chlorine. Open circles, 3 min after the addition of chlorine; points, 3 h after the addition of chlorine; and open triangles, 24 h after the addition of chlorine.

If the air containing chlorine is acidic, an excess of potassium hydroxide can be added initially to the absorbing reagent.

Three minutes are required for full colour development of the reaction product at pH 12·8. As shown in Fig. 4, its colour in alkaline solution is stable; after 24 h, the absorbance in the above pH range is diminished by only 5–6 per cent. At pH 14, the colour is even more stable, but the method is then slightly less sensitive. It is recommended, however, that the reaction be conducted at this pH when the spectrophotometric measurement cannot be carried out on the same day. The time required for full colour development at pH 14 is 15 min.

The coloured product obtained in this method is also formed at still higher levels of alkalinity (concentrations of alkali greater than 1 M), without the presence of barbitone sodium in the absorbing reagent, but the time required for full colour development under these conditions is much greater.

TABLE I

ABSORBANCE OF SAMPLES WITH DIFFERENT INITIAL CONCENTRATIONS OF CHLORINE AFTER DILUTION OF THE DEVELOPED COLOURED SOLUTION WITH ABSORBING REAGENT TO GIVE AN EQUIVALENT INITIAL CONCENTRATION OF 1 μg ml^{-1}

Initial chlorine concentration/ μg ml^{-1}	Absorbance after dilution
1	0·45
2	0·44
5	0·45
10	0·46
20	0·48
30	0·48
40	0·47
50	0·46
100	0·35

Effect of Temperature

The colour is not affected by heating the solution to 50 °C (a high temperature for subtropical conditions) prior to the addition of chlorine, nor by continued heating at this temperature for 3 h after the colour development.

Sensitivity

The sensitivity of the method is of the same order of magnitude as that of other colorimetric methods (Fig. 5), the calculated molar absorptivity at 485 nm being 19 000. Extraction of the coloured product with amyl or butyl alcohol increases the sensitivity.

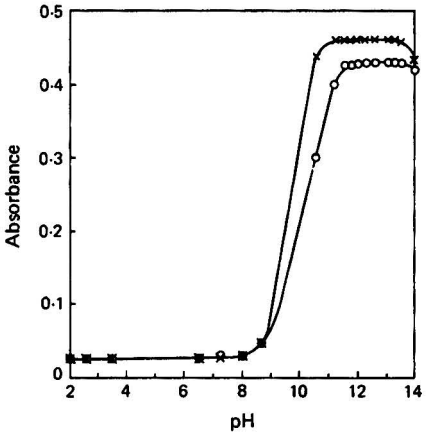


Fig. 4. Dependence of absorbance on pH (concentration of chlorine, 1 μg ml^{-1}). ×, 3 min after the addition of chlorine; and ○, 24 h after the addition of chlorine.

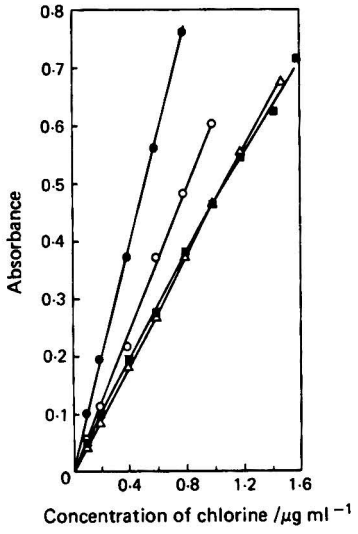


Fig. 5. Sensitivity comparison of various methods for the determination of free chlorine. ●, *o*-Tolidine method; ○, methyl orange method; △, 4-nitroaniline method; and ■, potassium iodide method.

Interferents

The effects of various potential interferents were investigated; in order to adapt the method for the determination of residual chlorine in water pollution analysis, some interfering compounds usually found in water were included. These compounds were added electrolytically prior to the addition of chlorine to the sample. The results of these experiments are presented in Table II.

Compounds Nos. 7–10, all of which are oxidising agents, do not interfere with the reaction even at high concentrations. Iodides do interfere, and it is therefore advisable to oxidise samples that contain iodides with potassium iodate prior to the addition of the absorbing reagent. Low iodine concentrations, however, do not interfere in the determination of chlorine by this method. The presence of oxidising agents such as ozone, high persulphate concentrations or permanganate causes a decrease in absorbance rather than the increase found when using the other methods. Sulphur reducing compounds, hydrogen peroxide and ammonium chloride (Nos. 14–19) interfere with the reaction. However, the interference from these compounds in the gaseous state can be eliminated by oxidising them by passing the air through the chromic acid scrubber prior to making contact with the absorbing reagent (Table III).

The chromic acid scrubber can therefore completely eliminate the effect of some of the interfering gaseous compounds.

Moreover, nitrogen dioxide, formed by oxidation of nitric oxide when the scrubber is used, does not interfere with the reaction of chlorine with 4-nitroaniline, a limitation on the use of the scrubber found with other methods.

With regard to interference by hydrochloric acid, when air containing 215 p.p.m. of hydrogen chloride was passed through the scrubber to the sampling system, less than 0·4 per cent. of it was oxidised to free chlorine. When large volumes of hydrogen gas were bubbled through the absorbing reagent before or after the addition of chlorine, no interference was found.

While high concentrations of ozone interfere in the determination of chlorine with 4-nitroaniline, the addition of 20 g l^{-1} of sodium nitrite to the absorbing reagent reduces the effect of the interference. In Fig. 6 the ratio of the absorbance of chlorine in the presence

TABLE II

INFLUENCE OF POTENTIAL INTERFERENTS IN THE DETERMINATION OF CHLORINE AT pH 12·8

Chlorine concentration used was 1 μg ml^{-1}.

Test No.	Interferent	Concentration of interferent/ μg ml^{-1}	Absorbance of the coloured reaction product
1	—	—	0·45
2	Sodium chloride	10 000	0·45
3	Potassium bromide	10 000	0·44
4	Potassium carbonate	200	0·45
5	Sodium nitrate	1000	0·44
6	Sodium nitrite	20 000	0·44
7	Potassium chlorate	10 000	0·47
8	Potassium iodate	10 000	0·45
9	Iron(III) chloride	50	0·46
10	Iodine (ethanolic)	100	0·47
11	Potassium persulphate	100	0·44
		300	0·37
12	Potassium permanganate	10	0
13	Potassium iodide	100	0
14	Sodium sulphide ($Na_2S.9H_2O$)	10	0
15	Methanethiol	10	0
		1	0·13
16	Sodium sulphite	10	0
17	Potassium chlorate or iodate + sodium sulphite	10 000	
		10	0·15
18	Hydrogen peroxide	30	0
		3	0·08
19	Ammonium chloride	150	0·08
		10	0·32
		5	0·41

of ozone to that of chlorine alone is plotted against the ratio (V/V) of ozone to chlorine in the air stream in the presence and absence of sodium nitrite.

At high chlorine concentrations the method with 4-nitroaniline can also distinguish between free chlorine and bromine; Fig. 7 shows that the initial absorbance of the coloured product of bromine plus the absorbing reagent is high; however, the colour fades and after 90 min becomes relatively negligible. The absorbance of 100 μg ml^{-1} of free bromine after

TABLE III

INTERFERENCE OF SOME GASEOUS COMPOUNDS IN THE DETERMINATION OF CHLORINE (0·15–0·30 p.p.m.) IN AIR

Interfering gas	Ratio (V/V) of interfering gas to chlorine	Ratio of absorbance of interfering gas + chlorine to chlorine	
		Without scrubber	With scrubber
—	—	1·00	1·02
Sulphur dioxide	1·6	0	1·00
Nitrogen dioxide	1·6	1·00	
Methanethiol	0·35	0·04	1·01
Hydrogen peroxide	0·38	0·50	1·00
Ammonia	7·0	0·70	1·00

90 min is equivalent to that of 0·37 μg ml^{-1} of chlorine; the absorbance of 4 μg ml^{-1} is equivalent to 0·13 μg ml^{-1} of free chlorine. Thus the interference of free bromine depends not only on the ratio of its concentration to that of chlorine but also on the absolute concentration of free chlorine. At small concentrations of chlorine better results can be obtained by using a calibration table in which the decay of the absorbance of free bromine within 90 min is related to the absorbance at the end of this interval.

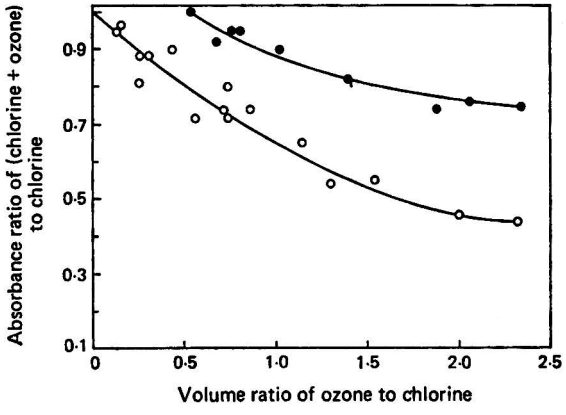


Fig. 6. Interference of ozone with and without sodium nitrite. ○, In the absence of nitrite; and ●, in the presence of nitrite.

Collection Efficiency

The collection efficiency of the absorbing reagent was found to be not less than 99 per cent. in the first impinger. This high collection efficiency is probably due to the rapid formation of hypochlorite. Variation of the sampling rate up to 2 l min^{-1} and of the temperature up to 50 °C did not affect the results.

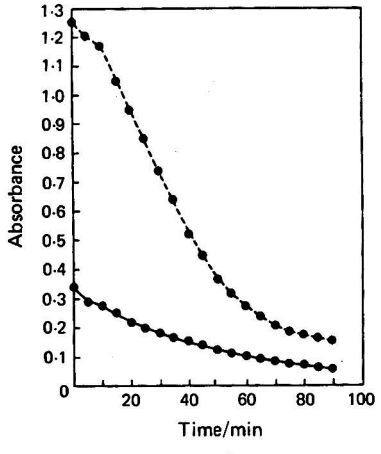


Fig. 7. Stability of the coloured product of bromine plus the absorbing reagent. Broken line, bromine concentration 100 μg ml^{-1}; and solid line, bromine concentration 4 μg ml^{-1}.

The reproducibility at various concentrations was found to be ± 1 per cent.

Further, the absorbing reagent, in the absence of bound chlorine (chloramines), is also suitable for the determination of residual chlorine in water pollution control. The sensitivity of the absorbing reagent to chloramines is currently under investigation.

We are indebted to Mr. Y. Almog for helpful discussions.

References

1. Katz, M., *in* Stern, A. C., *Editor*, "Air Pollution," Volume II, Second Edition, Academic Press, New York and London, 1968, p. 99.
2. "Methods of Air Sampling and Analysis," Intersociety Committee, American Public Health Association, Washington, D.C., 1972, p. 351.
3. "Methods of Air Sampling and Analysis," Intersociety Committee, American Public Health Association, Washington, D.C., 1972, p. 282.
4. Leithe, W., "The Analysis of Air Pollutants," Ann Arbor Science Publishers, Ann Arbor, 1970, p. 213.
5. Marks, H. C., *in* Ciaccio, L. L., *Editor*, "Water and Water Pollution Handbook," Volume III, Marcel Dekker, New York, 1971, p. 1213.
6. Nicolson, N. J., *Analyst*, 1965, **90**, 187.
7. Zabicky, Y., and Ehrlich-Rogozinsky, S., *in* Patai, S., *Editor*, "The Chemistry of the Carbon - Halogen Bond," John Wiley & Sons, London, 1973, p. 63.
8. Pilipenko, A. T., and Gakal, R. K., *Ukr. Khim. Zh.*, 1974, **40**, 528.
9. Saltzman, B. E., and Wartburg, A. F., *Analyt. Chem.*, 1965, **37**, 779.

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A Colorimetric Method for the Determination of Isoprenaline Sulphate in Pharmaceutical Preparations

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A rapid and convenient colorimetric method is described for the determination of isoprenaline sulphate in pharmaceutical preparations. This method is based on measuring the intensity of the orange colour developed when isoprenaline sulphate is allowed to react with thiosemicarbazide in an alkaline medium. Beer's law is obeyed in the concentration range 2·0–16·0 μg ml^{-1}. Data on precision and accuracy are presented. As the catecholic function with unsubstituted adjacent positions is required for the development of the colour, the method is highly specific.

Isoprenaline sulphate [1-(3,4-dihydroxyphenyl)-2-isopropylaminoethanol sulphate] is a sympathomimetic amine used in the treatment of bronchial asthma. Several methods for the determination of isoprenaline sulphate in pharmaceutical preparations are available. The official methods[1–4] have not proved to be completely satisfactory because they lack sensitivity to micro-amounts, and are non-specific and time consuming.

The BP[1] and USP[2] assays of isoprenaline sulphate powder are based on the determination of nitrogen and on a non-aqueous titration with 0·1 N perchloric acid solution, respectively. For tablets and aerosol inhalations, the BP[1] and BPC[4] methods depend upon the colour reaction given by the phenolic group of the molecule. The USP assay of isoprenaline sulphate inhalations requires previous separation of the isoprenaline from interfering substances followed by spectrophotometry. A spectrophotofluorimetric method has recently been described[5] for parenteral formulations containing isoprenaline hydrochloride. Hence the development of a simple, time-saving and specific method for the determination of isoprenaline sulphate in various pharmaceutical preparations is highly desirable.

Experimental

Materials and Reagents

Isoprenaline Sulphate BP. Obtained from Burroughs Wellcome & Co.

Isoprenaline Tablets BP. Obtained from Burroughs Wellcome & Co.

Isoprenaline sulphate tablets with ephedrine hydrochloride (25 *mg*) *and theophylline* (130 *mg*). Obtained from Silbe Ltd.

Isoprenaline sulphate aerosol inhalation. Obtained from Riker Laboratories.

Strong isoprenaline sulphate aerosol inhalation. Obtained from Riker Laboratories.

Isoprenaline Sulphate Inhalation USP.

Isoprenaline Spray BPC.—This spray contained Isoprenaline Sulphate BP (1·0 g), sodium metabisulphite (0·1 g) and propylene glycol (5 ml) in 100 ml of water.

Compound Isoprenaline Spray BPC. This spray contained Isoprenaline Sulphate BP (1·0 g), sodium metabisulphite (0·1 g), propylene glycol (5 ml), papaverine sulphate (2·5 g) and atropine methonitrate (0·2 g) in 100 ml of water.

Thiosemicarbazide reagent. Dissolve 100 mg of thiosemicarbazide in 75 ml of water by gently heating the mixture, cool the solution to room temperature and dilute it to 100 ml.

All the chemicals used were of analytical-reagent grade.

Procedure

Calibration Graph

Pipette several accurately measured aliquots in the range 0·5–4 ml of isoprenaline sulphate solution (100 μg ml^{-1}) into 25-ml calibrated flasks. Dilute each to 10 ml with water and then add, in the following order, 1·0 ml of thiosemicarbazide reagent and 0·5 ml of 1·0 N sodium hydroxide solution. Mix well and leave the solutions to stand for 45 min. Dilute

them to volume with water and measure the absorbances at 490 nm in a 1-cm cell against a blank prepared under the same conditions but using 1·0 ml of water instead of the thiosemicarbazide reagent.

Sample Preparation and Assay

Isoprenaline tablets

Weigh and powder 20 tablets. Dissolve an accurately weighed amount of the powder equivalent to 100 mg of isoprenaline sulphate in sufficient water to give 100 ml of solution. Filter, reject the first 20 ml of the filtrate, then dilute 10 ml of the filtrate to 100 ml with water.

Proceed as described for the calibration graph using 2 ml of the diluted filtrate. Calculate the amount of isoprenaline sulphate from the calibration graph.

Isoprenaline sulphate aerosol inhalation

The amount of isoprenaline sulphate available to a patient is determined by subtracting the amount retained in the oral adaptor from the amount delivered by the metering valve of the pressurised container as follows.

(*i*) *Amount of isoprenaline sulphate delivered by the metering valve.* Agitate the unit gently and inject ten sprays into a mixture of 25 ml of carbon tetrachloride and 25 ml of 0·01 N sulphuric acid contained in a beaker, swirling the mixture between sprays. After removing it from its position above the beaker, wash the unit with two 5-ml portions of 0·01 N sulphuric acid and shake the combined mixture and washings in a separating funnel.

Transfer the acidic layer into a 50-ml calibrated flask and wash the carbon tetrachloride layer twice with 5-ml portions of 0·01 N sulphuric acid. Combine the acid extracts and make the volume up to 50 ml with 0·01 N sulphuric acid. To 10·0 ml of this solution add 1·0 ml of thiosemicarbazide reagent and 0·6 ml of 1·0 N sodium hydroxide solution, leave the mixture to stand for 45 min, dilute it to 25 ml with water and proceed as described for the calibration graph. Calculate from the calibration graph the amount of isoprenaline sulphate in one spray delivered by the metering valve.

(*ii*) *Amount of isoprenaline sulphate retained in the oral adaptor.* Clean the oral adaptor and the valve of the unit with two 5-ml portions of methanol, and discard the washings. Shake the unit gently and inject 20 sprays into the air, remove the oral adaptor and immerse it in a mixture of 25 ml of carbon tetrachloride and 25 ml of 0·01 N sulphuric acid. Remove the oral adaptor from the mixture and wash it twice with 5-ml portions of 0·01 N sulphuric acid. Shake the combined mixture and washings in a separating funnel, then transfer the acidic layer into a 50-ml calibrated flask. Wash the carbon tetrachloride layer twice with 5-ml portions of 0·01 N sulphuric acid. Combine the acid extracts and washings and make the volume up to 50 ml with 0·01 N sulphuric acid. Treat 10·0 ml of this solution as described above (*i*) and calculate from the calibration graph the amount of isoprenaline sulphate in one spray retained in the oral adaptor.

Strong isoprenaline aerosol inhalation

The above procedure for the isoprenaline sulphate aerosol inhalation was followed except that the combined acid extracts and washings were diluted to 100 ml and 5·0 ml taken in each instance for the determination of isoprenaline sulphate delivered by the metering valve and of that retained in the oral adaptor.

Isoprenaline sulphate inhalations and sprays

Measure an aliquot of the isoprenaline sulphate preparation containing 10·0 mg of isoprenaline sulphate into a 100-ml calibrated flask and dilute to volume with water. Proceed as described above for the calibration graph but using 2·0 ml of the solution. Calculate the amount of isoprenaline sulphate from the calibration graph.

Interferences

The effect of citric acid, sodium metabisulphite, ephedrine hydrochloride and theophylline on the determination of isoprenaline sulphate was determined by preparing tablets containing these substances plus a known amount of isoprenaline sulphate and performing the analysis according to the assay procedure for isoprenaline tablets.

The effect of propylene glycol, sodium metabisulphite, papaverine sulphate and atropine methonitrate, which are commonly used in aerosol inhalations and sprays, on the determination of isoprenaline sulphate was also studied by preparing sprays containing specific amounts of these substances plus a known amount of isoprenaline sulphate and performing the analysis according to the assay procedure for the sprays.

Specificity to the Catecholic Function

The above procedure was also applied to solutions of other phenols and phenolic ethers that had different numbers of hydroxy groups, including phenol, catechol, resorcinol, guaiacol, pyrogallol and phloroglucinol.

Accuracy

Recovery trials were performed by adding known amounts of isoprenaline sulphate solution to different pharmaceutical preparations that contained isoprenaline sulphate. Analyses were made before and after the additions.

Results and Discussion

A characteristic orange colour with an absorption maximum at 490 nm develops when isoprenaline sulphate reacts with thiosemicarbazide in an alkaline aqueous medium. A standard graph was plotted for various concentrations of isoprenaline sulphate. The colour was found to obey Beer's law over the concentration range 2·0–16·0 μg ml^{-1}, reaching its maximum intensity after 45 min at room temperatures (20–30 °C) and remaining stable for an additional 2 h. The production of the orange colour can be explained on the basis of the reactions reported for 6-hydroxydopamine,[6] adrenaline[7] and isoprenaline hydrochloride.[5] The isoprenaline chromogenic derivative produced on oxidation of isoprenaline sulphate reacts with thiosemicarbazide to form a stable thiosemicarbazone.

Factors that Affect Colour Formation

The effect of temperature, alkali concentration and the presence of other chemicals on the colour development was studied. A colour development time of 45 min at 20 °C was found to be necessary in order to give a linear relationship between absorbance and concentration, whereas this time decreased to 30 and 25 min at 25 and 30 °C, respectively, the colour obtained in each instance being stable for an additional 2 h. Hence a development time of 45 min was selected so as to allow complete colour development and obtain a linear relationship between absorbance and concentration at room temperatures between 20 and 30 °C. Fig. 1 shows that the addition of 0·5 ml of 1·0 N sodium hydroxide solution gives the optimum alkali concentration for production of maximum intensity and stability of the colour.

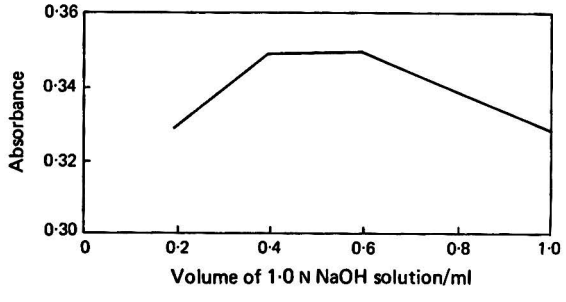

Fig. 1. Effect of alkali concentration on absorbance.

The presence of citric acid and sodium metabisulphite in the concentrations used in tablets produced no effect on the development, intensity or stability of the colour. Ephedrine hydrochloride and theophylline, which are sometimes included in isoprenaline tablets, have no effect on the colorimetric assay. Papaverine sulphate (2·5 per cent.) and atropine methonitrate (0·2 per cent.) when present in isoprenaline sulphate sprays produced no effect on colour development, stability or intensity.

It was found that mono- and trihydroxybenzene derivatives do not produce a colour under the experimental conditions described above. Moreover, dihydroxybenzenes with the hydroxy substituents in the *meta*- or *para*-positions fail to give the reaction. Methylation of one or both hydroxy groups in the catechol molecule also prevents colour development.

Samples of aqueous preparations containing isoprenaline sulphate were analysed before and after the addition of known amounts of isoprenaline sulphate solution. The results obtained are given in Table I.

TABLE I

RECOVERY OF ISOPRENALINE SULPHATE

Preparation	Isoprenaline sulphate added/μg	Absorbance		Recovery, per cent.	Error, per cent.
		Before addition	After addition		
Solution	100	0·340	0·510	100·0	0·0
Tablet	50	0·340	0·425	100·0	0·0
Spray	50	0·345	0·430	100·0	0·0
Compound spray ..	100	0·335	0·500	97·0	3·0

Comparative analyses by the proposed method and the BP, USP and BPC methods were also carried out on pharmaceutical preparations containing isoprenaline sulphate. The results obtained are shown in Table II.

TABLE II

COMPARATIVE ANALYSES OF PREPARATIONS CONTAINING ISOPRENALINE SULPHATE

	Labelled amount or concentration	Amount or concentration of isoprenaline sulphate found*			
		BP method	USP method	BPC method	Thiosemicarbazide method
Isoprenaline tablets	20 mg	19·0 mg	—	—	20 mg
Isoprenaline sulphate + ephedrine hydrochloride + theophylline tablets	15 mg	—	—	—	15·1 mg
Isoprenaline sulphate aerosol inhalation	80 μg†	—	—	90 μg	81 μg
Isoprenaline sulphate aerosol inhalation, strong	400 μg†	—	—	470 μg	405 μg
Isoprenaline sulphate inhalation ..	10 mg ml^{-1}	—	9·5 mg ml^{-1}	—	9·9 mg ml^{-1}
Isoprenaline sulphate + sodium metabisulphite + propylene glycol, spray	10 mg ml^{-1}	—	—	—	9·9 mg ml^{-1}
Isoprenaline sulphate + papaverine sulphate + atropine methonitrate + sodium metabisulphite + propylene glycol, compound spray ..	10 mg ml^{-1}	—	—	—	10·0 mg ml^{-1}

* Average of three determinations.
† Amount of isoprenaline sulphate delivered to patient in each metered dose.

References

1. "British Pharmacopoeia 1973," H.M. Stationery Office, London, 1973, p. 257.
2. "The United States Pharmacopoeia," XVIIIth Revision, Mack Publishing Co., Easton, Pa., 1970, p. 355.
3. "The International Pharmacopoeia," Third Edition, World Health Organization, Geneva, Switzerland, 1967, p. 297.
4. "British Pharmaceutical Codex 1973," The Pharmaceutical Press, London, 1973, p. 645.
5. Prasad, V. K., Ricci, R. A., Nunning, B. C., and Granatek, A. P., *J. Pharm. Sci.*, 1973, **62**, 1135.
6. Powell, W. S., and Heacock, R. A., *J. Pharm. Pharmac.*, 1973, **25**, 193.
7. Prasad, V. K., Ricci, R. A., Nunning, B. C., and Granatek, A. P., *J. Pharm. Sci.*, 1973, **62**, 1130.

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Communications

Material for publication as a Communication must be on an urgent matter and be of obvious scientific importance. Rapidity of publication precludes the use of diagrams, but tables and formulae can be included. Communications should not be simple claims for priority: this facility for rapid publication is intended for brief descriptions of work that has progressed to a stage at which it is likely to be valuable to workers faced with similar problems. A fuller paper may be offered subsequently, if justified by later work.

Manuscripts are not subjected to the usual examination by referees and inclusion of a Communication is at the Editor's discretion.

A Rapid Method for Detecting Erythrosine in Canned Red Fruits

Erythrosine and other permitted red dyes are added to many canned red fruits in order to mask the disappearance of the naturally occurring red pigments (anthocyanins) during storage. Present techniques for the detection and assay of artificial dyes in preserved foods involve lengthy procedures for purification and analysis.[1–3] Typically, these procedures involve extraction of the dye from the foodstuff and preliminary purification of the extract, *e.g.*, by column chromatography, followed by elution and concentration; separation and identification of the dye by paper or thin-layer chromatography; and confirmation of identity by spectrophotometry. Techniques that obviate the necessity for at least some of these steps would be of benefit for the identification of artificial dyes in preserved foods.

This communication reports a rapid technique that can be used to detect Erythrosine in canned red fruits that contain both naturally occurring pigments (and their breakdown products) and certain types of artificial dyes.

Method

The total contents of the can are macerated and a sample (20 g) is taken. An aqueous solution of sodium sulphite heptahydrate (0·5 g in 10 ml) is stirred into the sample so as to decolorise any anthocyanins present and to increase the pH to 4–6, thereby aiding the solubilisation of the Erythrosine. The mixture is shaken vigorously with 5 ml of 3-methylbutan-1-ol and centrifuged in order to separate the layers. A sample of the upper (alcohol) layer is transferred to a spectrophotometer cell and the spectrum recorded in the range 350–700 nm. A sharp peak at 545 nm indicates the presence of Erythrosine. This identification can be confirmed by adding 1–2 drops of concentrated hydrochloric acid to the cell, mixing and recording the spectrum again. The loss of approximately 95 per cent. of the absorbance at 545 nm is diagnostic of Erythrosine under these conditions.

Results and Discussion

The method has been used successfully for the qualitative identification of Erythrosine in cans of raspberries, loganberries, strawberries, plums and rhubarb that had been stored for up to 18 months. The cans also contained Ponceau 4R (in all samples) and Sunset Yellow (in strawberries and rhubarb only). However, neither of these pigments nor the yellow sulphite-reduction products of Ponceau 4R are extracted into 3-methylbutan-1-ol; these substances therefore do not interfere in the absorbance measurements. The red anthocyanin pigments are decolorised by sodium sulphite and are not extracted to a significant extent by the 3-methylbutan-1-ol under the conditions used. This was shown by demonstrating that the 3-methylbutan-1-ol extracts lost most of their absorbance at 545 nm on acidification (as expected for Erythrosine), rather than increasing in absorbance, as would be expected of decolorised anthocyanins on treatment with acid.[4] Other naturally occurring yellow and yellow - green pigments are extracted into the alcohol layer but do not interfere in the detection of Erythrosine as they have maximum absorbances at wavelengths far removed from that of the red dye. Acidification led to only small changes in the wavelength and intensity of maximum absorbance of these yellow pigments, whereas large spectral changes were observed for Erythrosine. Paper chromatography in butan-1-ol - acetic acid - water (4 + 1 + 5; upper phase) was used to confirm that Erythrosine was the only red pigment present in the alcohol extracts.

Preliminary investigations of the quantitative aspects of the method indicated that Erythrosine

is extracted by 3-methylbutan-1-ol in proportion to the amount of the dye present in the fruit macerate, thus showing that the method should also be suitable for quantitative analysis.

We believe that the method described represents a significant improvement on current techniques in that it provides a simple procedure that should greatly reduce the amount of time spent on analysis.

References

1. Dickinson, D., and Raven, T. W., *J. Sci. Fd Agric.*, 1962, **13**, 650.
2. Pearson, D., "The Chemical Analysis of Foods," Sixth Edition, Churchill, London, 1970.
3. British Food Manufacturing Industries Research Association, *Analyst*, 1963, **88**, 864.
4. Adams, J. B., and Woodman, J. S., *J. Sci. Fd Agric.*, 1973, **24**, 763.

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X-ray Analysis of High-alumina Cement Concrete

The analytical problems associated with set pre-stressed high-alumina cement concrete beams are: identification of beams that contain high-alumina cement; determination of the degree of conversion; and detection of beams where chemical attack on the products of conversion has taken place. X-ray diffractometry is suggested as the best analytical technique for all three problems.

Identification

The test recommended by the Building Research Establishment[1] is to determine the aluminum content by a chemical "oxine" method. The reliability of this test is suspect.

In situ identification by means of the iron content can be carried out with a relatively cheap and portable radioisotope X-ray analyser. Identification of high-alumina cement beams on this basis is 90–95 per cent. correct; Portland cement beams with a high iron content are incorrectly identified owing to the presence of iron in the aggregate. No beams that contain high-alumina cement are misidentified. Identification on the basis of aluminium content, determined on discrete samples by X-ray fluorescence, was also 90–95 per cent. correct.

For positive identification of high-alumina cement, the high iron- or aluminium-containing beams must be analysed further. X-ray diffractometry will positively identify beams by the presence or absence of compounds characteristic of high-alumina cement. This method is applicable whether or not the cement has undergone conversion. The peaks used for identification are listed in Table I.

TABLE I

X-RAY DIFFRACTION PEAKS USED FOR IDENTIFICATION

Compound	*d* spacing/nm	°2θ (Cu radiation)
$CaO.Al_2O_3.10H_2O$	1·42	6·2
$CaO.Al_2O_3.10H_2O$	0·716	12·36
$3CaO.Al_2O_3.6H_2O$	0·516	17·18
$Al_2O_3.3H_2O$ (gibbsite)	0·482	18·40

Determination of Degree of Conversion

Thermoanalytical techniques, in particular differential thermal analysis, have been recommended for determining the degree of conversion.[2] The degree of conversion can also be obtained by X-ray diffractometry.

Some advantages of X-ray diffractometry over differential thermal analysis are as follows: interpretation of peak position and measurement of peak height are much easier; interference due to peak overlap, *e.g.*, from gypsum or ettringite (a likely product of chemical attack), is minimal; there is no base-line drift. The analysis time is 15–20 min, compared with at least 35 min by differential thermal analysis. An automatic sample changer enables 35 samples to be processed overnight, with no operator present.

The disadvantage of X-ray diffractometry is its high cost. A diffractometer costs three to four times as much as differential thermal analysis equipment. There are, however, many diffractometers available in Universities, Polytechnics and Research Institutes.

Detection of Chemical Attack

During natural exposure, the compound $3CaO.Al_2O_3.6H_2O$ may be carbonated. Sulphate attack may also occur, leading to the formation of ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$). The extent to which both types of chemical attack have taken place can be assessed by the relative amounts of the various compounds detected on a diffractometer trace.

Sampling can be carried out as recommended for differential thermal analysis.[3] After passing it through a 150-mesh sieve, ideally a 200-mg sample is required, although satisfactory traces have been obtained from samples as small as 5 mg.

This contribution is submitted with the permission of the Director General, North Eastern Region, Central Electricity Generating Board.

References

1. Roberts, M. H., and Jaffrey, S. A. M. T., "A Rapid Chemical Test for the Detection of High-alumina Cement Concrete," Building Research Establishment, Garston, 1975.
2. "Recommendations for the Testing of High-alumina Cement Concrete Samples by Thermoanalytical Techniques," Thermal Methods Group, Analytical Division of The Chemical Society, London, 1975.
3. Department of the Environment, Circular BRA/1068, July 20th, 1974.

Received *December 22nd*, 1975

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Book Reviews

MANUEL PRATIQUE DE CHROMATOGRAPHIE EN PHASE LIQUIDE. By R. ROSSET, M. CAUDE and A. JARDY. Pp. xiv + 280. Orsay: Varian S.A. 1975. Price Fr85·60.

At present there are all too few books on the rapidly developing technique of high-speed or high-performance liquid chromatography (HPLC), and one warmly welcomes an introductory text which is simply and clearly written and which is firmly based upon theory and practical experience. This text should prove to be ideally suited to the beginner in HPLC, for it lays out the basic ideas in a straightforward, yet authoritative, way in a two-chapter section dealing with fundamentals and optimisation. Chapter 4 gives a sound, although not particularly comprehensive, account of equipment. Later chapters cover the various types of liquid column chromatography: liquid - solid adsorption, liquid - liquid partition, ion-exchange and exclusion chromatography. Throughout these chapters an excellent balance between theory and practice is maintained by the inclusion of illustrative examples and tables of data and materials. The references at the end of each chapter are well up to date and the publishers must be congratulated on rapid publication of the final manuscript.

A group of chapters then follow that deal with miscellaneous topics such as quantitative analysis, preparative liquid chromatography and the transfer to column chromatography of results obtained using thin-layer chromatography. Next, there is a valuable, 50-page bibliography of HPLC arranged under various headings. This will be invaluable to workers who wish to survey a particular area of application. Lastly, there is a comprehensive list of suppliers of HPLC equipment and accessories together with their addresses.

The book has obviously been prepared with much careful thought as to how one can provide, in the scope of 300 pages, the best balance of material as an introduction for the practical chromatographer. In this the authors have been most successful and one expects that their book will soon be found in laboratories in that well worn condition which indicates a favourite text-book.

It is perhaps worth remarking for the benefit of UK readers who may be discouraged from purchasing a book written in a foreign language, that the style of writing is straightforward and the text is sufficiently well supplied with diagrams that the French text should be no deterrent to the majority of UK chemists.

JOHN H. KNOX

AN INTRODUCTION TO THERMOGRAVIMETRY. Second Edition. By C. J. KEATTCH and D. DOLLIMORE. Pp. xii + 164. London, New York and Rheine: Heyden and Son. 1975. Price £4·00; $10·00; DM27·50.

The publication of this second edition inevitably invites comparison between the two editions. The first edition was enthusiastically received as being an extremely good introduction to the subject compressed into some 60 pages. The second edition has acquired 100 extra pages and a second author, namely Dr. David Dollimore. The extra pages are accounted for by the useful enlargement and updating of the original chapters, together with three additional chapters. One of these, namely the chapter on "Associated Equipment," serves as a brief survey of the increasing number of thermoanalytical techniques. One would have liked to see a part of the chapter given over to a discussion on simultaneous thermogravimetry with differential thermal analysis (TG - DTA). The other two chapters deal with two particular aspects of the operation of a thermobalance that are somewhat specialised, namely kinetic data from isothermal experiments and physical adsorption studies using a gravimetric technique.

One omission in the second edition is the Appendix on commercially available instruments. While it is difficult to compile an up-to-date list of equipment, it would have been helpful to include at least a list of the names and addresses of manufacturers. It would also have been helpful to include in the text a few paragraphs on the literature of thermogravimetry. The beginner can do no better than go to "Thermal Analysis Abstracts," also published by Heyden, and to the proceedings of the first four conferences of the International Confederation for Thermal Analysis, in order to gain a comprehensive introduction to this literature.

This second edition remains a remarkably good introduction to the subject, well written, well indexed and with correct nomenclature throughout. It is to be highly recommended to any person approaching the subject for the first time.

J. P. REDFERN

GAS CHROMATOGRAPHY IN INORGANICS AND ORGANOMETALLICS. By G. GUICHON and C. POMMIER. Pp. x + 332. Ann Arbor, Michigan: Ann Arbor Science Publishers Inc. 1973. Price £10.

Few techniques have had such an explosive effect on organic analysis as gas chromatography. With refinements of technique and instrumentation giving better resolution and lower and lower limits of detection, it is obvious that the methods must, with advantage, be applied to inorganic analysis, and here is a book which admirably indicates the state of work in this field. Unlike the Moshier and Sievers monograph published 10 years ago, which concentrated attention on the gas chromatography of metal chelates, the present text deals more generally with purely inorganic compounds as well as organometallic compounds. Two introductory chapters deal with theoretical concepts and apparatus and experimental technique. This is followed by chapters on inorganic gases, halogens and non-metallic halides, metals and metal halides, hydrides, organometallic compounds, metal chelates, isotopes and isotopic compounds. Two concluding chapters give examples of some analytical applications and some non-analytical applications. A useful feature is an index of analysed compounds.

This translation of the authors' 1971 French text provides a valuable source of information on the otherwise widely dispersed data on the gas chromatography of inorganic substances. Although the present reviewer has some misgivings about the rather sparse treatment of recent work on metal chelates, this is only a small part of the subject matter. What, perhaps, this book does unconsciously emphasise is the paucity of real analytical methods of inorganic analysis based on gas chromatography. It is fairly easy to obtain reasonable chromatography for a wide variety of inorganic substances, but less so to build this into a workable quantitative analytical method. If this book can encourage others to try their hand at the development of such methods it will have given valuable service. There is much here to merit the attention of environmentalists with interests in toxic gases in the atmosphere and poisonous organometallics accumulating in natural food chains. Work on the metal alkyls, particularly those containing mercury, provides a fine example of the power of the technique for trace detection and determination. No-one interested in the wider applications of gas chromatography should be without this book; those just beginning to take an interest in the subject will find it invaluable, and should not be put off by the somewhat unfortunate title; a translator's aberration?

WILLIAM I. STEPHEN

STRIPPING VOLTAMMETRY IN CHEMICAL ANALYSIS. By KH. Z. BRAININA. Translated from Russian by P. SHELNITZ. Pp. xii + 222. New York and Toronto: John Wiley and Sons; Jerusalem and London: Israel Program for Scientific Translations. 1974. Price £9·35.

I found this book extremely difficult to read, owing almost entirely to the necessity of translating it mentally from the distinctly clumsy English. While having the greatest admiration for the translator's command of a foreign language, literature at this level of technical complexity demands good presentation, and publishers should know by now that really readable texts are rarely produced outside one's mother tongue.

Having said this, it is still difficult to decide where this book is designed to fit on one's library shelves. The theory of electrode processes is adequately covered; the author seems to use his own symbols for some entities, although these are admittedly defined on the first page of the text, and the first 30 pages or so would be useful in a theoretical electrochemistry course.

The remainder of the book purports to be a practical manual, but I doubt if an experienced analyst who already uses electrochemical methods would find much to interest him; on the other hand, there is insufficient information in most instances for the less experienced worker to be able to follow the sketchy methods outlined. Sensitivities, precisions, and detection limits are quoted with no reference to the type of instrumentation used. Superficially, there appears to be adequate information on the manufacture of the electrodes described, but a beginner attempting this would be well advised to return to the original references; the oldest and probably most popular electrode, the Kemula hanging-drop electrode, is not mentioned.

I would have thought that for the average analytical laboratory needing a reference work for this field on its shelves, Rolf Nelb's "Inverse Polarographie und Voltammetrie" would be a much more useful work.

R. C. ROONEY

LECTURES AND COURSES

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Professor D. Thorburn Burns,
Department of Chemistry,
Queen's University of Belfast,
Belfast BT7 1NN, Northern Ireland.

An Improved Column-chromatographic Quantitative Isolation of Diosgenin and Yamogenin from Plant Crude Extracts Prior to Their Determination by Infrared Spectrophotometry

A previously described routine procedure involving the use of a silica gel column in determining diosgenin and yamogenin has been improved by using water-containing solvents. The advantages are that there is less variation between duplicate results, that each column can be used at least five times and that component bands are eluted in predictable volumes of solvents. An apparatus and solvent sequence is described that allows twelve columns to be developed simultaneously.

The method has been successfully applied to crude extracts from *Dioscorea deltoidea* tuber and to oily crude extracts from the seeds of *Trigonella foenum-graecum* (fenugreek) and *Balanites aegyptiaca*. The over-all error of the procedure, including sampling, extraction and infrared spectrophotometric determination for duplicate analyses of 2·5-g samples of the fenugreek seed used, expressed as a 95 per cent. confidence interval of the mean sapogenin value, was 1·04 $\pm$ 0·025 per cent. for diosgenin plus yamogenin, 0·64 $\pm$ 0·019 per cent. for diosgenin and 0·40 $\pm$ 0·023 per cent. for yamogenin.

As the method does not permit the separation of tigogenin from diosgenin nor that of neotigogenin from yamogenin, the results indicate maximum yields for diosgenin and yamogenin in fenugreek seed. The results exclude sterols, steryl esters, dihydroxysapogenins and spirostadienes.

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Analyst, 1976, **101**, 122–124.

Rapid Sample Dissolution and Determination of Total Iron in Iron Ore, Sinter, Concentrates and Agglomerates

A method is described for rapid and complete dissolution of iron ores with a wide range of composition in order to determine total iron. The sample is fused with a mixed flux of sodium carbonate and sodium peroxide in a vitreous carbon crucible and the melt is dissolved in hydrochloric acid. Iron is then determined by redox titration with dichromate. The wide range of composition of the samples for which the method can be used, as exemplified by results obtained for ISO, BCS and NBS reference standards, demonstrates its universal applicability. The method is rapid, free from tedious and time-consuming manipulations, suitable for routine control and yields results comparable with those obtained by the referee method.

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Analyst, 1976, **101**, 125–127.

Spectrophotometric Determination of Free Chlorine in Air

A spectrophotometric method that is suitable for the micro-determination of free chlorine in ambient air is described. When free chlorine is absorbed in an alkaline solution of 4-nitroaniline, an orange - brown colour develops, with a molar absorptivity (ϵ) of 19 000 at 485 nm. The method is suitable for the determination of chlorine in the range from a few parts per hundred million to about 20 p.p.m.

Ozone, ammonia and sulphur reducing gases interfere with the reaction, but these interferences can be reduced. Features of the method include high sensitivity, stability of the reagents and coloured reaction product, high collection efficiency, relative specificity to chlorine, reproducibility, simplicity and convenience.

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Analyst, 1976, **101**, 128–135.

A Colorimetric Method for the Determination of Isoprenaline Sulphate in Pharmaceutical Preparations

A rapid and convenient colorimetric method is described for the determination of isoprenaline sulphate in pharmaceutical preparations. This method is based on measuring the intensity of the orange colour developed when isoprenaline sulphate is allowed to react with thiosemicarbazide in an alkaline medium. Beer's law is obeyed in the concentration range 2·0–16·0 $\mu g\ ml^{-1}$. Data on precision and accuracy are presented. As the catecholic function with unsubstituted adjacent positions is required for the development of the colour, the method is highly specific.

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Analyst, 1976, **101**, 136–139.

A Rapid Method for Detecting Erythrosine in Canned Red Fruits

Communication

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Analyst, 1976, **101**, 140–141.

X-ray Analysis of High-Alumina Cement Concrete

Communication

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