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# Radioisotope X-Ray Spectrometry

## A Review*

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This paper reviews the present state of development of X-ray excitation with radioisotope sources and of relevant methods of non-dispersive energy selection and X-ray detection. Reduction of interferences arising from absorption, enhancement and particle-size effects is also discussed.

The compactness, cheapness and simplicity of the measuring head that result from the use of radioisotope excitation and non-dispersive energy selection are being exploited by portable and "on-stream" analysers now commercially available. The number of applications to ore and alloy analysis is already large and is increasing rapidly. The advantages of radioisotope X-ray spectrometry are less marked and less important in the laboratory where many facilities and alternative techniques exist. Nevertheless, applications for routine single-element determinations are increasing.

The basic techniques of excitation and energy selection have been worked out but not yet evaluated for all possible applications. In many of the problems that have been studied, alternative excitation and detection methods have been used but not directly compared. Physical methods for overcoming absorption and enhancement effects have been developed, mainly by analogy with conventional X-ray spectrometry. Suppression of particle-size effects in the analysis of heterogeneous materials remains a problem, especially as fusion techniques for removing the heterogeneity are virtually restricted to the laboratory. There is scope for the development of new techniques for overcoming particle-size effects, especially in "on-stream" analysis.

THE excitation of characteristic X-rays by radiations from a radioisotope source was first reported in 1946,[1] but nearly a decade passed before descriptions of potential applications to X-ray fluorescence analysis began to appear,[2,3] and over 12 years before applications were described.[4 to 8] X-ray filters for energy discrimination were suggested in 1955,[2,3] but analyses depending on the use of balanced filters to isolate $K\alpha$ X-rays of a particular element were not described until 1959.[5] In spite of this slow start, radioisotope X-ray fluorescence analysis is now an established technique. Twelve papers describing analyses were published at a single conference in 1965, one of which described methods for determining eleven elements.

Instruments now commercially available in the United Kingdom exploit the advantages of compactness and simplicity that result from replacing the conventional X-ray tube and its supplies by a small radioisotope source, and the diffracting crystal by non-dispersive energy selection. A battery-operated portable analyser (manufactured by Hilger and Watts Ltd.) weighing only 16 lb is available in laboratory and field versions, and has found immediate use in field assay of ores[9,10,11,12] and alloy identification[13] in the metallurgical industries. "On-stream" analysers are operational for continuous elemental analysis of aqueous mineral slurries and dry solids.[9,10,14,15,16] Even in the laboratory, where the advantages are neither as marked nor as important, applications are increasing in number.

The concept of X-ray fluorescence analysers that are simpler, cheaper and orders of magnitude more compact than the conventional apparatus demands a new approach to the application of X-ray analysis. Many uses not hitherto envisaged have been found and many more are likely to arise as this approach becomes more universal.

In this paper the present state of development of methods of X-ray excitation, energy selection and detection are reviewed, and the reduction of interferences caused by absorption, enhancement and particle-size effects is discussed.

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* Reprints of this paper will be available shortly. For details see Summaries in advertisement pages.

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## EXCITATION OF CHARACTERISTIC X-RAYS AND ENERGY SELECTION

One of the features of radioisotope X-ray fluorescence is the wide variety of possible sources and the consequent need for careful choice of source for a particular analysis.

Non-dispersive energy selection also involves the correct choice of excitation energy together with the use of absorption edge filters and energy sensitive detectors with electronic pulse height selection. These methods may be used separately or in combination, and it will become clear that, for a particular analysis, the source and method of energy selection are often chosen simultaneously.

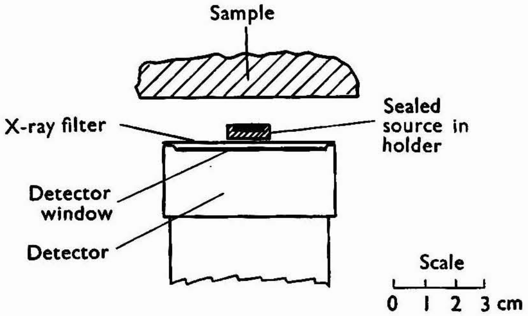

Fig. 1. "Central source" arrangement of source, sample and scintillation counter detector

### GEOMETRICAL ARRANGEMENT OF SOURCE, SAMPLE AND DETECTOR

The simple and efficient geometry (Fig. 1) made possible by the small size of sources and absence of crystal spectrometers is necessary because of the relatively low source output (about $10^7$ photons per second). The low outputs are, themselves, an advantage because

TABLE I

COMMONLY USED LOW ENERGY X-RAY AND $\gamma$-RAY SOURCES

| Source | Half-life | Useful radiations | Practical emission efficiency, photons per disintegration | Typical activity | Highest atomic number usefully excited, K X-rays |
|---|---|---|---|---|---|
| Iron-55 | 2·7 years | Manganese K X-rays, 5·9 keV | 0·15 | 2 mC | 24 (chromium) |
| Tritium - zirconium* | 12·3 years | Bremsstrahlung, 2 to 12 keV<br>Zirconium L X-rays, 2 keV | $4 \times 10^{-5}$<br>$10^{-5}$ to $10^{-4}$ | units of 1 to 3 C | 30 (zinc) |
| Cadmium-109† | 1·3 years | Silver K X-rays, 22 keV<br>$\gamma$-ray, 88 keV | 0·8<br>0·04 | 1 mC | 43 (technetium) |
| Promethium-147 - aluminium† | 2·6 years | Bremsstrahlung, 10 to 100 keV | $2 \times 10^{-3}$ | 0·5 C | 60 (neodymium) |
| Americium-241† | 470 years | $\gamma$-ray, 59·6 keV<br>$\gamma$-ray, 26 keV<br>Neptunium L X-rays, 11 to 22 keV | 0·35<br>0·02<br>0 to 0·2‡ | 1 mC | 69 (thulium) |
| Gadolinium-153 | 236 days | $\gamma$-ray, 103 keV<br>$\gamma$-ray, 97 keV<br>Europium K X-rays, 42 keV‡ | 0·2<br>0·2 | 1 mC | 88 (radium) |
| Cobalt-57† | 270 days | $\gamma$-ray, 136 keV<br>$\gamma$-ray, 122 keV<br>$\gamma$-ray, 14 keV<br>Iron K X-rays, 6·4 keV‡ | 0·10<br>0·88<br>0 to 0·06‡ | 0·5 mC | 98 (californium) |

* Tritium - titanium also available.

† Also used as primary source in source - target assemblies.

‡ Emission depends on self-absorption of source and on window thickness.

little shielding of the detector is required, and the radiation hazard is small even with unshielded sources.* Adequate shielding is usually afforded by the normal structures (including the sample) around the measuring head.

The geometrical efficiency of the "central source" arrangement shown in Fig. 1 is a few per cent. so that, assuming fluorescent excitation efficiencies are also a few per cent., count-rates of characteristic X-rays from pure elements are in the range of $10^3$ to $10^5$ per second. These are sufficient to give good statistical accuracy in counting times of 10 to 100 seconds.

Other geometrical arrangements have been used in special cases and are described where appropriate.

## LOW ENERGY X-RAY AND $\gamma$-RAY SOURCES

Useful sources have been selected by using criteria of long half-life, low cost and ready availability with high specific activity. They emit monochromatic X-rays or $\gamma$-rays, a continuous spectrum of X-rays (bremsstrahlung) or $\alpha$ or $\beta$-particles. Suitable low energy X-ray or $\gamma$-ray sources are listed in Table I. They are the most commonly used, and their choice for excitation of particular characteristic X-rays is discussed in detail under "Choice of source and detector for a given analysis." Other sources have specialised applications and these are also described in the same section.

The sources listed in Table I are normally available as disc-shaped pellets with over-all dimensions from 0·5 to 1·5 cm diameter and 2 to 5 mm thick. The back and sides are shielded so that emission takes place from one face only. Stainless-steel windows are used on sources emitting energies greater than about 30 keV, and aluminium is used when the required output is of lower energy. An exception is iron-55, which has a thin Terylene window protecting the electroplated iron layer.

The tritium bremsstrahlung sources are not constructed in this way, and are not "sealed" within the present meaning of the sealed-source regulations. They consist of a thin layer, usually of zirconium, melted on to a tungsten backing. Tritium is contained as a non-stoicheiometric zirconium tritide that is stable at temperatures up to about 200° C. At room temperature tritium escapes slowly (a few $\mu$C per curie per day) and gives rise to a concentration of tritium or tritiated water vapour in the atmosphere that is undetectable if the room is well ventilated. The rate of evolution has a negligible effect on the apparent half-life of the source.

### SOURCE - TARGET ASSEMBLIES—

Optimum excitation can be achieved by using spectrally pure characteristic X-rays from a secondary target excited by a primary source.[2,9,10,16,17,18] The target can be chosen to have its characteristic energy just above that of the absorption edge of the element to be determined, thus ensuring high analytical sensitivity. Detectable limits in the range 50 to 200 p.p.m. can usually be obtained. The system is also flexible because targets can be changed at will, and can be made of mixtures emitting more than one X-ray energy.

The highest spectral purities (greater than 90 per cent.) are achieved by using back-scatter geometry and primary excitation with low energy X-rays or $\gamma$-rays. The limited source outputs and extra losses imposed by secondary excitation make the geometrical design of the whole source - target sample detector system of critical importance. One design that we found satisfactory is shown in Fig. 2; it is seen that the "central source" principle is preserved.

The primary source used consists of a ceramic sphere with a truncated conical shield and an aluminium envelope. "Conical sources" of americium-241, cobalt-57, cadmium-109 and promethium-147 - aluminium (see Table I) are available, and each excites target X-rays efficiently in a limited region of the spectrum.

The targets are usually made from an oxide or other suitable compound of the required element mixed with the minimum of binder such as epoxy resin. A loading of about 60 per cent. w/w of the fluorescent element in the target is normally obtained. This gives a slightly lower spectral purity than is obtainable with an elemental target (see Fig. 3) but an almost unchanged fluorescent emission. If sufficiently workable the same metals can be used for elemental targets as those listed under "Balanced Filters" for filter materials.

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* Localised dose rates at 1 cm from the emitting surface of the sources given in Table I are about 1 Roentgen per hour, and at 1 foot are 1 milliRoentgen per hour.

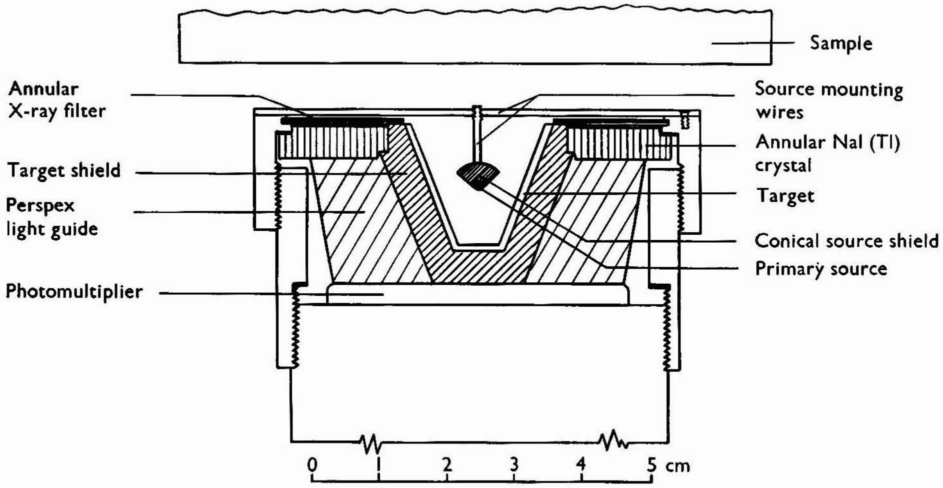

Fig. 2. Source - target assembly showing "central source" disposition with respect to detector and sample

Fig. 3 shows curves of spectral purity and target emission as functions of target atomic number and X-ray energy for a 2·5-mC americium-241 primary source. It is seen that high purities are obtained in the range silver K (22 keV) to thulium K (50 keV), but at lower energies both purity and emission fall off rapidly. In the range 10 to 20 keV the purities and emissions are higher than would be expected from excitation by the 60-keV americium-241 $\gamma$-ray alone, because of the emission of neptunium L X-rays from the primary source. The discontinuities in this energy range arise from the energies and relative abundances of the neptunium L X-rays.[19] The values of target output given are the total photon fluxes over a 4·2-cm diameter area, 1 cm from, and co-axial with, the detector window. This is the optimum sample position. An increase by a factor of about 3 in output can be obtained by using the maximum americium-241 activity available (14 mC) in conical sources of this size.

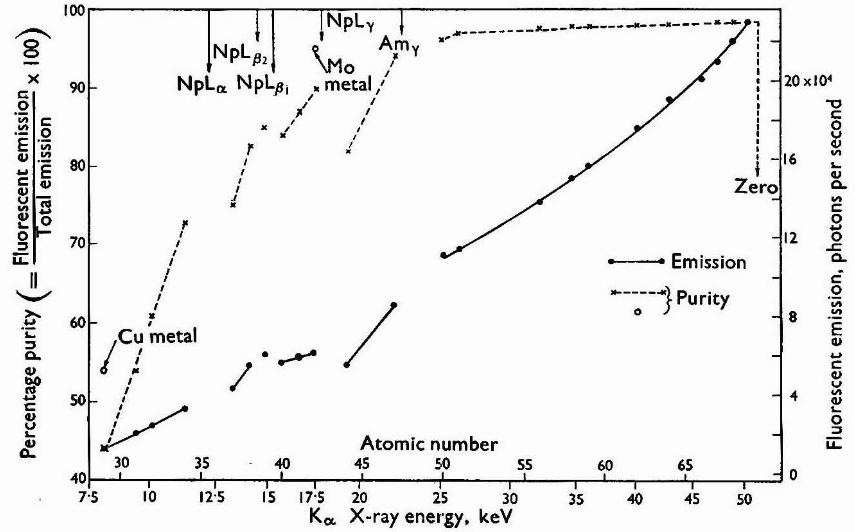

Fig. 3. Curves of spectral purity and emission as functions of target atomic number and K$_\alpha$ X-ray energy with a 2·5-mC americium-241 primary source

A further 3-fold increase in over-all efficiency of the system can be obtained, at the cost of slightly reduced spectral purity, by raising the source to the mouth of the target cone and raising the target base correspondingly.

The range of useful target emissions obtained with the other primary sources are: for cobalt-57, about 60 to 100 keV with osmium to uranium targets; for promethium-147 - aluminium, about 20 (rhodium K) to 27 keV (tellurium K); and for cadmium-109, about 9 (zinc K) to 17 keV (molybdenum K). One of the main limitations of cadmium-109 is the cost of sources of about 10 mC (several hundred pounds).

## ENERGY SELECTION

The purpose of energy selection is to increase both specificity and sensitivity by eliminating unwanted radiation which, for X-ray or $\gamma$-ray excitation, consists of other fluorescent X-rays and scattered X-rays from the matrix. Detectable limits are almost always set by the ratio of fluorescent "signal" to scattered "background." Scattering is particularly severe for high incident energies and matrices of low atomic number, such as may occur in the analysis of solutions or slurries. In alloy analysis, on the other hand, the main need is usually for discrimination between characteristic X-rays from neighbouring elements.

The methods of energy selection available include adjustment of detector response, balanced filters and pulse height analysis.

### ADJUSTMENT OF DETECTOR RESPONSE—

This procedure is generally used whether or not more refined techniques are needed in addition. Methods used include choice of window thickness to filter out unwanted low energies, and choice of detector atomic number or adjustment of detector mass per unit area to discriminate against high energies.

A third method is the use of a single absorption-edge filter on the detector window for cutting out the higher of two neighbouring energies.[8,20] With this method the unwanted X-rays are absorbed by factors of 10 to 100, by using filters which are a half-thickness for the required X-rays. However, the ready absorption of the unwanted radiation is synonymous with efficient conversion to fluorescent X-rays that are characteristic of the filter element. Detection of these X-rays considerably reduces the efficacy of this method of filtration. In particular, the use of heavy-element filters with correspondingly high fluorescent yields is often not warranted.

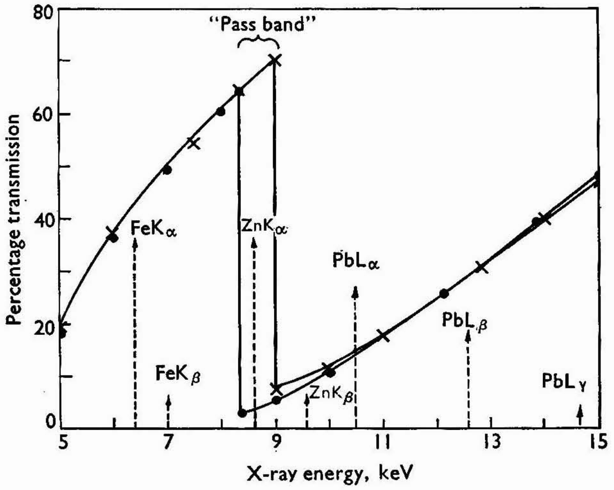

Fig. 4. X-ray transmission through balanced filters of copper (×, 9·8 mg per cm²) and nickel (●, 10·5 mg per cm²). Iron K, zinc K and lead L X-ray energies shown

BALANCED FILTERS—

By thickness adjustment the X-ray transmissions through two filters of adjacent atomic number can be made equal over a wide range of energies except for the "pass band" between their two absorption edges (see Fig. 4).[20,21] Thus the difference between the two transmissions is proportional to the X-ray intensity in the narrow energy band between the two absorption edges. With few exceptions* a pair of K absorption edges can be found that bracket any given K$\alpha$ X-ray energy.

In use, balanced filters require the subtraction of two measurements. The measurements can be made with the same detector by changing, oscillating or rotating the two filters. Alternatively, the outputs from twin measuring heads, each with its respective filter, can be continuously subtracted. Oscillating or rotating filters with, say, a tuned amplifier to pick up and rectify the appropriate part of the detector output could have advantages of stability under adverse signal-to-noise ratios.[5]

If possible, filters are made from metal foils, and the following metals can be used in this way: Mn (*plus* 12 per cent. of Ni), Fe, Co, Ni, Cu, Zn (suitable thicknesses, 0·0005 to 0·001 inch); Zr, Nb, Mo (0·002 inch); Rh, Pd, Ag, Cd, In, Sn (0·003 inch); most rare-earth elements; and Hf, Ta, W, Re, Ir, Pt, Au and Pb (0·01 inch). Filters of unworkable metals, non-metals and reactive elements are best made by encapsulating the oxide or other suitable chemical compound in the minimum of epoxy resin or plastics. In this case great care must be taken to mix the constituents thoroughly. Filters of elements from aluminium to calcium require special techniques because of their very low values of mass per unit area (1 to 3 mg per cm$^2$). For example, silicon filters have been made by depositing 1 to 2 mg of silicon per cm$^2$ on Terylene film 0·00025 inch thick.

Filters can be balanced by sequentially placing them in position on the detector window, together with the source, and comparing the count-rates by using pure element samples with characteristic X-ray energies in the region of interest. Even with pure element samples care must be taken to allow for scattered radiation as it might be quite different in energy and of comparable intensity to the characteristic X-rays.

A final check on over-all balance should be made with a sample typical of the material to be analysed, but containing none of the element to be determined. Thickness adjustment of the metals is made by chemical etching, and of the loaded plastics and resin filters by hot-pressing and abrading, respectively. Two basic problems militate against perfect balancing, unequal absorption-edge ratios and unequal excitation of filter X-rays by absorbed higher energy radiation. In principle, both difficulties can be overcome by including extra filters without nearby absorption edges,[20,21] but perfect balancing is sometimes quite tedious and hardly ever necessary.

In most applications the use of balanced filters renders further energy selection unnecessary and the detector can then be chosen on criteria of speed of response, reliability and simplicity of associated electronic equipment.

PULSE HEIGHT ANALYSIS—

The main problem with balanced filters is the rapid increase in statistical error of the difference count for increasingly smaller ratios of wanted to unwanted radiation. Detection limits below 300 p.p.m. are only achieved if some of the unwanted radiation can be eliminated. Efficient excitation of the characteristic radiation by using source - target assemblies has already been mentioned.

Another method is to choose the exciting energy so that the resulting scattered radiation is confined to an energy region that can be resolved from the fluorescence with a proportional counter and so discriminated against with a pulse height analyser (see Fig. 5). Unresolved fluorescent X-rays are isolated with balanced filters, as before. This technique is particularly useful at energies below about 20 keV where the energy change on Compton scattering is 2 keV or less, and proportional counters are efficient.

The advent of lithium-drifted silicon and other solid-state detectors promises to extend and improve this technique. A resolution of 2 keV (full width at half maximum) has been reported,[22] which is about equal to that of a proportional counter at 20 keV and appreciably

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* There is no K absorption edge between the K X-ray energies of the pairs titanium - vanadium, bromine - krypton, silver - cadmium, praseodymium - neodymium, tantalum - tungsten and uranium - neptunium.

better at 50 to 100 keV. Developments in this field have been rapid, and a closer approach to the theoretical limit of detector resolution (a fraction of 1 keV) is to be expected. However, the necessity to cool the detector and first stage of the pre-amplifier, and the high cost of large area detectors at present limit application in an otherwise cheap and rugged instrument.

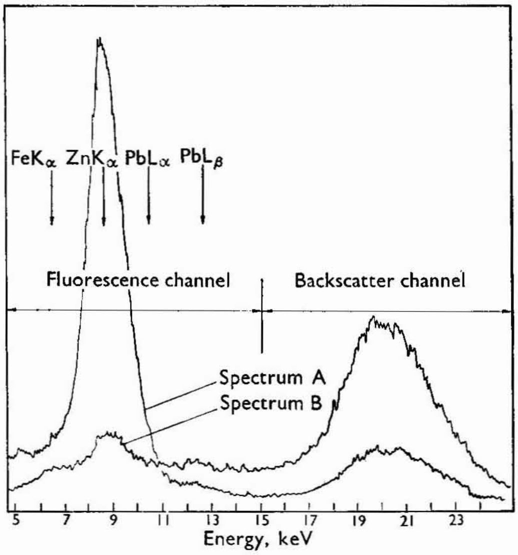

Fig. 5. Spectra from zinc ore slurries (15 per cent. solids) with a cadmium-109 source and proportional counter. Spectrum A; concentrate sample, 50 per cent. of zinc in solids: Spectrum B; ore sample, 1 per cent. of zinc, 1 per cent. of lead and 1 per cent. of iron in solids

## CHOICE OF SOURCE AND DETECTOR FOR A GIVEN ANALYSIS

It has been shown that a wide range of low energy X-ray and $\gamma$-ray sources is available for excitation and a number of suitable techniques for energy selection. This section reviews the methods available for determining elements in various regions of the periodic table.

### LIGHT ELEMENTS, CARBON TO CALCIUM

The proportional counter is the only satisfactory detector in this energy range (0·28 to 3·7 keV), combining high efficiency, low noise and rapid response with a degree of energy resolution. Sealed counters with beryllium windows as thin as 0·002 inch (type PX130L, manufactured by Twentieth Century Electronics Ltd.) have been used for detection of silicon K X-rays (1·74 keV), but at lower energies gas-flow counters are invariably used. Aluminised Terylene windows, 0·00025 inch thick, transmit X-ray energies down to about 1·25 keV (magnesium K), but below this, collodion windows or no windows at all are necessary. Air paths between source, sample and detector are practicable down to 2·0 keV (phosphorus K). Filters of elements from aluminium to calcium (except argon) can be made, but only the use of aluminium foil has been reported.[23,24]

Suitable X-ray sources are iron-55 and tritium - titanium for excitation of K X-rays from phosphorus to calcium. A difficulty can arise with argon-filled counters in this energy region due to the argon K escape peak. This is a second peak in the spectrum, 3·0 keV below the peak owing to the incident energy, which occurs when the latter is able to excite argon K X-rays (3·0 keV). These have a significant probability of leaving the counter undetected. For example, when the incident energy is 5·9 keV (with iron-55), the escape peak at 2·9 keV can interfere with detection of sulphur to calcium K X-rays. Tritium - zirconium sources selected for the high emission of zirconium L X-rays (2·0 keV) are particularly suitable for exciting K X-rays of magnesium to silicon. Tanemura[25] has shown that tritium β-particles emitted from the surface layers of tritium - zirconium sources are important in exciting fluorine K X-rays. Seibel and Le Traon[23] and Kühn[26] have described the use of tritium bremsstrahlung and iron-55 sources for the laboratory determination of magnesium, aluminium, silicon, calcium and iron in cements and iron ores, but do not appear to have satisfactorily solved the problem of energy selection for magnesium, aluminium and silicon K X-rays. Starnes[14] has described an "on-stream" analyser for determining calcium in cement raw-mix slurries, which involves the use of iron-55 excitation and a sealed proportional counter.

α-Particle excitation of soft X-rays has fundamental advantages, especially for the lighter elements in this range. The number of X-rays emitted per α-particle is comparable with the fluorescent excitation efficiency for atomic numbers 15 to 20, but increases with decreasing atomic number to a maximum (about $10^{-1}$) for carbon, whereas fluorescent excitation efficiencies fall off rapidly. In addition, back-scattered α-particles and α-bremsstrahlung have negligible intensities. Robert[27] has demonstrated the excitation of K X-rays of elements from carbon to chlorine by using a 6-mC polonium-210 α-source* with a 1 mg per $cm^2$ mica window and, for the detector, a windowless flow-proportional counter. Imamura *et al.*[24] have developed an instrument for the automatic analysis of fused samples of cement raw materials. This involves the use of sources of polonium-210 α-particles and tritium - zirconium bremsstrahlung; the former exciting aluminium, silicon and calcium K X-rays, and the latter iron K X-rays.

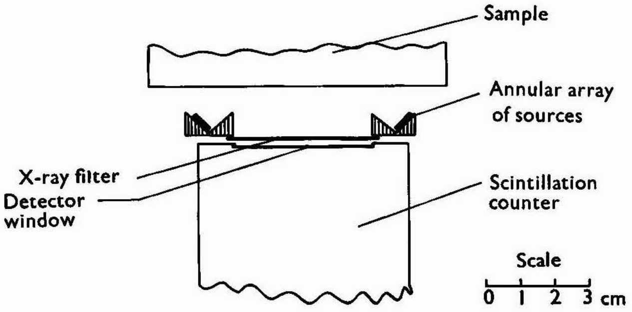

Fig. 6. Annular source arrangement used with tritium - zirconium sources and a scintillation counter

## ELEMENTS, SCANDIUM TO ZINC

Sodium iodide (thallium activated) scintillation counters and xenon - methane filled, sealed proportional counters are satisfactory detectors in this energy range (4 to 9 keV). Scintillation counters require simpler electronic equipment and have a theoretically unlimited life and are therefore preferred whenever possible. A portable analyser (manufactured by Hilger and Watts Ltd.) is available, which consists basically of a scintillation counter and rate-meter and relies solely on balanced filters for energy selection. Many of the applications mentioned below have been proved feasible with this instrument.[9 to 13]

For excitation of scandium, titanium and vanadium, iron-55 is ideal, and detection limits† of about 0·01 per cent. are possible in light matrices. Even in a steel matrix, vanadium can be determined down to 0·025 per cent.[13] Although tritium - zirconium bremsstrahlung gives the highest fluorescent-to-scatter ratios for excitation of K X-rays from chromium to zinc, available sources have low surface activity. The resulting low count-rates obtained with central source geometry can be increased up to 5-fold by using an annular source array as shown in Fig. 6. (This advantage is nullified when it is necessary to measure areas less than about 3 cm in diameter, as on curved small samples.[13]) With the portable analyser, balanced filters and the annular array of tritium - zirconium sources, detection limits of

* Half-life, 138 days; α-energy, 5·3 MeV.

† It is only possible to be semi-quantitative when quoting detectable limits because definitions of detectable limit differ, and also it is not always made clear what the detectable limit is.

0·1 to 0·2 per cent. in rate-meter time constants of 4 to 16 seconds (per filter) have been obtained for chromium or manganese in steels,[13] copper and nickel in copper alloys[13] and copper[12] and zinc (M. J. Gallagher in a private communication) in their respective ores. Niewodniczanski[28] and Florkowski *et al.*[29] also report the use of tritium - zirconium bremsstrahlung for the assay of copper ores and iron, copper and zinc ores, respectively, with a Geiger counter-operated portable analyser. Florkowski[30] also describes a simple method for determining iron in engine oil by using tritium - zirconium to excite iron K X-rays.

Much higher sensitivities can be obtained for determining elements from cobalt to zinc with cadmium-109 for excitation and a proportional counter with pulse height analysis to discriminate against the scattered radiation then localised at 20 to 22 keV. Copper and zinc in aqueous ore slurries have been determined with detection limits of about 40 p.p.m.,[15] and 10 p.p.m. of cobalt in hydrocarbons have been detected.[31] For the latter, the source used was promethium-147 - aluminium which, because of its continuous spectrum, was not expected to give as high a sensitivity as cadmium-109 (which was not available at the time).

At present, chromium, manganese and iron cannot be determined with high sensitivity. Source - target assemblies are not yet capable of giving spectrally pure characteristic energies below 10 keV, nor has direct excitation by iron K X-rays from cobalt-57, copper K X-rays from zinc-65, gallium K X-rays from germanium-68 or bismuth L X-rays from lead-210 been found advantageous. However, development of proportional counters especially for use with source - target assemblies will enable scattered primary radiation to be eliminated[17] and possibly provide a solution to this problem. Even so, highly sensitive measurements of small or curved samples will not be possible as source - target assemblies cannot be made small enough.

Much consideration has been given to the $\beta$-excitation of characteristic X-rays[2,4,5,32,33] but, although $\beta$-excitation of X-rays is most favourable in the energy region 5 to 15 keV,[33] there is no evidence to suggest that the ratios of characteristic to unwanted radiation obtained are higher than for fluorescent excitation. Further study of $\beta$-excitation may show advantages where matrix effects are important, as absorption of the incident $\beta$-particles is almost independent of the atomic number of the sample.

## ELEMENTS, GALLIUM TO LANTHANUM

For this range of elements high sensitivities are generally obtainable by one of the methods of excitation. Detection limits of tens of parts per million can be obtained for elements gallium to niobium with a cadmium-109 source and a proportional counter with pulse height analysis to discriminate against the back-scattered X-rays. Cadmium-109 is still the best source for the excitation of elements from molybdenum to ruthenium, but electronic resolution of the fluorescent and scattered radiation is no longer possible. Molybdenum and niobium in steel can be determined down to 0·04 per cent. by using the portable analyser with balanced filters and a cadmium-109 source.[13] Molybdenum in ores can be determined down to about 0·03 per cent. with the same instrument.

For atomic numbers above 44 (ruthenium) the preferred sources are americium-241 or promethium-147 - aluminium, either for direct excitation or in source - target assemblies. Promethium-147 - aluminium is better than americium-241 for direct excitation over the whole range and gives particularly good results for determining tin in tin ores[9] for which detection limits of 0·03 to 0·1 per cent. are obtained with the portable analyser,[9,11,12] by using a 0·5-C source and a 4-second rate-meter time constant.

The possibility of obtaining high sensitivity through excitation with americium-241, together with electronic discrimination against the back-scattered radiation at 48 to 60 keV, is ruled out because of interference in the region 15 to 35 keV caused by iodine or xenon escape peaks when using the most practicable detectors, sodium iodide (thallium activated) scintillation or xenon - methane-filled proportional counters.[9] The latter are inefficient above 20 keV (unless pressurised, when anode voltages of up to 5 kV are necessary) and in this context one looks forward to the availability of inexpensive silicon (lithium drifted) detectors of relatively large area and thickness.

Reference to Fig. 3 shows that americium-241-excited source - target assemblies are ideal for the efficient excitation of rhodium to lanthanum K X-rays. Americium-241 - barium and americium-241 - samarium are already being used for the "on-stream" determination of tin and barium, respectively, in ores.[9,16] Detection limits are better than 0·01 per cent. for both, with 25-second rate-meter time constants.

### THE RARE EARTHS

Apart from some early work by Yakubovich *et al.*,[7] who used thulium-170* for X-ray excitation, no analyses of rare earths have been reported. It is expected that efficient excitation of cerium to thulium K X-rays should be possible with americium-241 or americium-241-excited source - target assemblies. Also, metal foils of the rare earths are readily available for production of balanced filters.

### HEAVY ELEMENTS, HAFNIUM TO URANIUM

Cobalt-57 and gadolinium-153 (see Table I) excite the K X-rays of heavy elements efficiently. However, the relatively large energy loss (25 to 40 keV) on Compton scattering and the wide variation of scattered energy with scattering angle militates against high sensitivity with central source geometry. The increased scattering at these energies, especially from matrices of low atomic number, accentuates the problem. Nevertheless, the presence of 0·2 per cent. of lead in leaded steels is easily detectable by using gadolinium-153 excitation[13] and, with cobalt-57 and iridium - rhenium balanced filters with the portable analyser, lead in lead ores can be determined down to about 0·1 per cent. (M. J. Gallagher in a private communication). Cobalt-57 gives somewhat better results than gadolinium-153 for elements tungsten to lead because most of the scattered energy is then above the absorption edge of the element being determined.

Source - target assemblies with cobalt-57 primary sources would permit excitation with maximum efficiency, but it remains to be seen whether or not they would yield significant improvements in sensitivity; no experiments have yet been reported. In certain cases naturally occurring radioactive targets would increase backgrounds, perhaps unacceptably.

If collimated beam geometry is used, the energy loss on Compton scattering can be controlled and the energy spread limited; also, sources with high energy components can be more easily shielded. In fact, the highest source energy compatible with central source geometry is about 200 keV. Unfortunately, collimation renders the geometrical efficiency one or two orders of magnitude lower than that of central source geometry, necessitating correspondingly more active sources. Martinelli and Blanquet[34] exploit collimated beam geometry for determining lead in ore slurries and tungsten, bismuth and mercury in solution. The Compton scattering from the source used† is localised at 160 ± 30 keV and is resolved from the characteristic K X-rays by pulse height analysis with a sodium iodide (thallium activated) scintillation counter. The detection limits obtained were 0·1 per cent. or better. Gorski and Lubecki,[35] and Gorski[36] describe the determination of tungsten in steels to below 0·1 per cent. with a source of strontium-90 and yttrium-90 $\beta$-excited lead K X-rays. Here collimation is needed mainly to shield the detector from high energy bremsstrahlung.

The main advantage of exciting the K X-rays of heavy elements is that the use of high energies considerably reduces grain-size effects in the analysis of heterogeneous materials. In homogeneous matrices, excitation of the L X-rays (7·9 to 13·6 keV) by cadmium-109 or source - target assemblies, with discrimination against scattering by using a proportional counter and pulse height analyser, can make for extremely high sensitivities. We have shown that this method is feasible for determining lead compounds in petroleum. With a 0·4-mC cadmium-109 source and a xenon - methane-filled proportional counter (type PX130B, supplied by Twentieth Century Electronics), the detection limit for lead bromide was 3 p.p.m. in a counting time of 100 seconds. Lead L *plus* bromine K X-rays were isolated from the scattered radiation with a single-channel pulse height analyser. When, in addition, balanced filters of gallium and germanium were used to isolate lead $L_\alpha$ X-rays (for unknown lead-to-bromine ratios) the detection limit under otherwise similar conditions was 40 p.p.m.

Excitation of both K and L X-rays has been used for determining uranium in solution. MacKay[17] used an americium-241 source of activity of only 710 $\mu$C with a cadmium target to excite uranium L X-rays and obtained a detection limit of 50 p.p.m. of uranium in 10 minutes' counting time. Forberg[37] excited uranium K X-rays with a collimated beam of $\gamma$-rays from cobalt-57, detecting the fluorescence and scattering at 90° to the exciting beam. His geometrical arrangement compromises between the improvement in fluorescent-to-scattered ratio and the increase in difficulty of resolving the scattered and fluorescent energies

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* Half-life 127 days, emits 52-keV X-rays (4 per cent.), 84-keV $\gamma$-rays (3 per cent.) and bremsstrahlung up to about 900 keV (about 3 per cent.).

† Iridium-192, half-life 74 days, main $\gamma$-ray energy about 308 keV.

as the scattering angle is increased. It also compromises between the low efficiency of narrow beam geometry and the high efficiency of central source geometry. Nevertheless, the sensitivity is not significantly different from that obtained by MacKay.

## MATRIX EFFECTS

The three main sources of interference in X-ray fluorescence analysis are usually termed "matrix absorption," "matrix enhancement" and particle-size effects. They are all well known in conventional X-ray analysis, and the approach to their elimination is similar in both the conventional and radioisotope techniques as the effects occur in the sample and the basic physics is identical.

However, methods of elimination suited to routine multi-element laboratory analysis (such as the use of internal standards[38] and the computation of concentrations[39,40] following measurement of all significant characteristic X-rays) are likely to be confined to conventional X-ray spectrometry. On the other hand, the wide choice of nearly monochromatic X-rays now available from radioisotope sources increases the scope for physical methods of reducing interference.

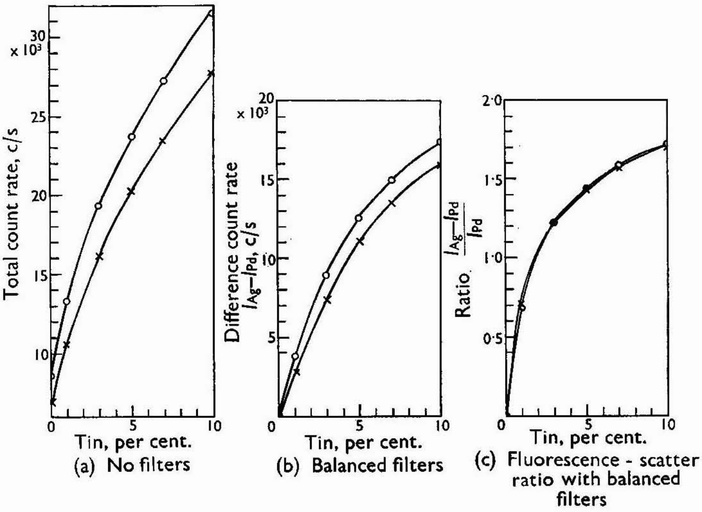


Fig. 7. Curves (○, 0 per cent. of iron; ×, 5 per cent. of iron) of (*a*) tin K fluorescence *plus* scatter; (*b*) fluorescence only; and (*c*) ratio of fluorescence to scatter against tin content, showing reduction of matrix effect due to iron, by the use of balanced filters. Excitation by americium-242 - barium source - target assembly

### MATRIX ABSORPTION

If the sample contains more than about 1 per cent. of an element with a relatively high mass attenuation coefficient at either the exciting or fluorescent energy, an increase in concentration of this element will significantly reduce the intensity of the characteristic X-rays to be measured. For example, the results in Fig. 7 (*b*) show that an increase from 0 to 5 per cent. of iron in tin ore reduces the intensity of tin K X-rays by up to 20 per cent.

The back-scattered intensity and, with samples of suitable mass per unit area, the transmitted intensity are also reduced with increasing concentration of the interfering element. These phenomena are the basis of several methods that have been used to overcome matrix absorption effects satisfactorily.

### SIMPLE METHODS OF OVERCOMING MATRIX ABSORPTION EFFECTS—

The simplest methods for overcoming matrix absorption effects have been considered for use with portable analysers. These are based on the requirements that: special sample treatment is not desirable; only back-scatter geometry is utilised; and that the number of readings per determination is as small as possible.

*The use of balanced filters*—The use of balanced filters to cut out back-scattered X-rays limits matrix absorption to the effect on the characteristic radiation. Sometimes this is sufficient to reduce errors satisfactorily, for example, in determining molybdenum or niobium in steels.[13] If balanced filters are not used to isolate molybdenum or niobium K X-rays, the matrix effect on the scattered radiation then measured is sufficient to render separate calibration graphs necessary for high and low alloy steels.

In ore analysis the higher scattered flux makes isolation of the characteristic X-rays even more essential. Also, as the matrix composition is more variable, its effect on the characteristic X-rays is often still important. This is illustrated in Figs. 7 (*a*) and (*b*). Fig. 7 (*c*) shows that, without increasing the number of readings, the matrix effect on the fluorescent X-rays can sometimes be eliminated by plotting what is effectively the fluorescence-to-scatter ratio against concentration. This method has been used successfully in the assay of tin[11,12] and copper[12] ores with the portable analyser and in "on-stream" analysis of tin,[16] barium[16] and lead[34] ores. It cannot be used if there is little scatter, such as from some alloys, but here the same measurement can provide inter-element correction in a different way. Measurement of copper content of copper alloys is often subject to matrix absorption arising from iron and manganese impurities. Excitation is by tritium - zirconium and there is little scattered radiation. Copper K X-rays are isolated from other fluorescent X-rays (*e.g.*, nickel K and zinc K) by cobalt and nickel balanced filters, the cobalt filter strongly absorbing copper K X-rays but transmitting iron K and manganese K X-rays. It is found that the cobalt filter reading is proportional to iron *plus* manganese content, and a suitable correction can thus be made to the copper K intensity.[13]

*Nomograms*—The closely related nomographic method has been used by Dziunikowski,[41] Florkowski *et al.*[29] and Niewodniczanski[28] for the analysis of copper and zinc ores, both containing iron as the interfering element. In this method one measurement is made for each independently variable component. Each measurement is a function of both components and the nomogram is a graphical representation of the two simultaneous equations. Within limits, the nomographic method corrects empirically for all interferences affecting the X-ray intensities.

In the analysis of copper ores, correction is made both for absorption of copper K X-rays by iron and enhancement of iron K X-rays by copper K X-rays. The two necessary readings can be made in several ways. A reading without filters is proportional to both iron K and copper K X-rays intensities, and one with a zinc filter is proportional mainly to copper intensity. Alternatively, the difference reading between cobalt and nickel filters (which need not be balanced) is proportional mainly to copper K intensity, while a reading with the cobalt filter is proportional mainly to iron K intensity.

The method has three main drawbacks. If there are more than two independent variables it becomes too complicated for simple nomographic presentation. If the sensitivities of each measurement for each variable are nearly equal the errors become large. If the back-scattered intensity is high a situation analogous to too many independent variables exists.

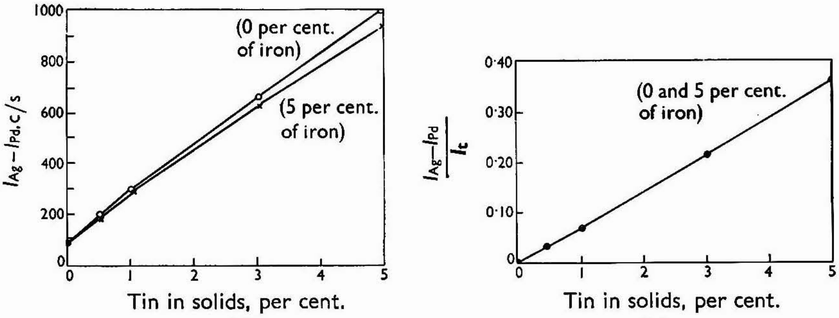
*Compensation*—The compensation method relies on excitation of fluorescence in the interfering element sufficient to just compensate for the decrease in intensity of the wanted radiation caused by the matrix absorption effect. As the required radiation and the fluorescent X-rays from the interfering element are counted simultaneously with the same detector, this method needs only a single measurement. The main application is to the measurement of coal-ash by X-ray back-scatter.[10,42] The back-scattered X-ray intensity varies with ash content but variations in iron content give rise to a severe matrix absorption effect. Simultaneous excitation and detection of iron K X-rays eliminates this source of error. It has also been shown possible to eliminate interference by iron from the determination of tin in tin ores.[9]

### METHODS MORE SUITED TO "ON-STREAM" ANALYSIS—

When the measuring head is a fixed installation such as in "on-stream" or laboratory analysis other methods of overcoming matrix effects are available. These are not suitable for use with portable analysers because they involve either special sample presentation or more than one measuring head.

*Sample dilution*—The dilution method[9,10,15,38] is ideally suited to the "on-stream" analysis of pulverised ores which are usually transported as aqueous slurries. The variability of the mass attentuation coefficient of the total sample is reduced by adding a large proportion of diluent. The intensity of the required radiation is also reduced, but to a smaller extent,[10,15] so that the net effect is to reduce errors arising from matrix absorption. Interference by lead and iron in "on-stream" analysis of zinc ores was reduced to acceptable proportions by ensuring that the water content exceeded 85 per cent. w/w.[15] However, dilution to 10 per cent. of solids did not eliminate the effects of iron in "on-stream" analysis of tin and barium ores,[9,16] and further dilution reduced the sensitivity of the method to an unacceptable extent.

*The "transmission correction" method*—Two further methods of eliminating matrix absorption effects have been used in "on-stream" and laboratory analysis. The first is "transmission correction,"[9,15,16] which involves additional measurement of the X-ray intensity transmitted through a sample of fixed or known mass per unit area. It can be shown[15] that the ratio of fluorescent to transmitted intensities can be made independent of changes in concentration of all elements likely to give matrix absorption errors, by suitable choice of sample mass per unit area or source energy,[9] or both. Fig. 8 shows that complete elimination of the effect of iron on the determination of tin in tin ore slurries[9] is possible. The method has also been used in the analysis of copper[15] and barium[16] ores.



(a) (b)

Fig. 8. Calibration graphs of (*a*) tin K fluorescence, and (*b*) ratio of fluorescence to transmission, against tin and iron concentration for tin ore slurries of 10 per cent. solid content. Excitation by americium-241 - barium source - target assembly

*Balanced targets*—The use of source - target assemblies in "on-stream" analysis has so far been restricted to twin measuring heads, each with the same source - target assembly to excite the required fluorescence, and each with one of the pair of balanced filters necessary to isolate the fluorescence.[16] Often the analytical line needs to be isolated only from the scattered radiation and this can sometimes be achieved satisfactorily with a single absorption-edge filter[18] (see under "Adjustment of detectable response"). Carr-Brion (in a private communication) has proposed[43] that the twin measuring head should then be fitted with two different targets, one to excite the desired fluorescence and the second, with its energy below the absorption edge of the element being excited, to provide back-scattered X-rays for correction of inter-element effects. The ratio of the two detector outputs is insensitive to matrix absorption effects as the fluorescent and back-scattered radiations are absorbed to an approximately equal extent in the sample. Interfering fluorescence, as it is excited nearly equally by both targets, is also corrected provided that its intensity is relatively low. It is found that the analytical sensitivity is comparable with that obtained by using balanced filters.

## MATRIX ENHANCEMENT

Enhancement of the required radiation caused by secondary excitation within the sample by fluorescent X-rays of higher energy is neither a large nor a widespread cause of error in ore analysis. The higher energy X-rays need never be excited if the optimum choice of source can be made. In alloys in which several adjacent elements often occur in high concentration, enhancement can be an important effect but has, to the author's knowledge, rarely been encountered in radioisotope X-ray spectrometry. The determination of chromium in steels[13] is facilitated by the enhancement of chromium K by iron K X-rays. Serious errors (comparable with statistical errors) are not introduced because the concentration of iron does not change by a large factor independently of that of chromium. However, in measuring the nickel content of nickel - copper - zinc alloys, enhancement caused by zinc K X-rays is a large effect and must be corrected by separately measuring the approximate zinc content.[13]

## EFFECTS OF FINITE PARTICLE SIZE

In heterogeneous materials the absorption of X-rays varies from particle to particle depending on the mass attenuation coefficient and size of the particles. Thus the integrated fluorescent intensity from a sample is a function of the size and composition of the particles. Claisse[44] has studied a relatively simple system containing "fluorescent" and "non-fluorescent" particles (*e.g.*, a tin ore composed entirely of tin(IV) oxide and silica). He has shown that the fluorescent intensity usually increases with decreasing particle size until the absorption in an individual particle is only a few per cent., when the dependence on particle size disappears. The maximum rate of change of fluorescent intensity with particle size depends on the exciting and fluorescent energies but generally coincides with the most common particle sizes of ground material (0·01 to 1 mm). An example of this effect is shown in Fig. 9 in which the calculated[44] lead K X-ray intensity from a lead sulphide - silica system is plotted against particle size. In this instance both exciting and fluorescent radiations are relatively penetrating, so that the "transition zone" occurs at larger particle sizes than usual.

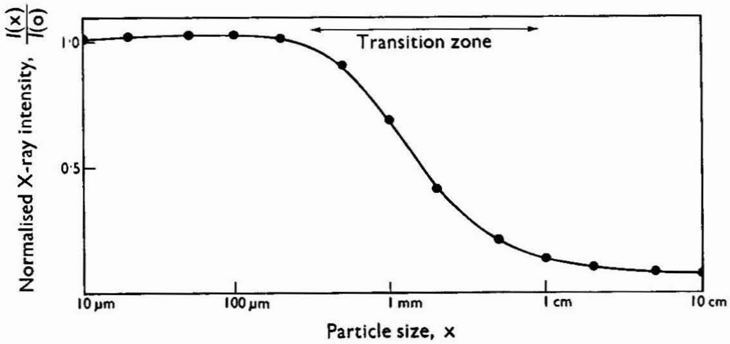


Fig. 9. Calculated variation of lead K X-ray intensity (excited by cobalt-57) with particle size for 10 per cent. w/w lead sulphide in silica

At relatively large sizes where the radiation only penetrates the surface, the fluorescent intensity again becomes independent of particle size. However, with sizes from 1 to 10 mm, surface irregularity and changes in geometrical packing can cause large errors. Also, representative sampling may be difficult. Even on a smooth rock surface the coarse granular structure gives rise to similar errors. These make *in situ* assay of rock surfaces and core samples with the portable analyser only semi-quantitative. Nevertheless, this type of assay is extremely valuable in the absence of alternative methods suitable for field use.

### METHODS OF OVERCOMING PARTICLE-SIZE EFFECTS—

The usual laboratory method of overcoming particle-size effects is to remove the heterogeneity by fusing the sample,[38] but this is considered to take too long for process control applications. However, Imamura[24] uses fusion to prepare samples for an instrument intended for the analysis of cement raw mix in plant control. Sample preparation time is stated to be 10 minutes. In Starnes' "on-stream" analyser[14] the primary sample can be rapidly ground before continuous presentation to the measuring head. This form of sample preparation will not necessarily reduce the maximum particle size below that which gives significant absorption, but can result in a fairly constant particle-size distribution. There is, of course, the danger of increasing the range of particle sizes if the hardness of the minerals present varies greatly.

White[45] has adopted an even simpler approach for the analysis of iron-ore sinter-mix. Portions of the primary sample are hydraulically pressed into moulds giving crushed pellets with a smooth surface and constant bulk density. These are presented automatically to the measuring head, counted and ejected from their moulds. Counts are totalled from enough pellets to make up a representative sample.

The design of flow cells for presenting slurries has, until recently, been concerned with ensuring sufficient turbulence to prevent segregation of solids while avoiding too rapid window wear.[14,16] It should be possible to design flow cells to promote controlled segregation of large and small particles. Holland-Batt[46] (in a private communication) has based development of an "on-stream" particle-size analyser on this principle. On the other hand, as coarse grains are responsible for the reduction in fluorescent intensity, controlled segregation could be used to make them pass closer to the measuring head than the finer grains[47] (P. E. Starnes in a private communication).

Physical methods of reducing errors caused by particle-size variations have not yet been thoroughly investigated, although the effects themselves are well known. The higher the fluorescent and exciting energies the larger the particle size can be before serious errors are caused. It is therefore preferable to excite K rather than L X-rays of heavy elements, and Martinelli[33] reports negligible error from particle sizes up to 0·16 mm in determining lead in lead ore slurries, which is to be expected (see Fig. 9). The use of high exciting energies, *i.e.*, energies well above the absorption edge of the element to be determined, is often incompatible with efficient fluorescent excitation.

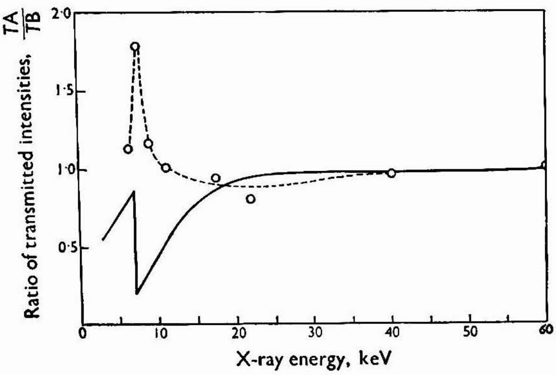


Fig. 10. Ratio of X-ray transmission through two iron ore samples as a function of energy, showing large particle-size effect near the iron K absorption edge. Sample A: iron content, 68·6 per cent.; approximate mean particle size, 65 μm. Sample B: iron content, 50·7 per cent.; approximate mean particle size 50 μm. The solid curve is the calculated transmission ratio for homogeneous samples

Radiation transmitted through, or back-scattered from, a heterogeneous sample is also a function of particle size. The intensity of back-scattered radiation varies in a similar manner to that of fluorescent radiation (see above) whereas the transmitted intensity increases with increasing particle size. The rapidity of this increase is greater the higher the attenuation coefficient of the particles. This is illustrated in Fig. 10, which shows experimental values of the ratio of X-ray intensities transmitted through two briquetted iron-ore samples of different particle size but similar composition. The expected variation of transmitted ratio for homogeneous samples, which is caused only by the different composition (*i.e.*, iron content), is seen to differ considerably from the experimental values at energies between 20 keV and the iron K absorption edge. With samples of this nature the transmission correction method for eliminating matrix absorption effects would fail completely. However, the large effect could be used for correcting errors from particle-size variations. Any matrix absorption effects would, of course, have to be measured and corrected by other means.

The above considerations indicate that a general physical approach is possible, aimed at correcting the characteristic X-ray intensity for the effects of both variable particle size and matrix absorption. For instance, the transmitted or back-scattered radiation of any energy when the mass attenuation coefficient of the sample is high would be particularly sensitive to particle size. Measurement of the back-scattered intensity at an energy near the characteristic energy could be used to correct matrix absorption. As this energy is below the absorption edge of the element to be determined it would be in a region of relatively low mass attenuation coefficient (provided that the element has a relatively high concentration) and so the effect of particle-size variation would be small.

It remains to be seen to what extent this approach to eliminating errors arising from variable particle size will be successful in practice.

## CONCLUSIONS

Radioisotope X-ray analysis is in a phase of rapid development. The basic techniques of excitation and energy selection have been worked out but have not yet been evaluated for all possible applications. In many applications that have been studied, alternative methods have been used but not directly compared.

Excitation of atomic number 14 (silicon) and above presents no difficulty with X-ray, $\gamma$-ray or bremsstrahlung sources. The range of sources already available has been augmented by the development of source - target assemblies that emit nearly monochromatic secondary X-rays with high efficiency.

Elements of low atomic number (carbon to calcium) are readily excited with $\alpha$-particles. The use of $\beta$-particle excitation is limited to special cases.

For atomic numbers below 20 (calcium) high absorption coefficients present difficulties. The short radiation paths associated with the high efficiency geometry permit the use of air paths for atomic number 15 and above (phosphorus $K\alpha$ energy 2·0 keV); in a dispersive X-ray spectrometer the longer paths necessitate evacuation or helium flushing for detection of X-rays below calcium K (3·7 keV).

Detection limits vary from a few parts per million to 0·1 per cent. in counting times of up to a few minutes. The sensitivity obtainable depends on the available source energy, the energy of the required characteristic radiation, the composition of the matrix and the sophistication of the detection equipment. The simplest equipment in common use is a portable analyser in which a sodium iodide (thallium activated) scintillation detector and backed-off rate-meter are used. It relies entirely on physical methods of energy selection. Detectable limits obtained vary from 0·03 to 1 per cent. with rate-meter time constants of 4 and 16 seconds. With more sophisticated equipment, "on-stream" determination of atomic number 14 (silicon) and above is practicable, and detection limits for elements of atomic number 27 (cobalt) and above are in the order of 0·01 per cent.

A range of methods has been applied to the elimination of matrix absorption effects. Most of these methods are variants of those already well known to conventional X-ray spectrometry, and in most applications matrix absorption or enhancement effects can now be satisfactorily eliminated.

Analysis of heterogeneous materials, such as ores, is subject to errors arising from variations in particle size. These effects are difficult to correct and the heterogeneity is not easily removed except by fusion techniques, which are virtually limited to the laboratory. Most progress has been made with methods of rapid sample preparation and presentation designed to minimise particle-size effects. There seems to be scope for development of physical methods of correcting errors arising from variable particle size.

Excitation of the K rather than the L X-rays of heavy elements considerably reduces the effects of heterogeneity and, when radioisotope sources are used, presents no special problems. In contrast, the established practice in conventional X-ray spectrometry has been to excite L X-rays of heavy elements because otherwise it is necessary to use high X-ray tube voltages and special crystal monochromators.

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# Rapid Determination of Molybdenum in Alloy Steels by Atomic-absorption Spectroscopy in a Nitrous Oxide - Acetylene Flame

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Atomic-absorption spectroscopy at 3132 Å in a nitrous oxide - acetylene flame provides a rapid and precise determination of molybdenum in low and high alloy steels. The steel sample (1 g) is dissolved in hydrochloric and nitric acids which are then diluted to volume and sprayed directly into the flame. The observed absorbance is compared with that obtained from a calibration graph prepared from solutions containing known amounts of molybdenum and about the same amount of iron as the steel sample. The method proposed here operates in the range down to 0·2 per cent. of molybdenum and is free from interference from other alloying elements, including tungsten, in steel. The proposed method can be applied to any type of steel by using a single calibration graph.

The determination of elements that form refractory oxides in an air - acetylene flame requires that the flame be luminous (fuel-rich) to provide reducing conditions, before appreciable absorption by atomic species can be observed. David,[1] and later Mostyn and Cunningham,[2] have described the determination of molybdenum in steels by using such a flame. It is possible, however, to obtain a population of ground-state atoms suitable for atomic-absorption spectroscopy by the use of a non-luminous nitrous oxide - acetylene flame,[3] which is both oxygen-free and sufficiently hot to promote dissociation of most salts. This paper reports the determination of molybdenum in alloy steels by direct atomic-absorption spectroscopy at 3132 Å in a flame of this type.

The sample is dissolved in a mixture of hydrochloric and nitric acids and the diluted solution is sprayed directly into the flame, when the molybdenum absorbance at 3132 Å is measured. The molybdenum content of the sample is then determined from a calibration graph obtained from pure aqueous molybdate solutions containing amounts of acid and iron similar to those present in the sample.

## Experimental

The equipment used in this work was the Unicam SP900A flame spectrophotometer with a Unicam molybdenum hollow-cathode lamp. The instrument conditions used throughout were: slit width, 0·02 mm; wavelength, 3132 Å; lamp current, 15 mA. The burner supplied with the SP900A for atomic-absorption measurements in air - acetylene was replaced by a brass burner of similar dimensions for the nitrous oxide - acetylene flame (*cf.* Fig. 1). The burner head-plate used, however, had a slit 2 inches long and 0·015 inch wide, and was cooled by an attached water-cooled plate clamped to the side of the burner. This system requires that a larger acetylene jet (0·052 inch in diameter) be used at the base of the burner than when an air - acetylene burner and flame are used. Aspiration via the SP900A atomiser was by nitrous oxide (pressure 15 lb per sq. inch) and the acetylene pressure used was just sufficient to produce the maximum height of red "feather" in the flame without luminosity. The burner height was adjusted so that as much as possible of the converging light beam from the hollow-cathode lamp passed through the red "feather" above the primary reaction zone. The strongest absorbance for molybdenum is always obtained in this band, which is highly characteristic of the nitrous oxide - acetylene flame. The flame was first ignited on an air - acetylene mixture, and the air was then gradually replaced by nitrous oxide (via two rotameters and a T-piece arrangement) until the air was completely shut off.

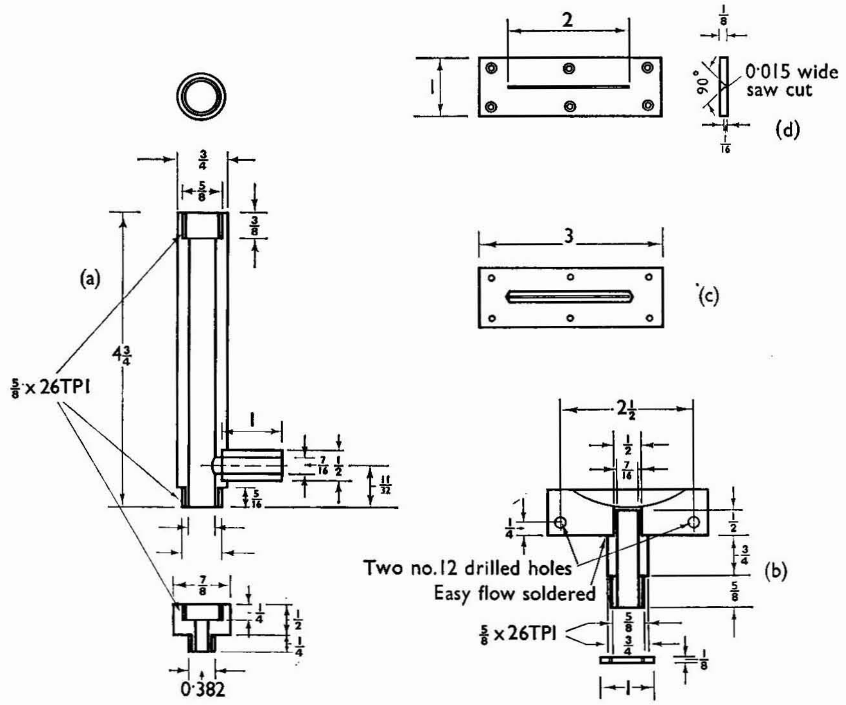

Fig. 1. Diagram showing burner parts with dimensions; all measurements are in inches. (*a*) Burner pre-mixing chamber, side view; (*b*) burner head, side view; (*c*) under surface of burner-head plate; (*d*) upper surface of burner-head plate

### REAGENTS—

*Molybdenum(VI) solution,* 0·1 M—Dissolve 17·66 g of analytical-reagent grade ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in 1 litre of distilled water in a calibrated flask.

*Iron(III) chloride solution*—Weigh 48·46 g of analytical-reagent grade iron(III) chloride, $FeCl_3.6H_2O$, and dissolve in 100 ml of distilled water.

1 ml of solution ≡ 0·1 g of iron(III).

### PREPARATION OF CALIBRATION GRAPH—

Transfer accurately 0·5, 1·0, 2·0, 3·0 and 4·0 ml of 0·1 M molybdenum solution to a series of 100-ml calibrated flasks. Add 10 ml of the standard iron solution, 20 ml of concentrated hydrochloric acid and 2 ml of nitric acid to each, and dilute to 100 ml with distilled water. Measure the absorbance of the solutions at 3132 Å in the nitrous oxide - acetylene flame. The calibration graph is linear and passes through the origin.

### PREPARATION OF SAMPLES—

Weigh accurately about 1·0 g of the steel sample into a 100-ml beaker. Add 20 ml of concentrated hydrochloric acid and 2 ml of concentrated nitric acid, and warm to aid dissolution. After effervescence has ceased, boil the solution. Cool, dilute to 50 ml with distilled water, and transfer to a 100-ml calibrated flask. For low alloy steels, dilute to 100 ml with distilled water. For high alloy steels, add the calculated volume of iron(III) chloride solution to make the total weight of iron present about 1 g, and then dilute to 100 ml with distilled water. Spray the solutions into the nitrous oxide - acetylene flame using the instrumental conditions described above, and measure the absorbance of the 3132 Å molybdenum line for each sample. By interpolation, determine the molybdenum content of each from the calibration graph.

## RESULTS AND DISCUSSION

A calibration graph was prepared for molybdenum in the range 20 to 200 p.p.m. in an aqueous solution (absorbance 0·06 to 0·39, 2 p.p.m. of molybdenum giving 1 per cent. absorption at 3132 Å). When the molybdenum solutions were 2 M with respect to hydrochloric acid and contained a similar amount of iron (1 g) to that present in the steel samples taken, it was found that the absorbance values were severely depressed. A more detailed investigation of the effect of iron on the molybdenum absorbance revealed that, provided the solution aspirated was about 1 per cent. with respect to iron(III), the ratio of excess of iron to molybdenum was not critical for the production of a rectilinear calibration graph.

Determination of the atomiser efficiency for a pure aqueous 200 p.p.m. molybdenum solution and for a similar solution which contained 1 per cent. of iron and was 2 M with respect to hydrochloric acid, revealed only slightly lower efficiency of sample transfer to the flame for the solution containing iron. The suppression of the molybdenum signal therefore results from the presence of the iron itself in the flame. It was therefore decided that if 1-g samples of low alloy steels were to be taken, their molybdenum content would have to be obtained by comparison with a calibration graph prepared from standards containing similar amounts of iron (1 g per 100 ml) and hydrochloric acid. This calibration graph is linear, passes through the origin, and produces absorbance values between 0·08 and 0·49 for 50 and 400 p.p.m. of molybdenum (3·3 p.p.m. of molybdenum produce 1 per cent. absorption). This procedure works well for the rapid determination of molybdenum in low alloy steels, as shown in Table I.

TABLE I

DETERMINATION OF MOLYBDENUM IN ALLOY STEELS

| Sample number | Certificate analysis, molybdenum, per cent. | Molybdenum found, per cent. | Other major constituents, per cent. | | | | | |
|---|---|---|---|---|---|---|---|---|
| *Low alloy steel*— | | | | | | | | |
| B.C.S. 252/1 .. | 1·05 | 1·06, 1·04 | Nickel | 2·23 | — | | — | |
| B.C.S. 253/1 .. | 0·67 | 0·66, 0·67 | Nickel | 1·00 | Chromium | 0·99 | — | |
| B.C.S. 251/1 .. | 1·57 | 1·53, 1·56 | Nickel | 1·24 | Manganese | 1·5 | — | |
| B.C.S. 255/1 .. | 0·30 | 0·30, 0·31 | Nickel | 4·98 | — | | — | |
| B.C.S. 256/1 .. | 0·53 | 0·53, 0·52 | Chromium | 2·3 | Manganese | 1·02 | — | |
| B.C.S. 258/1 .. | 0·83 | 0·83, 0·84 | Chromium | 1·29 | — | | — | |
| *Alloy*— | | | | | | | | |
| B.C.S. 219/2 .. | 0·43 | 0·46, 0·42 | Nickel | 2·54 | Chromium | 0·8 | — | |
| B.C.S. 220/1* .. | 5·20 | 5·15, 5·30 | Chromium | 5·13 | Tungsten | 6·8 | Vanadium | 2 |
| B.C.S. 241/1* .. | 0·52 | 0·52, 0·53 | Chromium | 5·03 | Tungsten | 19·6 | Cobalt | 5·6 |
| B.C.S. 246 .. | 2·89 | 2·89, 2·86, 2·98 | Chromium | 18·8 | Nickel | 12 | Niobium | 0·8 |
| B.C.S. 336 .. | 2·42 | 2·50, 2·42, 2·40 | Chromium | 17·6 | Nickel | 9·5 | Manganese | 0·8 |
| 62/16/2 XB stainless .. | 1·10 | 1·17, 1·10 | Chromium | 13·6 | Nickel | 10·2 | Manganese | 1·4 |
| 62/16/3 XC stainless .. | 2·25 | 2·28, 2·24 | Chromium | 15·46 | Nickel | 10·13 | Manganese | 1·37 |

* 2 ml of 40 per cent. hydrofluoric acid was added to both sample and standards to retain tungsten in solution.

When applied to high alloy steels, however, the incorporation of 1 g of iron into the standard solutions used to prepare the calibration graph results in over-compensation, as the steel samples taken contain only 60 to 80 per cent. of iron. The procedure adopted for these samples was, therefore, modified, and additional iron in the form of standard iron(III) chloride solution was added to the 1-g steel samples after dissolution to make the total weight of iron present about 1 g. This procedure enables the correct result to be obtained for this type of steel. The results for these analyses are also shown in Table I.

It is also possible, when only high alloy steels are to be analysed, to construct a calibration graph from standard solutions containing the same weight of iron (0·6 to 0·8 g) as that present in the high alloy steel samples. This would allow a more sensitive means of determining molybdenum in high alloy steels, but would necessitate the use of two calibration graphs. The method proposed here sacrifices some sensitivity for these high alloy steels, but is applicable to all types of steel with only one calibration graph.

After sample dissolution and dilution, two steel samples and two standard check solutions may be aspirated and measured in 10 minutes. The method is, therefore, easy to operate, and is rapid and precise in practice. No chemical manipulation or pre-treatment of the steel sample is required other than its dissolution in acid. A method could be devised to analyse steels of lower molybdenum content with some sacrifice of rapidity and simplicity by the introduction of a concentration stage involving extraction of the molybdenum from the iron into an organic solvent, either as molybdenum 8-hydroxyquinolinate or molybdenum(V) thiocyanate. It should then be possible to determine as little as 0·01 per cent. of molybdenum in mild and carbon steel by atomic-absorption spectroscopy. We have not examined this possibility here as most interest appears to lie in steels with molybdenum contents greater than 0·2 per cent.

### COMPARISON OF METHODS

David,[1] and Mostyn and Cunningham,[2] both used fuel-rich luminous air - acetylene flames for determining molybdenum. The sensitivities they report benefit from both scale-expansion of the signal attentuation and from the use of relatively long absorbance path lengths. The molybdenum absorbance also varies markedly with the composition of the air - acetylene mixture, and the sensitivities quoted are those obtained with the recommended flow-rates. These are not expressed in litres per minute of air and acetylene, and are thus difficult to compare. The sensitivity is higher in the richer flames, but the noise-to-signal ratio becomes rather great. Mostyn and Cunningham sacrifice considerable sensitivity by using the 3798 Å resonance line of molybdenum to reduce null meter noise. We have examined several other resonance lines of molybdenum, in addition to the 3132 Å line, and found them to give either inadequate sensitivity or high noise levels. Our findings for the 3798 Å resonance line with the nitrous oxide - acetylene flame agree well with those of David for luminous air - acetylene, *i.e.*, about half the sensitivity is obtained compared with that available at 3132 Å. The sensitivity, expressed as p.p.m. required to produce 1 per cent. absorption per unit path length, is, therefore, greater when using a non-luminous nitrous oxide - acetylene flame than both of those previously quoted and than that obtainable with our instrumentation when using a luminous air - acetylene flame, (*cf.* Table II). The sensitivity found by us for the air - acetylene flame agrees quite well with the manufacturer's quoted sensitivity (2 p.p.m.). It is physically more pleasant to work with the nitrous oxide - acetylene flame because it radiates less heat into the monochromator than the luminous air - acetylene flame, and the noise levels are considerably less than those obtained with air - acetylene. In addition, the absorbance owing to a given amount of molybdenum is not as dependent on the flame composition as it is with air - acetylene.

TABLE II

COMPARISON OF SENSITIVITIES FOR ATOMIC-ABSORPTION SPECTROSCOPY OF MOLYBDENUM

| | Flame and instrumental conditions | Molybdenum, sensitivity for 1 per cent. absorption, p.p.m. | |
|---|---|---|---|
| | | At recommended conditions | At unit path length |
| David[1] .. .. .. | A.C., scale-expansion, luminous air - acetylene, 10-cm path length, 3132 Å | 3·3* | 33* |
| Mostyn and Cunningham[2] .. | A.C., scale-expansion, luminous air - acetylene, 10-cm path length, 3798 Å | 1·3† | 13† |
| Proposed method .. .. | A.C., no scale-expansion, 3132 Å<br>(*a*) luminous air - acetylene, 7-cm path length | 2·3 | 16 |
| | (*b*) nitrous oxide - acetylene, 5-cm path length | 2·0 | 10 |

* Corrected for scale-expansion by David's own results.
† Uncorrected for scale-expansion (no results available).

The procedure recommended here for determining molybdenum in alloy steels requires considerably less sample pre-treatment than those used by David and by Mostyn and Cunningham. David points out that the addition of aluminium chloride to both sample and standard solutions will suppress all major interferences with molybdenum absorption and give a result for any sample solution to about 10 per cent. accuracy. He also suggests, to obtain more accurate results, that the major element composition be taken into account and the standards prepared accordingly, and that aluminium chloride should be added as before. Our results for the analysis of steels of different minor element compositions reveal that the addition of aluminium chloride is not necessary to suppress interference or to obtain accurate results if the major element is incorporated in the standards used to prepare the calibration graphs. Mostyn and Cunningham, however, found that addition of aluminium chloride and nitric acid to all solutions was not always effective in controlling interferences. They recommended the use of ammonium chloride as an interference suppressor in the determination of molybdenum in iron(III) alloys, and did not add iron to the standard solutions.

It is probable that these conflicting reports arise from the fact that the fuel-rich, air - acetylene flame acts as a rather inefficient medium for the production of molybdenum atoms. Our procedure reveals that the nitrous oxide - acetylene flame is more efficient and that these additions are not required. Mostyn and Cunningham also used the method of standard additions for their analyses, and did not achieve notably accurate results. In the method proposed here the only pre-treatment of samples arises with higher alloy steels when an addition of iron(III) chloride is made to compensate for matrix composition.

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# Determination of Small Amounts of Molybdenum in Niobium and Tantalum by Atomic-absorption Spectroscopy in a Nitrous Oxide - Acetylene Flame

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Between 0·006 and 0·06 per cent. of molybdenum can be determined in niobium or tantalum by extracting molybdenum(VI) 8-hydroxyquinolinate from a medium containing fluoride and EDTA as masking agents into butanol at pH 4·5, and atomic-absorption spectroscopy of the extract in a nitrous oxide - acetylene flame at 3132 Å without recourse to scale expansion. The most suitable conditions for the determination have been established, and a study of the effect of other cations and anions is presented. Vanadium(V) and chromium(VI) interfere when present in 100-fold excesses, but their interference can be eliminated by the addition of potassium sulphite to the solution before extraction.

THE determination of refractory elements in matrices which also form refractory oxides can be accomplished by atomic-absorption spectroscopy, if good sensitivity can be obtained by the provision of flame conditions suitable for the production of a large population of ground-state atoms of the element to be determined. Elwell and Gidley[1] have shown that use of the organic solvent effect, after separation by solvent extraction of the element to be determined, can produce increased sensitivity, and such a separation stage can make the procedure virtually specific. Our studies have been concerned with the determination of trace elements in niobium and tantalum by atomic-absorption spectroscopy.[2] Several workers[3,4] have reported the determination of molybdenum by atomic-absorption spectroscopy in an air - acetylene flame. They had to use a fuel-rich luminous flame to provide suitable reducing conditions to obtain a sufficiently large population of atoms and thus achieve a good sensitivity for molybdenum. However, the use of strongly luminous flames is physically unpleasant, and the photomultiplier receives high background radiation that can cause fatigue of the photo-responsive surfaces of the cathode, even although the continuum radiation is not amplified.

The use of a non-luminous nitrous oxide - acetylene flame[5] to obtain a population of ground-state molybdenum atoms suitable for atomic-absorption spectroscopy is reported here. Molybdenum is separated from niobium and tantalum by extraction of molybdenum(VI) 8-hydroxyquinolinate from fluoride medium at pH 4·5 into butanol. The butanol extract, to which butylamine is added to maintain molybdenum(VI) 8-hydroxyquinolinate in solution, is then aspirated into the nitrous oxide - acetylene flame for absorbance measurement at 3132 Å.

## EXPERIMENTAL

### APPARATUS—

The equipment used was the Unicam SP900A flame spectrophotometer, with a Unicam molybdenum hollow-cathode lamp. The instrument conditions used were: lamp current, 15 mA; wavelength, 3132 Å; and slit width, 0·02 mm. The burner for atomic-absorption measurements in air - acetylene supplied with the SP900A was replaced by a brass burner of similar dimensions for the nitrous oxide - acetylene flame. This burner, which has a slit 2 inches long and 0·015 inch wide, has already been described.[6] A nitrous oxide pressure of 15 p.s.i. was used, and sufficient acetylene to produce the maximum height of red "feather," above the primary reaction zone, without luminosity elsewhere in the flame. Measurements of absorption arising from molybdenum were made in the red "feather" zone of the flame. The flame was first ignited on a fuel-rich air - acetylene mixture (air pressure 15 p.s.i.) and the air was then gradually replaced by nitrous oxide (via two rotameters and a T-piece arrangement) until the air was completely shut off.

REAGENTS—

*Molybdenum solution*, $10^{-2}$ M—Dissolve 1·766 g of analytical-reagent grade ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in 1 litre of distilled water in a calibrated flask. Dilute this stock solution (960 µg of molybdenum per ml) to $10^{-3}$ M as required.

*Tantalum solution*—Dissolve 10 g of tantalum powder (obtained from Murex Ltd., Rainham, Essex) in 30 ml of 40 per cent. hydrofluoric acid and 3 ml of nitric acid (sp.gr. 1·42). Dilute the solution to about 500 ml, adjust to pH 4·5 with 4 M ammonia solution, and dilute to 1 litre to produce a 10,000-p.p.m. tantalum solution.

*Niobium solution*—Dissolve 10 g of niobium metal (obtained from Murex Ltd., Rainham, Essex) in 30 ml of 40 per cent. hydrofluoric acid and 12 ml of nitric acid (sp.gr. 1·42). Dilute the solution to 500 ml, adjust to pH 4·5 with 4 M ammonia solution, and dilute to 1 litre to produce a 10,000-p.p.m. stock solution.

*Buffered 8-hydroxyquinoline reagent*—Prepare a 1 per cent. solution of 8-hydroxyquinoline in pH 4·5 sodium acetate - acetic acid buffer. (100 g of hydrated sodium acetate and 150 ml of glacial acetic acid diluted to 1 litre.) All other reagents used should be of analytical-reagent grade.

PROCEDURE—

*Calibration graph for molybdenum in niobium (or tantalum)*—Transfer 1 to 10-ml aliquots of $10^{-3}$ M molybdenum solution to a series of 500-ml separating funnels. Add to each solution 150 ml of the 10,000-p.p.m. niobium (or tantalum) solution, 10 ml of a 0·1 M EDTA solution and 50 ml of the 1 per cent. 8-hydroxyquinoline reagent - buffer solution. Add 20 ml of butanol to each funnel and shake the flasks for 1½ minutes. Allow the solutions to stand for 15 minutes for complete phase separation to occur, and discard the aqueous layer. Add 5 ml of butylamine to each organic phase. Spray the clear organic phases directly into the nitrous oxide - acetylene flame and measure the absorbance at 3132 Å against a butanol solvent blank. The use of a butanol - butylamine mixture is not necessary, because the latter does not affect the absorbance readings.

*Preparation of samples*—Dissolve 1·5 g of niobium or tantalum in 4·5 ml of 40 per cent. hydrofluoric acid and add nitric acid (sp.gr. 1·42), 0·5 ml for tantalum and 1·75 ml for niobium. Dilute to about 75 ml, adjust the pH to 4·5 with 4 M ammonia solution, and then dilute the solution to 150 ml with distilled water.

## RESULTS AND DISCUSSION

A calibration graph for molybdenum in aqueous solution can be obtained in the range 20 to 200 p.p.m. of molybdenum (absorbance 0·06 to 0·39). This sensitivity is insufficient to permit the direct determination of small amounts (less than 0·1 per cent.) of molybdenum in niobium and tantalum to be made, and it is not possible to achieve these concentrations by dissolving a large sample of either metal in a small volume of solution suitable for atomic-absorption measurements. The preliminary separation of the molybdenum by extraction of molybdenum(VI) 8-hydroxyquinolinate into butanol was, therefore, adopted to provide a concentration of the molybdenum and to take advantage of the higher spraying efficiency of the organic solvent.

EXTRACTION PROCEDURE—

Chloroform has been the most extensively studied solvent for the extraction of molybdenum(VI) 8-hydroxyquinolinate from aqueous solution, and according to Starý,[7] quantitative extraction may be obtained with 0·01 M 8-hydroxyquinoline in chloroform in the pH range 1 to 5·5. Chloroform, however, is unsuitable as a solvent for atomic-absorption spectroscopy in a nitrous oxide - acetylene flame because during its aspiration it is not possible to make the flame sufficiently non-luminous to obtain the characteristic red "feather" of the nitrous oxide - acetylene flame. The noise-to-signal ratio is, therefore, high, and the flame resembles a luminous air - acetylene flame in its properties. For this reason we preferred to use butanol. Atomic-absorption measurements on both the aqueous and butanol phases over a range of pH values revealed that molybdenum(VI) 8-hydroxyquinolinate was extracted quantitatively into butanol from an aqueous solution, 0·016 M with respect to 8-hydroxyquinoline, in the range of pH 2 to 5. The extraction of molybdenum at pH 4·5 was not inhibited when the solution was also 0·08 M or 0·04 M with respect to niobium or tantalum, respectively, and 0·6 M and $5 \times 10^{-3}$ M in fluoride and EDTA, respectively. The presence of this concentration of EDTA permits the quantitative extraction of molybdenum from aqueous solutions containing large amounts of other ions (*e.g.*, copper, nickel and cobalt) that would otherwise interfere by consumption of the 8-hydroxyquinoline reagent. The concentration of fluoride present in the aqueous medium (0·06 M) is sufficient to retain the niobium and tantalum in solution as their fluoride complexes, and also to supplement the EDTA as a masking agent for foreign ions that would otherwise form their 8-hydroxyquinolinates and deplete the 8-hydroxyquinoline available for formation and extraction of molybdenum(VI) 8-hydroxyquinolinate.

### ORGANIC SOLVENT EFFECT—

Butanol, sp. gr. 0·8, is appreciably soluble in water (7·9 g per 100 ml at 20° C). An aqueous phase volume of 220 ml at room temperature should, therefore, dissolve about 20 ml of butanol. The high ionic strength of the aqueous phase containing the niobium or tantalum, fluoride and EDTA, however, suppresses the miscibility so that when 20 ml of butanol is equilibrated with the aqueous phase (220 ml) at room temperature, 4 ml of butanol solvent phase remain after separation. Over [the normal range of laboratory temperatures encountered, this phase volume is quite reproducible. The use of 25 or 30 ml of butanol for the extraction provides only one-half or one-third of the absorbance on measurement. This decrease in sensitivity is caused by the effective 2 or 3-fold increase in the butanol phase volume to 10 and 15 ml, respectively, after extraction.

After extraction of the molybdenum(VI) 8-hydroxyquinolinate into butanol at pH 4·5, the solution was allowed to stand for 15 minutes for complete phase separation to occur, and the aqueous layer was then rejected. The remaining butanol phase was cloudy and contained an appreciable amount of solid material, whereas the blank solutions that contained no molybdenum did not. This indicated that the precipitate was molybdenum(VI) 8-hydroxyquinolinate, and it was identified as such by filtering off, ashing and testing the dissolved residue (molybdenum trioxide) with 2-amino-4-chlorobenzenethiol hydrochloride.[8] The precipitate, caused by the limited solubility of hydrated molybdenum 8-hydroxyquinolinate in butanol, gave rise to poor reproducibility and lack of sensitivity when the butanol phase was directly aspirated for atomic-absorption measurements. A 5-ml portion of butylamine was, therefore, added to the butanol phase after separation. The amine displaces the water molecules coordinated to the molybdenum in the chelate and thus promotes solubility of the complex in butanol. This addition causes an improvement in reproducibility of the absorbance measurements, and effects an enhancement in sensitivity, even after allowing for the dilution effect, arising from the high atomiser efficiency of butylamine.

### CALIBRATION GRAPHS AND SENSITIVITY—

The calibration graphs obtained by the recommended procedure are linear in the range 96 to 960 $\mu$g of molybdenum, and correspond to the added 64 to 640 p.p.m. (0·006 to 0·064 per cent.) of molybdenum in the niobium or tantalum sample taken, which is equivalent to 1·5 g of either metal. The absorbance values corresponding to these concentrations are 0·07 and 0·735, respectively, for molybdenum in niobium, and 0·067 and 0·710, respectively, for molybdenum in tantalum. Both calibration graphs pass through the origin, and reveal that the niobium and tantalum metal available to us contained no detectable amount of molybdenum. Although the lowest amount of molybdenum determined in this study corresponded to 0·006 per cent. of niobium or tantalum, the adoption of scale expansion of the 80 to 100 per cent. transmission range, in a manner similar to that described by David,[3] would readily allow the determination of molybdenum to be effected down to 0·001 per cent.

### PRECISION AND ACCURACY—

To evaluate the precision of the method, nine simulated niobium-sample solutions containing the equivalent of 320 p.p.m. (0·032 per cent.) of molybdenum in niobium were analysed by the recommended procedure. The standard deviation obtained was 2·9 per cent. of the average absorbance. The analysis of nine similar tantalum-sample solutions gave a standard deviation of 2 per cent. of the average absorbance.

A measure of the accuracy of the method was obtained by the determination of molybdenum in synthetic niobium and tantalum solutions treated as unknown samples. The results of these analyses are shown in Table I.

TABLE I

DETERMINATION OF MOLYBDENUM IN NIOBIUM AND TANTALUM SOLUTIONS

| Molybdenum present, per cent. $\times 10^{-2}$ | Molybdenum found, per cent. $\times 10^{-2}$ | Metal present |
|---|---|---|
| 3·2 | 3·0 | tantalum |
| 4·5 | 4·7 | tantalum |
| 5·1 | 5·1 | tantalum |
| 1·9 | 1·9 | tantalum |
| 3·2 | 3·4 | niobium |
| 4·5 | 4·7 | niobium |
| 1·9 | 1·9 | niobium |
| 3·5 | 3·6 | niobium |
| 2·3 | 2·3 | niobium |

### INTERFERENCES—

The effect of foreign ions on the determination was investigated by observing their influence on the absorbance produced in the determination of 0·032 per cent. (480 $\mu$g) of molybdenum in niobium and tantalum. An ion was considered not to interfere, for the purpose of this study, when less than 5 per cent. error in absorbance was produced. In the presence of 10 ml of 0·1 M EDTA and from 0·6 M fluoride solution, the presence of a 100-fold excess by weight of the following ions produced no interference: Al, Ca, Co(II), Cu(II), Fe(III), Hg(II), K, Mg, Mn(II), Na, $NH_4$, Ni, Pb, Sn(IV), Ti(IV), Th, W(VI), Zn, Zr, acetate, chloride, fluoride and sulphate. The presence of a 100-fold excess of vanadium(V) and of chromium(VI) caused low results, but this was eliminated by the addition of 2 g of potassium sulphite to the aqueous solution before addition of the 8-hydroxyquinoline and extraction, and by boiling to promote formation of the chromium(III) - EDTA complex. It is well known that molybdenum(VI) is not reduced under these conditions, and we have checked this by observing no difference in molybdenum absorbance for synthetic mixtures of molybdenum with niobium and tantalum in the presence and absence of potassium sulphite. The vanadium(V) is easily reduced to the vanadium(IV) - EDTA complex, and the reduction of chromium(VI) to chromium(III) is similarly assisted by the EDTA present.

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# Excitation Gradients in Acetylene - Oxygen Flames

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The position of maximum emission in the flame gases and the optimum ratio of acetylene to oxygen has been established for representative atomic and ionic lines of eight elements. The elements and their lines (in millimicrons) are: antimony, 259·8; barium, 553·6; barium II, 493·4; boron, 249·7; cobalt, 345·4; iron, 372·0; iron II, 238·2; niobium, 405·9; tin, 254·7; and vanadium, 440·8.

DIFFERENT excitation conditions are encountered by metal atoms as they pass through the various zones of an acetylene - oxygen flame. Extending outwards and upwards from the tip of the burner are zones of over-excitation (the blue inner cone or primary combustion zone), reduction (the inter-conal gases in which occurs the transition from non-equilibrium to conditions of chemical and thermal equilibrium) and oxidation (the plume or outer mantle, the zone of secondary combustion with entrained air). In physical size these zones vary with the mixture ratio of acetylene to oxygen; in particular, the thickness of the inter-conal gases.

When one of the alkali metals is supplied to the flame, strong radiations emanate from all three zones.[1,2] For other elements their emission may be markedly stronger in a particular zone. For example, the spectrum of the inner cone of hydrocarbon flames provides a rich source of lines not observed in the plume of a flame.[3] Also, lines of a number of elements that are either absent or very weak in the plume of a normal lean acetylene - oxygen flame appear in unusual strength in the spectrum of a rich acetylene flame.[4] Workers in flame emission spectrometry tend to use only a single flame composition for all elements and to collect spectral emission from a fixed location within the flame gases. This tendency is to be deplored. Location of the site of maximum emission intensity within the flame and the selection of the optimum mixture ratio of acetylene to oxygen become critical if the analyst is to elicit a maximum signal (or, sometimes, a recognisable signal) for individual elements.

In this preliminary survey, the strongest atomic line for each of eight elements was studied. The selections include a representative group with respect to energy of excitation and energy of monoxide dissociation. Two ionic lines were included for comparison.

The mixture ratio or strength of a flame is defined as the actual volume of oxygen introduced into the flame divided by that required for the complete oxidation of the combustibles. The stoicheiometric equation for the combustion of acetylene to the products carbon dioxide and water requires 2·5 moles of oxygen per mole of acetylene. It can be assumed that an organic solvent would be burned to the same final products. The contribution of a combustible solvent must be included in computing the mixture ratio. In the experimental work the oxygen flow was maintained constant at 0·119 mole per minute (3·00 litres per minute). Thus, for a given solvent, the amount of solvent and oxygen introduced into the flame remained constant throughout the entire series of experiments. Only the acetylene flow was varied to alter the mixture ratio. The mixture strength is given by the appropriate expression—

$$\text{Mixture strength} = \frac{(\text{oxygen flow, } 0{\cdot}119 \text{ mole per minute})}{(\text{acetylene flow, mole per minute } (2{\cdot}5) + \text{ethanol aspirated, mole per minute } (3{\cdot}0))}$$

$$= \frac{(\text{oxygen flow, } 0{\cdot}119 \text{ mole per minute})}{(\text{acetylene flow, mole per minute } (2{\cdot}5) + \text{isobutyl methyl ketone aspirated, mole per minute } (8{\cdot}5))}$$

## EXPERIMENTAL

### REAGENTS—

Metals were added to the flame in the form of salts, soluble in ethanol or in isobutyl methyl ketone.

*Antimony*, 5000 *μg per ml*—This was prepared by dissolving 0·5986 g of antimony oxide, $Sb_2O_3$, in the minimum volume of fuming hydrobromic acid, evaporating the solution to about 10 ml on a steam-bath, and diluting to a final volume of 100 ml with isobutyl methyl ketone.

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*Barium,* 2000 *μg per ml*—This was prepared by dissolving 4·896 g of anhydrous barium perchlorate, $BaClO_4$, in 1 litre of ethanol.

*Boron,* 1000 *μg per ml*—This was prepared by dissolving 5·715 g of analytical-reagent grade boric acid in 1 litre of ethanol.

*Cobalt,* 5000 *μg per ml*—This was prepared by dissolving 6·175 g of fresh crystals of cobalt nitrate, $Co(NO_3)_2.6H_2O$, in 250 ml of ethanol.

*Iron,* 5000 *μg per ml*—This was prepared by dissolving 4·475 g of iron(III) sulphate, $Fe_2(SO_4)_3.6H_2O$, in 200 ml of 5 M hydrochloric acid and equilibrating the solution with exactly 200 ml of isobutyl methyl ketone for 10 minutes. All of the iron passes into the organic phase.

*Niobium,* 1000 *μg per ml*—This was prepared by dissolving 0·250 g of the metal in the minimum volume of a 1 + 1 solution of 48 per cent. hydrofluoric acid and concentrated nitric acid. The resulting solution was evaporated to incipient dryness and the residue was dissolved in 250 ml of ethanol.

*Tin,* 5000 *μg per ml*—This was prepared by dissolving 9·504 g of analytical-reagent grade tin(II) chloride dihydrate in 1 litre of ethanol.

*Vanadium,* 2000 *μg per ml*—This was prepared by dissolving 0·500 g of ammonium vanadate in about 50 ml of warm water, then adding 1 ml of concentrated hydrochloric acid and, slowly, about 5 g of hydroxylammonium chloride. The deep blue solution was evaporated to a volume of 5 ml, and concentrated nitric acid was added dropwise to destroy excess of the hydroxylamine. After effervescence from the nitric acid treatment had ceased, the solution was evaporated until it assumed the consistency of a thin paste, which was then dissolved in 100 ml of ethanol.

### EMISSION GRADIENTS—

The optical arrangement for measurement of emission gradients in a flame has been described by Carnes and Dean.[5] A hollow metal tube (light guide), 140 mm long and 6 mm in diameter, was placed on the optical axis between the Beckman total consumption nebulizer-burner and the mirror at the entrance to the Beckman DU monochromator. The mirror in the burner housing was blanked out. The inside diameter of the light guide corresponded to the usual height of the entrance and exit slits in the monochromator. Consequently, in the subsequent discussion, a region of observation in the flame is considered rather than a point source. From reversed optics, the circle of light observed over the burner was 15 mm in diameter. However, as shown by Carnes,[6] about 75 per cent. of the light gathered by the optical arrangement lay within a projected circle of radius 3 mm about the optical axis.

At height increments of 2 mm, the profiles shown in Fig. 1 were obtained when each species was emitting radiation. Emission readings are net emissions (line above background) *versus* burner height, and were measured relative to the tip of the inner cone because the height of the inner cone increases as the flame is made richer in acetylene. Each excitation profile was scanned past the light guide by movement of the flame, which was accomplished by vertical traversing screws attached to the burner support.[5] Readings were taken at each 2 mm of traverse.

## DISCUSSION

One feature observed for all ten emission lines is the richness of the flame that is required to elicit the stronger emission readings. A mixture strength of about 0·57 was the optimum for four of the emission lines that were studied, and a range of from 0·32 to 0·40 was the optimum for the remainder of the lines. The flame is nearly saturated with carbon vapour (smoke-point is generally stated to occur at 0·44). These mixture strengths strongly suggest that a burned gas composition corresponding to carbon monoxide and water vapour prevails and provides an environment favourable for existence of free atoms in the flame owing to the strong chemical reducing action of carbon. Rich flames are absolutely necessary if one is to obtain any signal from vanadium and niobium. This probably is owing to the large values for the dissociation energies of their monoxides. As the acetylene content of the flame gases is increased, a critical value is attained. The emission lines suddenly appear and increase markedly in brilliance as the mixture strength is further decreased until the optimum value is attained.

The boron line emission is critically dependent upon mixture strength; the optimum value lies within the range 0·37 to 0·40. Although not as critically dependent, the emission

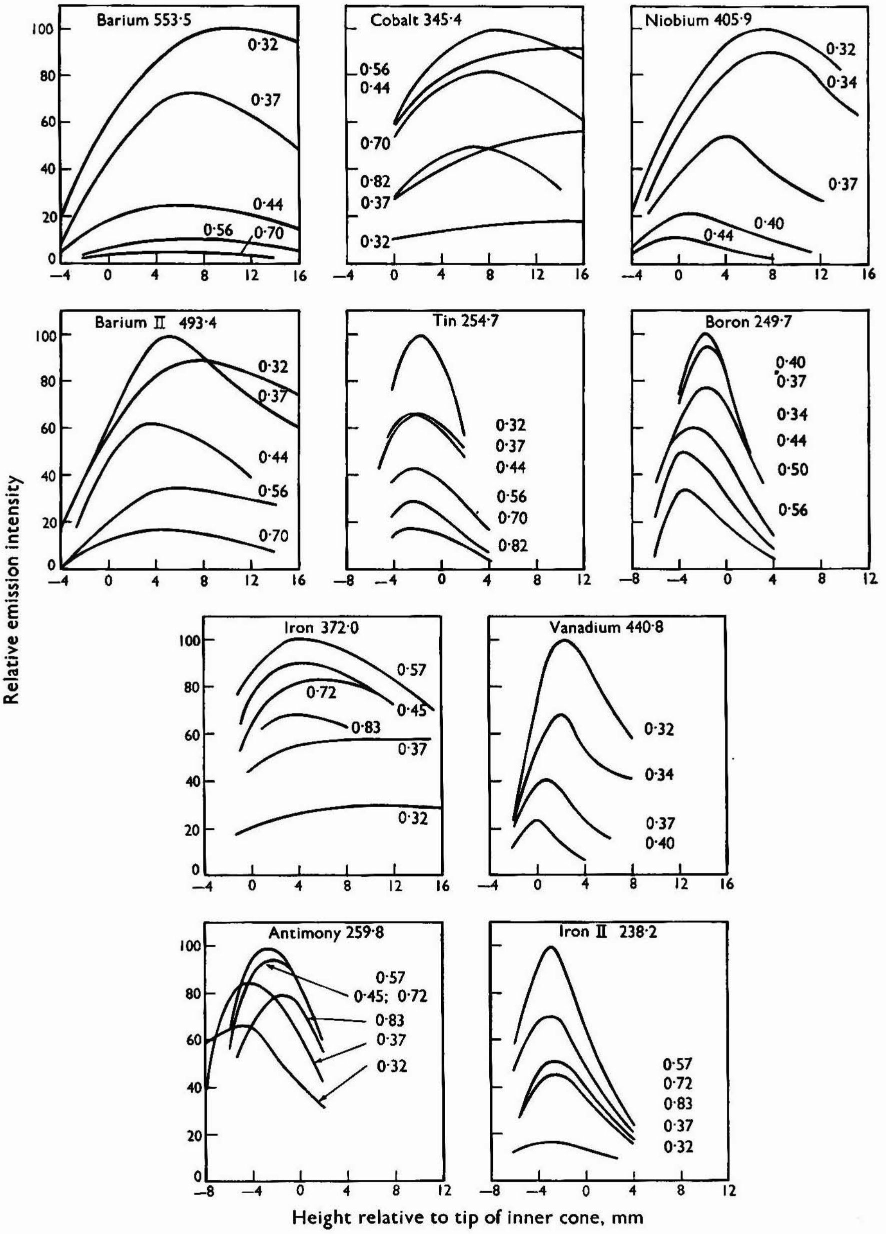

Fig. 1. Emission intensity as a function of height, relative to the tip of the inner cone with mixture strength of the flame as parameter

of both the atomic and ionic lines of barium and the atomic line of tin is strongest in very rich flames. For boron, the emission line at 248·7 m$\mu$, which appears only in the reaction zone, offers virtually the same signal strength as do the oxide bands in the interval 450 to 600 m$\mu$, while rendering it a simple matter to correct for background radiation as compared with the difficulty encountered with the overlapping oxide band systems.[7,8]

A second important parameter is the variation of the emission intensity through the flame front. Emission profiles reach a peak near the top of the inner cone for tin, boron, antimony and the ionic line of iron, and fall off rapidly in the outer mantle of the flame. At this point the fuel has been consumed completely. Occasionally, the location of the maximum signal shifts when the mixture strength changes (for example, antimony and the iron ionic line), but, generally, the position remains virtually fixed within the flame. It is unfortunate that commercial flame emission spectrometers do not generally possess facilities by which the vertical position of the burner may be quickly adjusted to take advantage of the enhanced emission features from within the inner cone, or the optimum location anywhere within the flame gases. Adjustable mounts have been described elsewhere.[9,10]

The emission gradient for barium 553·6 correlates well with the distribution of barium atoms in lean and rich air - acetylene flames recently reported by Rann and Hambly,[11] who used atomic-absorption measurements in their investigation. However, the peak emission readings show large differences between the rich and less rich flames, whereas the peak absorbances in Rann and Hambly's work show little difference (ratio of absorbances was 1·4). This could mean that a different mechanism exists for the production of excited atoms than for the production of ground-state atoms.

In agreement with previous results published by Buell[2] and by Zhitkevitch and co-workers,[12] the spectral lines that required excitation energies of 4·0 eV or less exhibited maximum emission above the tip of the reaction zone, whereas spectral lines requiring energies of excitation greater than 4·0 eV exhibited optimum emission within the inner cone (Table I). The notable exception is antimony, for which no explanation is offered. Excitation potentials not greater than 3·5 eV, but relatively high oxide dissociation energies, probably prevented the appearance of the line spectra of niobium and vanadium in ordinary lean flames.

For those interested mainly in the analytical utility of the spectral lines studied, the limit of detectability is included in Table I. The limit of detectability is considered to be the concentration of metal that results in a signal $2\sqrt{2}$ times larger than the root mean square *noise* signal (taken as the *fluctuation* of the background signal).

TABLE I

OPTIMUM REGIONS OF OBSERVATION, OPTIMUM MIXTURE STRENGTHS AND LIMITS OF DETECTABILITY

| Element | Wave-length of emission line, m$\mu$ | Optimum height above tip of inner cone, mm | Optimum mixture strength | Excitation energy of line, eV | Oxide dissociation energy, eV | Limit of detect-ability, $\mu$g per ml |
|---|---|---|---|---|---|---|
| Barium .. | 553·6 | 10 | 0·32 | 2·2 | 5·4 ± 0·5 | 1·1 |
| Cobalt .. | 345·4 | 8 | 0·56 | 4·0 | 4 | 0·8 |
| Niobium .. | 405·9 | 7 | 0·32 | 3·2 | 7·5 ± 0·6 | 8·0 |
| Barium II .. | 493·4 | 5 | 0·37 | 2·5* | 5·4 ± 0·5 | 3·0 |
| Iron .. .. | 372·0 | 4 | 0·57 | 3·3 | 4 ± 1 | 1·0 |
| Vanadium .. | 440·8 | 2 | 0·32 | 3·1 | 6·4 | 3·0 |
| Tin .. .. | 254·7 | −2 | 0·32 | 4·9 | 5·7 | 4·0 |
| Boron .. | 249·7 | −2 | 0·40 | 5·0 | 7·6 ± 0·4 | 15·0 |
| Iron II .. | 238·2 | −3 | 0·57 | 5·2† | 4 ± 1 | 11·0 |
| Antimony .. | 259·8 | −3 | 0·57 | 3·7 | 3·7 | 2·6 |

* Ionisation potential is 5·2 eV.
† Ionisation potential is 7·9 eV.

There are two important operating parameters which must be specified if maximum emission reading is to be attained from a particular emitting species in flame emission spectrometry. These parameters are the optimum region of observation within the flame and the optimum strength of the fuel gases. It is imperative to use a burner whose vertical traverse can be varied, and to insert flow-meters in the gas lines, if optimum emission conditions are to be explored and utilised. The sharper the excitation profile, the more critical becomes the burner position. Likewise, the mixture strength defines conditions for attainment of maximum emissivity.

Limits of detectability have been tabulated for each of the spectral lines studied.

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# The Absorption Spectra and Determination of Hexanitrodiphenylamine Complexes of Potassium, Sodium, Calcium and Magnesium

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A procedure is given for the determination of hexanitrodiphenylamine and some of its metal complexes, either individually, or in mixtures with each other. The reported similar behaviour of some related amines indicates that the procedure should be of general utility for the analysis of such complexes.

THE use of sequestering agents such as nitrated secondary amines has been suggested as a method for the separation of metals from solution. For example, Kolthoff and Bendix[1] reported the use of hexanitrodiphenylamine (dipicrylamine) for the determination of potassium. Kielland[2,3] reported similar specific behaviour of a large number of related amines (highly nitrated secondary amines) towards potassium.

The authors are interested in such separations, and have recently reported[4] a study of a procedure in which use was made of dipicrylamine for the selective recovery of potassium from saline water that contained multi-component mixtures of metallic ions. In the recovery procedure it was necessary to develop analytical methods for the determination of compositions in solid-phase mixtures of these complexes, and, as a consequence, the properties of individual metal complexes were also determined.

The procedures given here relate primarily to the identification and determination of the individual metal complexes of hexanitrodiphenylamine by absorption spectra methods. As a secondary objective, the method for determining mixtures of amine complexes of sodium, potassium, magnesium and calcium are discussed in relation to procedures used for the pure components and to applications such as the potassium recovery process.

## EXPERIMENTAL

### PROPERTIES OF THE INDIVIDUAL COMPLEXES—

In pure form, the metal complexes of these amines appear as highly coloured (red), crystalline solids. To identify these complexes, optical properties were studied and the spectrometric results for the visible, ultraviolet and infrared regions are given below.

### VISIBLE SPECTRA (350 TO 800 m$\mu$)—

Individual spectra of the four metal complexes with dipicrylamine in distilled water and acetone solutions were obtained with a recording double-beam instrument, the Bausch and Lomb Spectronic 505, with the solvent in the reference cell. For the aqueous solutions, the spectra of all of the complexes had very similar shapes with almost identical absorption peaks at 426 m$\mu$. The quantitative values for the absorbances determined for the potassium and sodium complexes and expressed as extinction coefficients in the Lambert - Beer model, are given in Table I.

The spectra of the four complexes in acetone solution were also quite similar. The absorption peak for the potassium complex occurred at a slightly lower value (415 m$\mu$) than in aqueous solution; the extinction coefficient for these conditions is also included in Table I. The absorbance of dipicrylamine was determined in acetone solution because the material is only slightly soluble in water. The shape of the absorbance curve of dipicrylamine in acetone was similar to that for the complexes, but the absorption peak occurred at 395 m$\mu$.

Close examination of the absorption values for the potassium complex in acetone revealed a small but significant deviation from the linear form of the Lambert - Beer model. For

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slightly ionised materials, the pertinent absorbance relationship contains two terms, these being absorbance by the amine ion as well as the metal complex. Absorption values for the potassium complex were interpreted on this basis, as shown in Table I. The excellent fit obtained suggests that the potassium complex is slightly ionised and that the potassium complex and the amine ion are characterised by extinction coefficients in acetone solution that differ.

TABLE I

EXTINCTION COEFFICIENTS IN THE VISIBLE REGION

| | | | Extinction coefficient* | | Concentration ($C$), mg per litre | |
|---|---|---|---|---|---|---|
| Compound | Solvent | Wave-length, mμ | litre per mg-cm | litre per gram-mole-cm | Range tested | Standard deviation† |
| Sodium - dipicrylamine complex | water | 426 | 0·0582 | 26,850 | 5 to 21 | 0·06 |
| Potassium - dipicrylamine complex | water | 426 | 0·0489 | 23,230 | 1 to 11 | 0·11 |
| Potassium - dipicrylamine complex | acetone | 415 | 0·0619‡ | 29,550‡ | 4 to 20 | 0·24 |

* Measured at 23° ± 3° C with a 1·0-cm cell by using 4 to 7 samples.

† Uncertainty, based on absolute differences between measured and calculated concentrations.

‡ All five values were fitted exactly (to three figures in absorbance) by the expression—

$$\frac{\text{absorbance}}{\text{cell length}} = mC + \sqrt{nC}$$

where $m$ = 0·0575 litre per mg-cm and $n$ = 0·000188 litre per mg-cm$^2$.

ULTRAVIOLET SPECTRA (200 TO 350 mμ)—

The absorbances of aqueous solutions were studied with the same instrument as was used for the visible region. Absorbance curves of similar shape and identical peak locations at 210 mμ were found for the sodium and potassium complexes. It is probable that the behaviour of the other complexes is the same. Extinction coefficients for the ultraviolet region are given in Table II.

TABLE II

EXTINCTION COEFFICIENTS IN THE ULTRAVIOLET REGION

| | | | Extinction coefficient* | | Concentration ($C$), mg per litre | |
|---|---|---|---|---|---|---|
| Compound | Solvent | Wave-length, mμ | litre per mg-cm | litre per gram-mole-cm | Range tested | Standard deviation† |
| Sodium - dipicrylamine complex | water | 210 | 0·0703 | 32,410 | 5 to 27 | 0·17 |
| Potassium - dipicrylamine complex | water | 210 | 0·0588 | 28,050 | 2 to 11 | 0·12 |

* Measured at 23° ± 3° C with a 1·0-cm cell by using 5 to 6 samples.

† Uncertainty, based on absolute differences between measured and calculated concentrations.

INFRARED SPECTRA (2·5 TO 18 μ)—

Absorbances were measured in this region with a double-beam instrument (Perkin-Elmer model 421). Spectra were obtained by using standard 300-mg potassium bromide pellets, 13 mm in diameter, containing about 0·2 per cent. of the metal complex in solid form. Reference pellets were not used.

The spectra for dipicrylamine and for the potassium and sodium complexes are given in Fig. 1. A major difference between curves is noted near 5·9 μ (1700 cm$^{-1}$); at this point, the sodium - dipicrylamine complex has a well defined absorption peak exhibited by none of the other materials. No such peak occurs in either the calcium or magnesium spectra, as may be seen in Fig. 2. Distinction between other complexes may be possible from an interpretation of the spectra between 6 and 8 μ, although these differences are not as well defined as the absorption peak for the sodium complex.

DETERMINATION OF MIXTURES—

We then considered the problem of determining the content of each of four metals in a solid-phase mixture of metal complexes. Direct determination of the metal content by emission spectra is not feasible because the compounds are mild explosives at temperatures above 200° C. From the visible, ultraviolet and infrared results given above for the individual complexes, it can be seen that optical properties are largely dictated by the amine molecule rather than the metals. It was therefore concluded that such absorption spectra cannot be used for the analysis of mixtures.

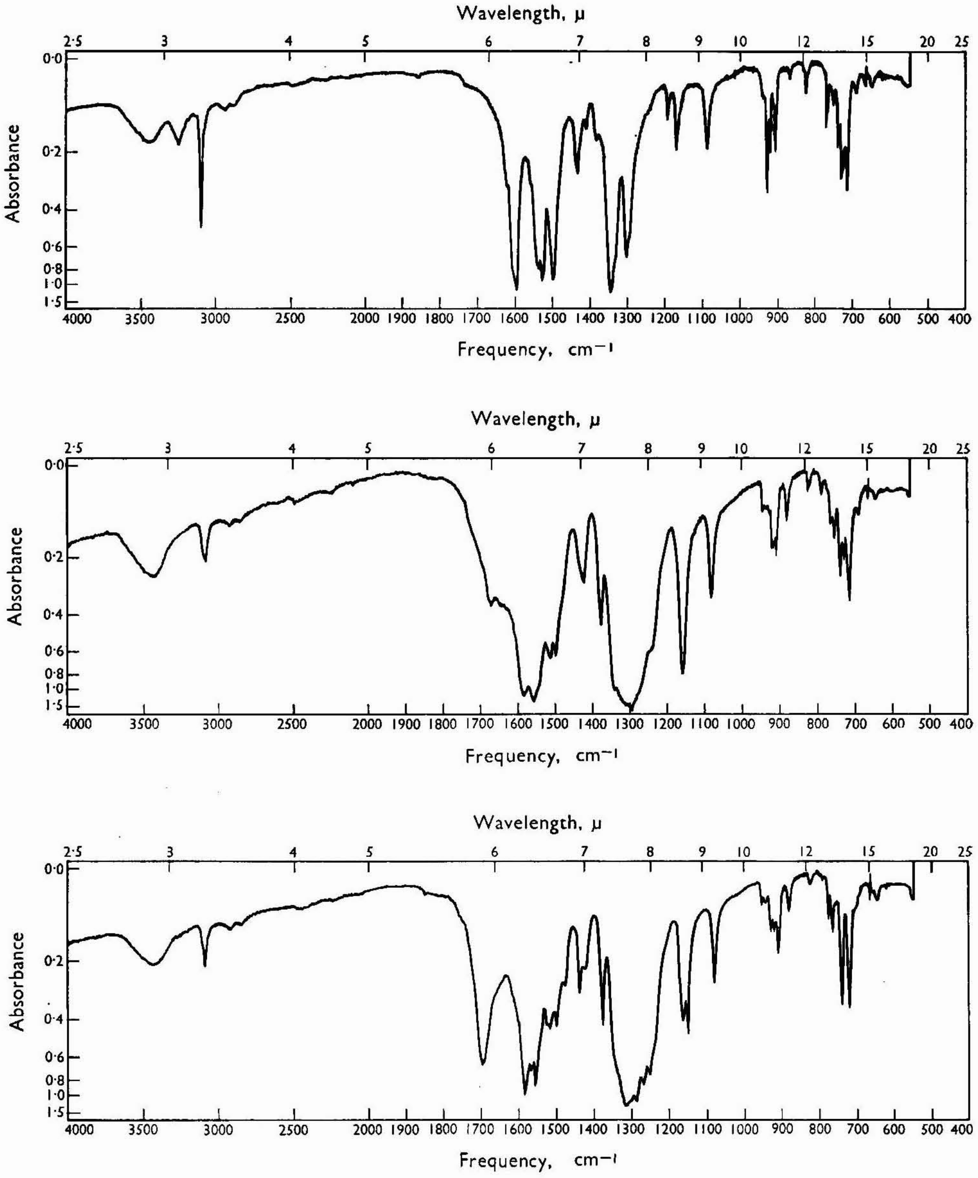

Fig. 1. Infrared spectra: top, dipicrylamine; middle, potassium dipicrylamine; bottom, sodium dipicrylamine

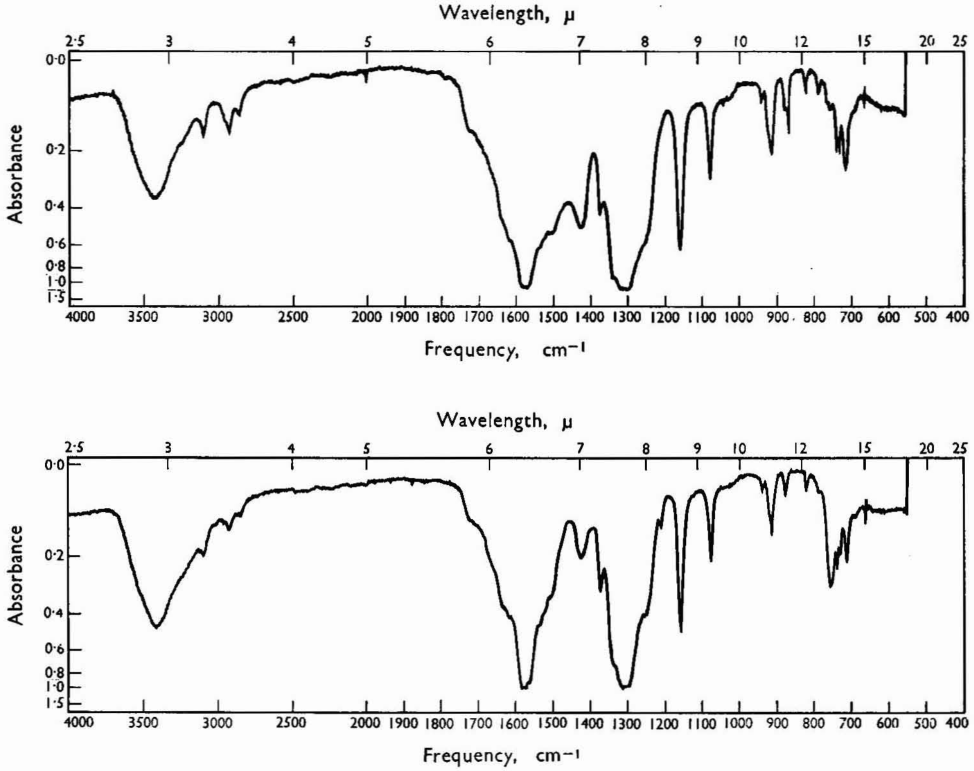

Fig. 2. Infrared spectra: top, calcium dipicrylamine; bottom, magnesium dipicrylamine

This problem was resolved by using a method that involved the decomposition of the complexes. In this method the complexes are quantitatively decomposed by mineral acid into insoluble dipicrylamine and soluble metal cations, the two phases are separated, and the dipicrylamine and metal compositions then determined by classical procedures. The amount of dipicrylamine produced may be determined gravimetrically,[4,5] and the metals present in the acid solution determined either gravimetrically or by flame photometry.

TABLE III

APPLICATION OF THE METHOD OF ANALYSIS*

| | Weight in sample† | | | | Calculated weight‡ | | Total weight of sample | |
|---|---|---|---|---|---|---|---|---|
| Sample or run number | Potassium, mg | Calcium, mg | Sodium, mg | Magnesium, mg | Potassium - dipicrylamine complex, mg | Calcium chloride, mg | Calculated | Determined§ |
| 26 | 22·5 | 10·5 | 0·15 | $<0·4$ | 273·5 | 30·5 | 304·0 | 301·8 |
| 31 | 23·3 | 9·5 | 0·2 | $<0·4$ | 282·8 | 27·8 | 310·6 | 308·4 |

* Chosen for comparison purposes, from the typical runs of Butt *et al.*[4]

† By flame-photometric analysis, in which the acid solution was diluted to 250 ml for magnesium, calcium and sodium, and to 2500 ml for potassium. These volumes are recommended for convenience of photometric calibration.

‡ Calculated stoicheiometrically from the potassium and calcium content.

§ The weight determined corresponds to the representative sample weight given by Butt *et al.*[4]

Some details of this decomposition method are as follows: the decomposition was effected by reacting about 300 mg of the mixture with about 2 ml of concentrated nitric acid in a 10-ml beaker at room temperature; the acidic solution of metallic ions was prepared for flame-photometric analysis by evaporating the solution to dryness at 150° C to remove the nitric acid, dissolving the residue in distilled water and diluting to a known volume; the gravimetric techniques were based on the precipitation of the potassium with chloroplatinate, precipitation of the calcium with oxalate and precipitation of the sodium with magnesium uranyl acetate. Other details of this method are available.[4,5]

This decomposition method was successfully used[4] to analyse solid precipitates obtained by treating sea water with the sodium complex of the amine. These precipitates could contain any of the four metal complexes, the pure amine, or other impurities such as chlorides or carbonates of the four metals. The success of this analytical method is illustrated by the two typical analyses given in Table III. These results indicate that the test samples contained a negligible amount of sodium and, within the precision of the method, no magnesium. The agreement between the calculated and determined values obtained for the total weight demonstrates the reliability of this method of analysis. Further applications of this method and discussion of the results obtained are reported elsewhere.[4]

Because the secondary amines studied by Kielland[2,3] have properties similar to those of dipicrylamine, the decomposition procedure outlined above should be of general use for the analysis of these materials and their metal complexes.

This work was supported by a grant from the Office of Saline Water, United States Department of the Interior. We thank the Perkin Elmer Corporation for assistance in determining the infrared spectra.

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# The Determination of Some Impurities in High Purity Beryllium by Differential Cathode-ray Polarography*

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Methods are described for the determination of copper, lead, cadmium, zinc, nickel, cobalt, iron and manganese in high purity beryllium by differential cathode-ray polarography. Impurities are separated by solvent extraction of diethyldithiocarbamates from buffered beryllium chloride solutions at pH 4·5 to 5·0, and elements determined in suitable supporting electrolytes. A technique has been developed for the separation of zinc and cobalt in 0·5 M pyridine - M potassium chloride by subtractive polarography by using reverse potential sweep. The methods give limits of detection of 0·2 p.p.m. for each element with a single 500-mg beryllium sample and have been applied to electrolytically refined metal.

Beryllium metal of 99·9 per cent. purity may now be obtained as a commercial product. At this and lower purity it has a low ductility, and fabrication of components requires melting and casting, or powder metallurgical routes before machining. In recent years metallurgists seeking a more fundamental understanding of the inherent properties of this metal have, to some extent, been successful in increasing the purity of the commercial product. This has necessitated improving analytical methods, and techniques such as radioactivation and spark-source mass-spectrometry have been used for metal that has been refined by zone-melting or vacuum distillation.[1,2,3] Emission spectrography has also been used successfully for the determination of many impurities at p.p.m. levels. These techniques, however, do not satisfy all requirements for the analysis of refined metal, and differential cathode-ray polarography has been examined as a supplementary method for a number of elements. Polarography has been applied to the analysis of beryllium to a limited extent, generally for low purity materials.[4,5,6] In differential cathode-ray polarography with the subtractive technique,[7] full instrumental sensitivity is readily obtainable, and this paper describes the application of this technique to the determination of copper, lead, cadmium, zinc, nickel, cobalt, iron and manganese to a limit of 0·2 p.p.m. with a single 500-mg sample.

## Experimental

Although beryllium is not electro-active, direct polarography at such low impurity concentrations was clearly impracticable. The impurities to be determined were therefore extracted from beryllium as diethyldithiocarbamates into ethyl acetate from buffered beryllium chloride at pH 4·5 to 5·0. Although offering little specificity, this system gives a clean and rapid separation, and the high solubilities of sodium diethyldithiocarbamate in water and of the metal chelates in the solvent enable small volumes to be used. Reagent blanks have been minimised by application of semi-micro solvent extraction techniques by using glass transfer pipettes for the separation of phases, and by using high purity reagents whenever available. Dry oxidation was used to destroy organic matter before applying polarography. This is effected by igniting below 500° C for a few minutes in the presence of a small amount of potassium chloride. No apparent loss of trace elements has been observed under these conditions, which is in agreement with the work by Gorsuch,[8] who used radiotracers.

A summary of the separation scheme is shown in Fig. 1.

### Supporting electrolytes—

Table I shows the supporting electrolytes used with approximate peak potentials referred to the mercury-pool anode.

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* Presented at a meeting of the Microchemistry Group on September 24th, 1965.

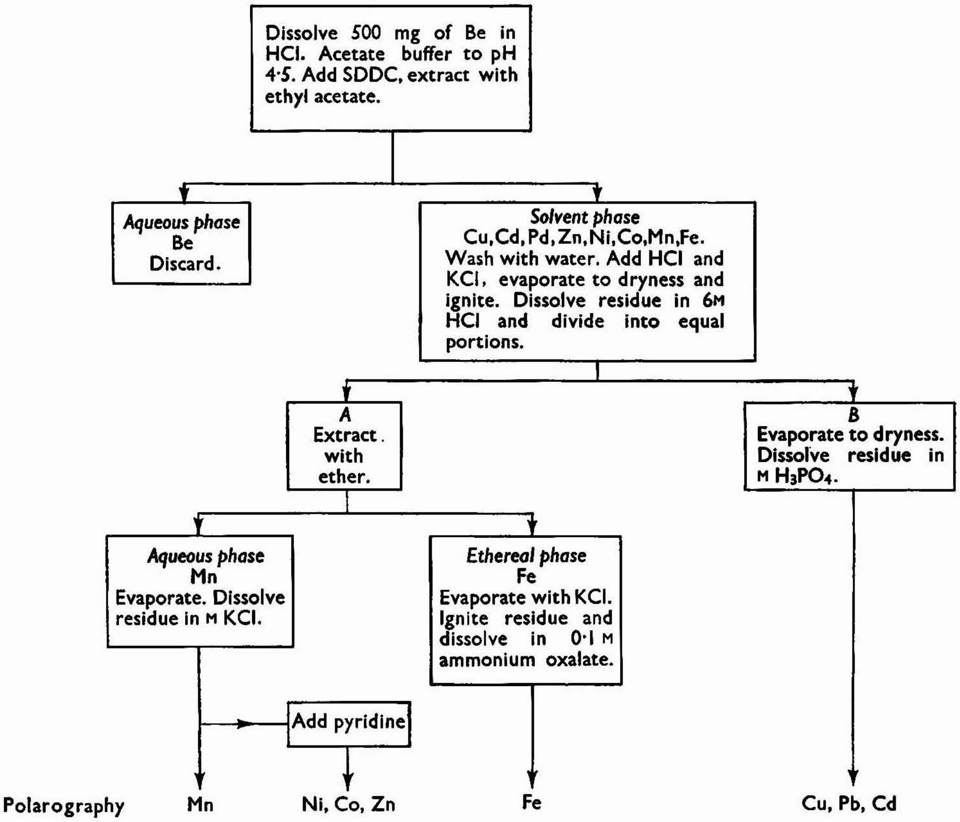

Fig. 1. Separation scheme

*Orthophosphoric acid*, M—The behaviour of a large number of ions in this medium has been studied by Milner and Slee.[9] The advantage of this medium is the non-interference of tin with lead and of indium with cadmium. Interference from the irreversible reduction of molybdenum(VI) in the determination of lead has also been observed, but can be eliminated by reverse potential sweep.

Attempts to determine zinc at low concentrations in this electrolyte, even by the subtractive technique, were unsuccessful owing to the close proximity of the hydrogen-ion reduction.

TABLE I

SUPPORTING ELECTROLYTES

| Electrolyte | Element | Approximate peak potential, volt (against mercury-pool anode) |
|---|---|---|
| Orthophosphoric acid M | Copper | −0·20 |
| | Lead | −0·65 |
| | Cadmium | −0·80 |
| | Zinc | −1·33 |
| Pyridine 0·5 M - potassium chloride M | Copper | −0·41 |
| | Cadmium | −0·67 |
| | Nickel | −0·83 |
| | Zinc ⎫ Forward | −1·05 |
| | Cobalt ⎭ sweep | −1·09 |
| Potassium chloride M | Manganese | −1·54 |
| | Iron | −1·45 |
| Ammonium oxalate 0·1 M | Iron | −0·34 |

*Pyridine*, 0·5 M - *potassium chloride*, M—Copper, cadmium and nickel are readily determined in this medium, although at low concentrations the copper wave is poorly defined. From Table I it may be seen that mutual interference arises for zinc and cobalt on the forward sweep. The composite wave for a mixture of 0·5 μg of cobalt per ml and zinc is shown in Fig. 2 (*a*). Resolution has been effected by utilising the differences in reversibility for the two reductions. Zinc may be determined on the reverse sweep, a single wave owing to the anodic oxidation of zinc being obtained (Fig. 2 *b*). The negligible contribution from cobalt is shown in Fig. 2 (*c*).

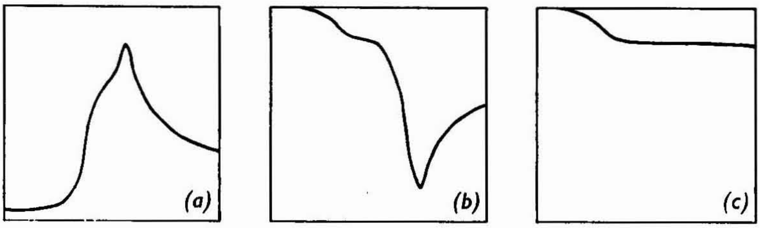

Fig. 2. Polarographic waves for: (*a*), 0·5 μg of zinc and 0·5 μg of cobalt per ml on forward sweep; (*b*), 0·5 μg of zinc and 0·5 μg of cobalt per ml on reverse sweep; (*c*), 0·5 μg of cobalt per ml on reverse sweep

For the determination of cobalt on forward sweep, the subtractive technique is used in which the zinc reduction wave is eliminated by equalising zinc concentrations in the two polarographic cells. This is conveniently carried out by adding a small volume of zinc standard to the blank cell from an Agla syringe pipette. This method has been shown applicable to solutions containing up to a 10-fold excess of zinc. The determination of cobalt in the presence of zinc by using a 0·5 M ammonia - ammonium chloride - dimethylglyoxime supporting electrolyte has been reported,[10] but the above technique was preferred as it utilises the solution used for the manganese determination.

*Potassium chloride*, M—This is used for manganese in preference to more selective supporting electrolytes, as well defined waves are observed at very low concentrations. Iron(III) is a serious interference in this medium, but is conveniently removed by extraction into ether from 6 M hydrochloric acid solution, and it can be subsequently determined in 0·1 M ammonium oxalate.

## METHOD

### APPARATUS—

*Davis differential cathode-ray polarograph, model A*1660—Manufactured by Southern Analytical Ltd.

*Agla micrometer syringe pipette.*

*Glass transfer pipettes*—Prepare from 5 mm i.d. Pyrex tubing and fit with a 2-ml rubber teat.

### REAGENTS—

If possible use foodstuffs or transistor grade reagents, or else a recognised analytical grade.

*Ammonia solution, sp.gr.* 0·88.

*Orthophosphoric acid*, M.

*Pyridine.*

*Nitric acid*, 6 M.

*Sodium hydroxide solution*, 10 M.

*Hydrochloric acid*, 6 M.

*Potassium chloride solution*, M.

*Ammonium oxalate solution*, 0·1 M.

*Ethyl acetate.*

*Diethyl ether*—Equilibrate with an equal volume of 6 M hydrochloric acid.

*Sodium diethyldithiocarbamate solution*, 10 *per cent.*, *w/v*—Dissolve 1 g of the reagent in 10 ml of water and filter the solution through a No. 41 filter-paper. Prepare a fresh solution daily.

*Sodium acetate buffer solution, pH* 5·0—Dissolve 82 g of anhydrous sodium acetate in 450 ml of water, and adjust the pH of the solution to 5·0 by the addition of 6 M hydrochloric acid.

PROCEDURE—

All polarographic potentials are referred to the mercury-pool anode and concentrations are calculated from suitable calibration graphs.

Accurately weigh 500 ± 5 mg of beryllium into a 50-ml conical flask. Stand the flask in a cold water bath and add 5 ml of water. Gradually add 10 ml of concentrated hydrochloric acid. When the reaction is almost complete, remove the flask and gently warm to ensure complete dissolution. Transfer the solution with the minimum of washing to a 50-ml beaker and adjust the pH to 4·5 to 5·0 by the dropwise addition of ammonia solution with a mechanical stirrer to assist in the re-dissolution of locally precipitated beryllium hydroxide. Transfer, with washings, to a 50-ml stoppered measuring cylinder.

Add 5 ml of sodium acetate buffer, 1 ml of the 10 per cent. sodium diethyldithiocarbamate (SDDC) solution, 10 ml of ethyl acetate, and shake the cylinder thoroughly. Allow the phases to separate, and then transfer the solvent phase to a 25-ml stoppered cylinder by using a glass transfer pipette. Repeat twice with 5-ml portions of ethyl acetate. Wash the combined extract with 5 ml of water and transfer the solvent phase to a 50-ml silica evaporating basin. Add 1 drop of M potassium chloride and 1 ml of concentrated hydrochloric acid. Cover with a watch-glass and remove the solvent by evaporation under an infrared lamp, blowing a gentle stream of air over the surface to assist evaporation. To the dry residue add 5 drops of concentrated hydrochloric acid and re-evaporate. Destroy organic matter by careful ignition for a few minutes, below 500° C. Dissolve the residue by warming with 5 ml of 6 M hydrochloric acid, transfer to a 10-ml stoppered cylinder and dilute to 10 ml.

(*a*) *Determination of copper, lead and cadmium*—Transfer 5 ml of the prepared solution to a silica basin, add 0·2 ml of M orthophosphoric acid and evaporate to dryness. Add 3 ml of M orthophosphoric acid and warm to dissolve the residue. Cool the solution and transfer a portion to the polarographic cell.

De-oxygenate, and determine copper, lead and cadmium subtractively against a blank prepared as above but omitting the sample. Record peak heights at −0·20, −0·65 and −0·80 volt, respectively.

(*b*) *Determination of manganese and iron*—To the remaining 5 ml of sample solution add 3 ml of diethyl ether, saturated with 6 M hydrochloric acid. Shake the solution and transfer the ether phase to a 50-ml silica basin. Repeat twice with 3 ml of ether and combine the extracts. Add 0·5 ml of concentrated hydrochloric acid and 0·1 ml of M potassium chloride solution to the ether and evaporate to dryness under an infrared lamp. Destroy the organic matter by dry oxidation. Moisten the residue with 0·5 ml of concentrated hydrochloric acid and re-evaporate. Dissolve the residue in 3 ml of 0·1 M ammonium oxalate and transfer a portion to a polarographic cell.

De-oxygenate and measure the peak height for iron subtractively at −0·34 volt.

For the determination of manganese, evaporate the aqueous phase from the ether extraction to dryness and then ignite to remove organic matter. Re-evaporate after adding 0·5 ml of concentrated hydrochloric acid, then again after the addition of 1 ml of water, and dissolve the residue in 3 ml of M potassium chloride. Transfer a portion to the polarographic cell, de-oxygenate and determine the peak height subtractively at −1·54 volt.

(*c*) *Determination of nickel, cobalt and zinc*—Add 0·1 ml of pyridine to the solution in the polarographic cell used for the manganese determination. Add an equal volume to the reference cell and de-oxygenate. Determine the nickel peak height at −0·83 volt. Switch the polarograph to the reverse potential sweep mode of operation and determine the zinc peak height by using a starting potential of 1·20 volt. Determine the zinc concentration by the standard addition technique. With an Agla micro-syringe pipette add a calculated volume of zinc standard to the reference cell to equalise the zinc concentration in both cells. Finally, equalise the volume in both cells by the addition of M potassium chloride solution to the sample cell. De-oxygenate and measure the cobalt peak height on the forward sweep at −1·00 volt.

## RESULTS

The methods described have been evaluated by the analysis of synthetic solutions prepared by the addition of metal standards to pre-extracted beryllium solutions. The results, together with total reagent blanks accumulated during the procedures, are shown in Table II.

TABLE II

RECOVERY EXPERIMENTS IN THE PRESENCE OF BERYLLIUM

| Element | Amount added, µg | Amount found (compensated for blank), µg | Reagent blank, µg |
|---|---|---|---|
| Copper | 1·0 | 1·07 | 0·12 |
|  | 1·0 | 1·02 | 0·10 |
|  | 1·0 | 0·99 | 0·09 |
| Lead | 1·0 | 0·95 | 0·08 |
|  | 1·0 | 0·96 | 0·07 |
|  | 1·0 | 0·94 | 0·07 |
| Cadmium | 1·0 | 1·00 | 0·07 |
|  | 1·0 | 0·96 | 0·05 |
|  | 1·0 | 0·92 | 0·05 |
| Zinc | 1·0 | 1·10 | 0·18 |
|  | 1·0 | 1·00 | 0·18 |
|  | 1·0 | 1·20 | 0·17 |
| Nickel | 1·0 | 0·98 | 0·02 |
|  | 1·0 | 1·06 | 0·04 |
|  | 1·0 | 0·90 | 0·03 |
| Cobalt | 1·0 | 1·02 | <0·1 |
|  | 0·5 | 0·50 | <0·1 |
| Manganese | 1·0 | 0·90 | 0·13 |
|  | 0·5 | 0·48 | 0·15 |
| Iron | 1·0 | 0·85 | 0·30 |
|  | 1·0 | 1·06 | 0·33 |

Reagent blanks are of satisfactory reproducibility, and with the exception of iron are less than 0·2 µg. For this element a blank of 2 to 3 µg is obtained, which originates largely from the sodium acetate buffer solution. Pre-extraction of this reagent with ethyl acetate after the addition of sodium diethyldithiocarbamate reduces the value to 0·30 µg.

### DETERMINATION OF COBALT AND ZINC—

The subtractive procedure for the separation of cobalt and zinc was examined separately, and the results are shown in Table III.

TABLE III

DETERMINATION OF COBALT AND ZINC

| Amount taken, µg |  | Amount found, µg |  |
|---|---|---|---|
| Cobalt | Zinc | Cobalt | Zinc |
| 0·20 | 0·20 | 0·20 | 0·23 |
| 0·32 | 0·64 | 0·30 | 0·65 |
| 0·20 | 1·20 | 0·24 | 0·95 |
| 0·20 | 1·00 | 0·20 | 1·09 |
| 0·20 | 2·00 | 0·19 | 2·58 |
| 0·20 | 1·60 | 0·25 | 1·53 |

### ANALYSIS OF BERYLLIUM—

The results shown in Table IV were obtained on samples of electrolytically refined beryllium flake. Although not of the highest purity available, these were selected to enable some intercomparison with emission spectrography to be made. Values in parentheses represent estimated limits of detection for spectroscopic methods; these are 0·2 p.p.m. for all polarographic determinations.

## CONCLUSIONS

The methods described give quantitative recoveries for all of the elements by using synthetic solutions containing beryllium. Results for electrolytically refined beryllium flake are in satisfactory agreement with other methods where intercomparison is possible.

TABLE IV

ANALYSIS OF BERYLLIUM

| Element | Sample A | | Sample B | |
|---|---|---|---|---|
| | Polarography | Emission spectrography | Polarography | Emission spectrography |
| Copper | 1·7, 2·6, 3·0 | < 5 (5) | 0·5, 0·8, 0·5 | < 5 (5) |
| Lead | 0·6, <0·2, <0·2 | < 3 (3) | <0·2, <0·2, <0·2 | < 3 (3) |
| Cadmium | <0·2, <0·2, <0·2 | < 2 (2) | <0·2, <0·2, <0·2 | < 2 (2) |
| Zinc | 31, 29, 31, 29 | <25 (25) | 6·0, 6·0 | <25 (25) |
| | | 20* (1) | | 5·5* (1) |
| Nickel | 26, 17, 17 | 18 (3) | 5·0, 6·2, 8·0 | 7·5 (3) |
| Cobalt | <0·2, <0·2, <0·2 | <2 (2) | <0·2, <0·2, <0·2 | < 2 (2) |
| Manganese | 19, 18, 20, 23 | 25 (2) | 1·6, 1·2, 1·0 | < 2 (2) |
| Iron | 40, 38, 39 | 30 (6) | 20, 16, 18 | 17 (6) |
| | | 35† (0·5) | | 19† (0·5) |

* Atomic absorption.
† Spectrophotometry by using bathophenanthroline.

Although requiring a certain amount of chemical manipulation, the use of semi-micro techniques has considerably reduced the over-all working time, and the methods have proved useful for the analysis of high purity research materials.

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# The Determination of Nickel with Dimethylglyoxime in Iron and Steel Containing Cobalt and Copper

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The separation of nickel from cobalt and copper with dimethylglyoxime in solutions containing iron has been examined. A double precipitation is always required in test solutions containing more than 3 to 5 mg of copper. Errors owing to the formation of a soluble nickel(IV) compound occur when the reagent solution is added to solutions with a pH above about 4.

For the determination of nickel in samples with up to 10 mg of cobalt in the test solution, precipitation in weakly acid solution is recommended. For the separation from cobalt in high cobalt samples, method A of the British Standard 1121 : Part 37 : 1961 is accurate, provided that unprecipitated nickel(IV) in the filtrate is recovered by extraction and determined separately.

AS is well known, the gravimetric determination of nickel with dimethylglyoxime is complicated by the presence of cobalt. This problem is encountered, for example, in the analysis of steels and magnetic alloys.

Most papers and handbooks, as well as the standard methods of the A.S.T.M.,[1] specify the use of additional reagent to take account of the amount of reagent consumed by cobalt(II). In the absence of iron this gives a good separation from amounts of cobalt that are not too large. When iron(III) is present, however, precipitation of nickel from the usual ammoniacal tartrate or citrate solution gives rise to slimy, red - brown precipitates that are difficult to filter off[2]; this effect even occurs in the presence of relatively small amounts of cobalt. In their presence the nickel dimethylglyoxime produced is contaminated with a compound of iron, cobalt and dimethylglyoxime.[2,3,4,5] The precipitation of nickel is complete with small amounts of cobalt, but incomplete with large amounts of cobalt.

If the iron is present in the iron(II) state no such contamination occurs, so that precipitation in a reduced solution can give good results.[2,5] This method is of limited application, however, as will be shown below.

It was found that a pure precipitate of nickel dimethylglyoxime could also be obtained when the amount of cobalt present was not excessive if the iron was kept completely in the tervalent state. As iron(III) is partly reduced with ease by tartrate or citrate in hot solutions, precipitation has to be carried out in the cold. Consequently, it appears probable that it is the combined presence of iron(II) and iron(III) that causes the contamination of the precipitate with the iron - cobalt complex mentioned above.

In connection with a revision of the Dutch standard method[6] (which is practically identical with the A.S.T.M. method[1]) for determining nickel in iron and steel, we were interested in a method that would permit the determination of nickel in the presence of considerable amounts of cobalt and copper. The only standard method that appeared to be applicable for this purpose is method A of the British Standard[7]; it is based on the work of the B.I.S.R.A. Methods of Analysis Committee.[8] This procedure has been adopted, with slight modification, as a French standard.[9] In this procedure, cobalt(II) is oxidised to non-interfering cobalt(III) by hydrogen peroxide in ammoniacal citrate solution; a single precipitation is made and the nickel in the precipitate is determined by titration with standard potassium cyanide and silver nitrate.

The first part of this paper is concerned with an investigation of this procedure.

## EXPERIMENTAL

### QUALITATIVE INVESTIGATION OF THE SEPARATION OF NICKEL FROM COBALT AND COPPER—

We first tested the British Standard procedure to determine the degree of separation obtainable from cobalt and copper. Decomposition of the precipitate was effected with sulphuric and nitric acids, and the cobalt and copper were determined photometrically with

2-nitroso-1-naphthol[10] and diethyldithiocarbamate,[11] respectively. Nickel in the filtrates was recovered by extracting the ammoniacal solutions several times with chloroform and the nickel in the combined chloroform extracts determined photometrically as described by us in a previous paper.[12] In the British Standard procedure, a constant addition of 25 ml of a 1 per cent. ethanol solution of dimethylglyoxime in a final volume of about 350 ml is used; if cobalt or more than 30 mg of copper is present, the addition of 75 ml of this reagent is prescribed (final volume 350 to 400 ml), providing for up to 150 mg of cobalt and 200 mg of copper.

For our tests with this procedure solutions were used containing various amounts of iron, nickel, cobalt and copper. In all instances when peroxide was used to oxidise the cobalt, the amount of cobalt found in the precipitate proved to be below 5 μg. The amount of iron was always below 10 μg. The separation from cobalt and iron is therefore excellent. The separation from copper, on the other hand, is less satisfactory. In experiments with 1 g of iron, 40 mg of nickel, 10 mg of cobalt and various amounts of copper, the precipitate obtained by using 75 ml of reagent was contaminated with amounts of copper as follows—

| | | | | | |
|---|---|---|---|---|---|
| Copper present in solution, mg . . . . . . | 5 | 25 | 50 | 100 | 200 |
| Copper present in the precipitate, μg . . . . | 40 to 50 | 100 to 120 | 200 | 300 | 300 to 400 |

Experiments showed that the apparent amount of nickel, calculated by using the gravimetric factor 0·2032, is higher by an amount approximately equal to the amount of copper in the precipitate. As the accuracy of the gravimetric nickel determination is within about ±0·04 mg, it is clear that with a single precipitation not more than about 5 mg of copper can be tolerated. With a double precipitation 200 mg of copper may be present. In these experiments care was taken to follow the direction of the British Standard as to the temperature of precipitation. It was confirmed that with a lower temperature of precipitation the contamination by copper increases strongly.

It was further shown that the presence of ethanol in the solution is essential for a satisfactory separation from copper to be effected; this explains why precipitation with a reagent dissolved in sodium hydroxide or ammonia solution results in heavy contamination, even when only a few milligrams of copper are present.

Precipitation of 40 mg of nickel with 75 ml of reagent is complete in the presence of 1 to 5 g of iron and up to 150 mg of cobalt. With 200 mg of cobalt, about 2 mg of unprecipitated nickel is found in the filtrate, increasing to about 10 mg when 300 mg of cobalt is present. In all of these instances the precipitate contained less than 5 μg of cobalt.

Complete precipitation by this procedure means that the filtrate contains 50 to 60 μg of nickel at 25° C, corresponding to the solubility of the nickel complex in about 350 ml of solution containing 75 ml of ethanol. Cooling to 15° C decreases the solubility to about 30 μg.

Applying this procedure to iron-free solutions, it was found that up to 300 mg of cobalt does not interfere with complete precipitation of nickel.

Although the British Standard method prescribes the use of 30 ml of 6 per cent. hydrogen peroxide for the oxidation of cobalt, this volume is excessive and much less is adequate. In most of the experiments described above, 10 ml of 3 per cent. hydrogen peroxide was used; no difference could be detected. It was also established that the separation from copper and the increased solubility of the nickel complex in the presence of cobalt above 150 mg were not affected by the amount of peroxide.

The 25 ml of reagent specified in the British Standard method for determining up to 40 mg of nickel in solutions containing no cobalt and not more than 30 mg of copper leaves an excess of reagent that is barely enough for complete precipitation. Therefore, to complete our investigation, experiments were also made with the constant addition of 40 ml of reagent; this leaves sufficient excess for up to 45 mg of nickel. The separation from copper proved to be much the same as when 75 ml of reagent were used, the results obtained for contamination of the precipitate by copper being almost identical. The limit tolerated for a single precipitation should again be set at about 5 mg of copper.

Complete precipitation of nickel is obtained in the presence of 1 g of iron and 100 mg of cobalt when using 10 ml of 3 per cent. hydrogen peroxide. With 150 mg of cobalt and above, precipitation of nickel is incomplete. Increasing the amount of iron decreases the tolerance for cobalt; with 2 to 5 g of iron and only 50 mg of cobalt, 2 to 10 mg of nickel is found in the filtrate. Increasing the amount of peroxide has no effect. With complete precipitation the filtrate contains about 30 μg of nickel at 25° C and about 23 μg at 20°C.

THE QUANTITATIVE ASPECT OF THE BRITISH STANDARD PROCEDURE—

Tests were made with prepared solutions or with standard steels to which varying amounts of cobalt or copper had been added. All of the determinations were made by weighing the precipitate of nickel dimethylglyoxime after drying at 140° to 150° C. A gravimetric finish was chosen as it was considered that it gave greater accuracy than the volumetric procedure.

Surprisingly, the results showed a definite tendency to be too low, with a larger range than expected. These low results were at first inexplicable as the filtrates contained the normal amount of nickel corresponding to the solubility of the nickel complex in the ethanol concentration concerned, as found earlier.[13]

When, however, the extracted filtrate was strongly acidified with hydrochloric acid, boiled with nitric acid and then adjusted in the cold with ammonia solution to pH about 8, further amounts of nickel could be extracted with chloroform. These amounts varied from 80 to 300 $\mu$g, thereby explaining the low results. This behaviour can only be explained by the formation of a soluble nickel(IV) compound[14] that is not extractable by chloroform, but is converted to nickel(II) in acid solution. For complete decomposition of the nickel(IV) complex it is necessary to acidify the solution to pH 4 or below and boil the solution.

Repeating the determinations with practically cobalt-free samples and, therefore, omitting the use of peroxide, we still found in the filtrates considerable amounts of nickel(IV) that varied from 80 to 200 $\mu$g. In these determinations nickel(IV) could have been formed only through oxidation by air. That this is so was shown by the following experiment. A solution containing 300 mg of an 18/8 steel and 2 g of pure iron was carried through the procedure up to the point where the solution was made strongly alkaline with ammonia solution and diluted to 300 ml. This solution was filtered through a slow-running filter with the funnel so placed that its tip touched the wall of a glass beaker at the rim. In this manner maximum contact with air was obtained during the filtration. After precipitation of the nickel with dimethylglyoxime, about 2 mg of nickel(IV) were found in the filtrate, showing that under suitable conditions, and without the use of hydrogen peroxide, large amounts of nickel(IV) can be formed. That so large an amount is not found after oxidation with peroxide is strange; possibly part of it is destroyed during the digestion at 60° to 90° C. Long boiling of a solution oxidised with peroxide, however, did not diminish the amount of nickel(IV) perceptibly.

A remarkable fact is that in iron-free solutions no oxidation to nickel(IV) takes place when cobalt is absent, even when hydrogen peroxide is used. With increasing amounts of cobalt the amount of nickel(IV) increases. It appears, therefore, that iron(III), as well as cobalt(III), catalyses the oxidation of nickel to nickel(IV) by air or peroxide.

We have not been successful in finding a reducing agent that reduces nickel(IV) without also reducing cobalt(III). It is thus evident that the British Standard procedure gives results that are too low. In unfavourable cases there may be a loss of 0·2 to 0·3 mg of nickel, resulting in a negative relative error of 0·5 to 1 per cent., when amounts of nickel in the range from 20 to 40 mg are determined. Accurate results can only be obtained if the nickel(IV) in the filtrate is determined by extraction.

In the practical application of the British Standard, the loss of nickel(IV) will often be compensated by the co-precipitation of copper as only a single precipitation is made. In this respect the French Standard[9] will be subject to larger errors as it specifies a double precipitation.

INVESTIGATION OF OTHER PROCEDURES—

It appeared probable that all other procedures in which nickel is precipitated in ammoniacal solution are also subject to the formation of nickel(IV). We therefore investigated two A.S.T.M. methods. In the first of these[1] (for determining nickel in iron and steel), an ammoniacal tartrate solution is first filtered, then slightly acidified with hydrochloric acid and heated to between 60° and 80° C. After adding the alcoholic reagent solution, precipitation is effected by adding ammonia solution until slightly alkaline. In a few experiments with 300 mg of an 18/8 steel about 30 $\mu$g of nickel(IV) was found in the filtrate (pH about 8·2).

In the second A.S.T.M. method[15] (for determining nickel in nickel - chromium alloys) the filtered acid solution is first neutralised in the cold with ammonia solution and an excess of 3 ml of concentrated ammonia added. The solution is then diluted to volume, heated to 70° C and the reagent added. In several experiments with the same steel large amounts of nickel(IV), ranging from 60 to 300 $\mu$g, were found. The pH of these solutions was about 9·1.

The amount of nickel(IV) found by the first method is low; it can probably be explained by assuming that any nickel(IV) formed during the filtration is, for the most part, decomposed by acidifying the solution. Addition of the reagent to the acid solution then prevents further oxidation, as, while the solution is still slightly acid, precipitation is practically complete. The large amount of nickel(IV) present in the second method is readily understandable, because the ammoniacal solution is in contact with air for a considerable time.

In view of the errors inherent when precipitating in ammoniacal solution, we turned our attention to precipitating in slightly acid solution buffered by acetate. With this procedure citrate cannot be used for complexing iron and other elements, for in citrate solution precipitation is incomplete below pH 7·0.[13] Precipitation must therefore be effected in tartrate solution in which it is complete above pH 5·4.[13]

Preliminary experiments with 18/8 steels showed that nickel(IV) was not formed when the nickel was precipitated by adding ammonium or sodium acetate to an acid solution containing nickel and dimethylglyoxime.

Contamination of the precipitate by iron and cobalt is heavy when the solution contains both iron(II) and iron(III) in appreciable amounts. Precipitation in reduced solution[2,5] is effective in preventing this contamination. This, however, is only possible when the amount of iron is below 0·3 to 0·5 g, as larger amounts of iron(II) prevent complete precipitation of nickel owing to consumption of reagent by the iron(II). When iron is present predominantly as iron(III), large amounts of it can be present. An extensive study of this method showed that when cobalt is present the precipitate always contains both iron and cobalt. Some examples are given in Table I.

TABLE I

CONTAMINATION OF NICKEL DIMETHYLGLYOXIME BY IRON AND COBALT

Precipitation of about 28 mg of nickel in acetate buffered solution

| Solution contains— | | | Precipitate contains— | |
|---|---|---|---|---|
| 18/8 steel, mg | pure iron, g | cobalt, mg | iron, µg | cobalt, µg |
| 300 | — | — | <5 | — |
| 300 | — | 10 | 20 | 15 |
| 300 | — | 25 | 200 | 100 |
| 300 | 3 | — | <5 | — |
| 300 | 3 | 10 | 130 | 140 |

From these and other experiments it can be concluded that by using a single precipitation not more than about 3 mg of cobalt or 3 mg of copper may be present. The figure for cobalt applies in the most unfavourable instance, *i.e.*, a maximum sample weight of 5 g. With smaller samples more cobalt, up to about 10 mg, may be present, as Table I shows. Amounts of cobalt above 10 to 15 mg can give rise to brown, slimy, heavily contaminated precipitates. By using a double precipitation, the amount of cobalt allowed is still about 10 mg and that of copper is increased to about 200 mg.

The procedure used for these experiments was as follows—

An oxidised solution of the steel was filtered after adding tartaric acid (and copper or cobalt), and adjusted in the cold with ammonia solution to about pH 4. After diluting to 200 to 250 ml and heating to between 70° and 80° C, the reagent solution (1 per cent. in ethanol) was added. Experiments have shown that above the theoretical volume of 0·4 ml of reagent for every mg of nickel *plus* cobalt, an excess of 15 to 20 ml is necessary for complete precipitation in solutions containing appreciable amounts of iron and other elements. Additional reagent to take account of the presence of even large amounts of copper is not required. Precipitation was completed by adding about 5 g of ammonium acetate or ammonia solution until a pH above 5·4 was obtained. After it had stood for at least 3 hours, and, if necessary, been cooled to about 20° C, the solution was filtered and the precipitate washed with cold water and dried at 140° to 150° C. The solubility of the nickel complex in about 300 ml of solution containing 35 to 40 ml of reagent corresponds to 25 to 30 µg of nickel. If a double precipitation is made, the loss by solubility can be decreased by cooling the first precipitate to 15° C or below (below 15° C excess of reagent crystallises out).

Application of this procedure to prepared solutions and to 18/8 steel samples gave excellent results (see below). Difficulties arose when it was applied to sample weights above about 0·3 g. In this event, the large amount of tartaric acid (about 7 times the sample weight) necessary to complex iron, chromium, etc., causes the solution to be so strongly buffered that it is impossible to reach a pH high enough for complete precipitation after adding only ammonium acetate to a solution of pH 4. The solution has first to be adjusted to pH 5·2 to 5·3 to obtain a pH above 5·4 after adding the acetate. When this was done, low results were obtained and the filtrate contained appreciable amounts of nickel(IV).

Experiments were therefore conducted in which steel solutions containing tartrate and nickel were adjusted to various pH values with ammonia solution and then stirred mechanically for 5 minutes in open beakers. At a pH of 3·0 the formation of nickel(IV) was doubtful, at pH 4·0, about 10 $\mu$g of nickel(IV) was found, increasing with pH to 300 $\mu$g at pH 6·0, and to about 1 mg at pH 7·5. This shows that it is dangerous to neutralise to a pH above 4. In practice, it is therefore advisable to neutralise the solution to a pH between 3 and 4. This can easily be done with the help of indicator paper and leaves a sufficient margin of safety for the lack of sensitivity of these indicator papers. The reagent should then be added to the hot solution and the pH increased to at least 5·4 by adding ammonium acetate for a small sample weight, with additional 7 M ammonia solution for large samples. There is no objection to continuing to add ammonia solution until the solution shows a weakly alkaline reaction; this is perhaps simpler than adjusting to a pH between 5·4 and 7. As the greater part of the nickel is already precipitated at pH about 4, there is no risk of nickel(IV) being formed at a higher pH.

Large amounts of nitrate do not interfere with the complete precipitation of even small amounts of nickel; this finding is not in agreement with statements made by Harwood and Theobald.[16] It should be noted that phosphoric acid cannot be used for dissolving the steel sample as iron(III) phosphate precipitates between pH 3 and 7 in tartrate solution. With steels containing tungsten, the tungsten therefore cannot be kept in solution and tungsten trioxide should be filtered off after oxidising the solution.

Citrate solutions showed the same behaviour as tartrate solutions with regard to oxidation of nickel in the pH range 4 to 7.

### ACCURACY—

To assess the accuracy of the procedure in which nickel is precipitated in weakly acid solution, tests were made with accurately known amounts of nickel. Spectroscopically pure nickel, free from cobalt and oxygen, was dissolved in nitric acid and the solution diluted in a calibrated flask to a known weight of solution. Aliquots taken by pipette were weighed so that the weight of nickel taken for analysis (about 31 mg) was known within 0·003 mg. The nickel was precipitated at about 70° C from a solution of pH 3 containing 2 g of tartaric acid, by adding the required amount of reagent followed by the addition of ammonium acetate and, if necessary, ammonia solution. After it had stood for about 3 hours, the solution was cooled to 20° C and filtered on a weighed quartz filter crucible. The precipitate was washed with cold water[13] and finally dried overnight at 140° to 150° C. All weighings were made on a Mettler semi-micro balance. The results were calculated by using the gravimetric factor 0·20319. The standard deviation calculated from a series of 17 determinations, spread over several days, was 0·013 mg of nickel. Without applying corrections for buoyancy, the mean of the determinations was 0·010 mg of nickel below the calculated weight. Taking the buoyancy into account a correction of about 0·06 per cent. should be applied to the amount of nickel dimethylglyoxime (density about 1·4) and thus to the weight of nickel, thus raising the mean by about 0·018 mg. Considering that the filtrate from these determinations contains about 0·03 mg of nickel in a final volume of about 300 ml, it can be concluded that the dried precipitate of nickel dimethylglyoxime appears to be somewhat heavier than the theoretical formula requires. For all practical purposes, however, the theoretical formula gives accurate results.

A series of determinations was made in the same way with N.B.S. standard Cr–18 - Ni–9 steel sample 101e (nickel 9·48 per cent., chromium 17·98 per cent., copper 0·36 per cent.). The aliquots taken were equivalent to 400 mg of steel containing about 38 mg of nickel. A single precipitation was made. One operator obtained a standard deviation (for a single determination) of 0·010 per cent. (11 determinations) and a mean of 9·485 per cent. A second operator with another batch from the same standard obtained a standard deviation of 0·008 per cent. and a mean of 9·477 per cent. (8 determinations). The standard deviation of about 0·010 per cent. of nickel corresponds to about 0·04 mg of nickel; this standard deviation is thus considerably larger than that obtained with pure nickel solutions.

Applications of this procedure to two 5-g samples of N.B.S. standard sample 10e of open-hearth steel with 0·093 per cent. (range 0·083 to 0·100) of nickel and 0·166 per cent. of copper gave results of 0·092 and 0·089 per cent. of nickel after a double precipitation, showing that this procedure can also be used for very low contents of nickel.

## DISCUSSION

The following points emerge from this investigation—

(*a*) The addition of dimethylglyoxime to test solutions with pH above about 4 leads to losses caused by the formation of nickel(IV).

(*b*) In all procedures, whether precipitation takes place in ammoniacal or in weakly acid solution, the presence of copper in excess of 3 to 5 mg requires a double precipitation.

(*c*) The most accurate method of determining nickel in iron and steel with low cobalt contents (less than 10 mg of cobalt in the test solution) requires the precipitation to be effected in weakly acid solution; a double precipitation is required when more than 3 mg of cobalt are present in the test solution.

(*d*) An excellent separation from cobalt (with up to 150 mg in the test solution) is obtained with method A of the British Standard. Owing to the formation of nickel(IV) in this procedure, unprecipitated nickel must be recovered by extraction of the filtrate (see below). The recovered nickel can be determined photometrically or, if a double precipitation is made, it can be re-extracted from the chloroform extract and added to the solution of the first precipitate.

### RECOMMENDED PROCEDURE FOR THE RECOVERY AND DETERMINATION OF NICKEL IN THE FILTRATE FROM THE DETERMINATION MADE ACCORDING TO THE BRITISH STANDARD METHOD—

Boil the filtrate for about 10 minutes to volatilise most of the excess of ammonia and to decompose hydrogen peroxide. Acidify to a pH of about 4 (at least 20 ml of 6 M hydrochloric acid are required), heat again to boiling and add 5 ml of concentrated nitric acid. Cool to about 20° C, neutralise with 7 M ammonia solution to about pH 4, add 10 ml of 1 per cent. dimethylglyoxime in ethanol and again add 7 M ammonia solution until the solution is slightly ammoniacal. The pH should be 7·5 to 8. Transfer to a separating funnel and extract twice with 15 to 20 ml of chloroform; shake the funnel about ½ minute each time. Wash the combined chloroform phases twice with a mixture of 20 ml of water and 2 ml of 7 M ammonia solution; one wash is sufficient if only a few milligrams of copper were originally present. Discard the washings. Shake the chloroform extract for 1 minute with 10 ml of M hydrochloric acid. The hydrochloric acid solution now contains all of the nickel present in the filtrate. This solution can be added to the solution of the first precipitate if a double precipitation is made, or the nickel contained in it can be determined photometrically after boiling off the chloroform.

### PHOTOMETRIC DETERMINATION[12]—

Transfer the hydrochloric acid solution to a 250-ml beaker, dilute to about 50 ml, add 1 ml of 10 per cent. w/v citric acid, 5 ml of freshly prepared 2 per cent. potassium persulphate, 15 ml of 2 N sodium hydroxide and 1 ml of 1 per cent. dimethylglyoxime in ethanol, in the order given. Heat the solution on a water-bath to about 60° C and keep it for 5 minutes at a temperature between 60° and 70° C. Cool to room temperature and dilute to 100 ml in a calibrated flask. Determine the optical density against water at 465 $m\mu$ in a suitable cell. Calculate the amount of nickel from a standard graph prepared with known amounts of nickel. The colour developed in this way is stable for at least 24 hours.

We have not been able to confirm the claim by Green[17] that during the washing of the chloroform extract with dilute ammonia solution a loss of nickel occurs owing to oxidation.

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# The Determination of Diquat Residues in Potato Tubers

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Calderbank, Morgan and Yuen's method for the determination of residues of diquat has been modified. Five samples are hydrolysed simultaneously in a household autoclave with perchloric acid. Diquat is separated with Dowex 50W–X2, 200 to 400 mesh, and measured spectrophotometrically after reduction with hydroxostannate(II) solution. The modified procedure is more sensitive, requires smaller samples, and is considerably faster than the original procedure.

IN a method[1] for the determination of diquat (1,1′-ethylene-2,2′-bipyridylium ion) residues in potato tubers, the macerated sample, 500 g of potatoes, is hydrolysed by refluxing for 5 hours with sulphuric acid. The acid is neutralised with calcium carbonate and sodium carbonate, and the solid material is filtered off by suction and washed with water. The pH of the solution is adjusted to between 7·1 and 7·5 with sodium carbonate. EDTA is added, and the solution is run through a Permutit Zeo-Karb cation-exchange resin, 52 to 100 mesh, containing 8 per cent. of divinylbenzene, in the sodium form, on which the diquat is retained. The column is washed with water, 2 M hydrochloric acid and water. The diquat is eluted with a saturated sodium chloride solution, 25 ml of the eluate are collected, and 5 ml are used for the spectrophotometric measurement, which is performed after reduction of the diquat with dithionite.

When we used this method, the recoveries of diquat added to samples of diquat-free potatoes before the refluxing were irregular and low.

Attempts to develop another type of method involving thin-layer chromatography or precipitation with sodium tetraphenyl borate were unsuccessful. Further investigations led to the development of the method given below, which is based upon the same principles as the original method.

The modifications described gave a more than 10-fold increase in the sensitivity of the method, and therefore made it possible to use only 100 g of sample for the chemical procedure. This resulted in a considerable speeding-up of the operations to be carried out, *e.g.*, five samples can be hydrolysed at once in beakers in a household autoclave. The higher temperature obtained reduces the amount of perchloric acid required to 3 ml, and the heating time to 60 minutes at top temperature for the hydrolysis. Of course, all neutralisation, sorption, washing and elution steps are much faster and more convenient with the smaller samples.

## APPARATUS—

*Meat mincer.*

*Macerator.*

*Flex-Seal household autoclave*—Pressure, 1 kg; height, 21 cm; diameter, 21 cm; available from Moderna Kök Inc., Sweden, or other apparatus of similar dimensions.

*Ion-exchange columns*—About 9 mm i.d., with a capillary stopcock at the lower end and, at the upper end, a short, wide part, about 30 mm i.d.

*Vacuum regulator* (*Fig.* 1) *and suction flask for exchange columns.*

*Recording spectrophotometer*—Use a Beckman DB, or a similar instrument that is provided with a slit mask or other accessory for measuring in micro cuvettes with a 40-mm light path and 4 to 5 ml of solution.

## REAGENTS—

*Perchloric acid,* 70 *to* 72 *per cent.*

*Glacial acetic acid.*

*Potassium carbonate solution,* 4·5 M.

*EDTA solution*—Dissolve 9 g of EDTA (disodium salt), $2H_2O$ in water, and dilute to 100 ml.

*Carbonate buffer*—Dissolve 10 g of sodium hydrogen carbonate in 800 ml of water, and add 25 ml of the EDTA solution. Adjust the pH of the solution to 10·0 with 3 M sodium hydroxide solution, and dilute to 1 litre with water.

*Sodium chloride solution*—Dissolve 350 g of sodium chloride in 1 litre of water.

*Hydroxostannate(II) solution*—Dissolve 1 g of a good, not too old specimen of tin(II) chloride dihydrate, $SnCl_2.2H_2O$, in 20 ml of 3 M sodium hydroxide solution and dilute with water to 30 ml. Prepare a fresh solution daily. Use only clear, unoxidised crystals of tin(II) chloride.

*Ion-exchange resin*—Use Dowex 50W-X2 spheres, 200 to 400 mesh, ionic form $H^+$, moisture content 78·0 per cent. Pack the column with 1·5 g of the resin between thin, flat layers of glass-wool. Wash by gentle suction with 5 ml of water, 25 ml of sodium chloride solution and 25 ml of water. Use a new filling of resin for every determination.

## PROCEDURE—

Take about 2500 g of potato tubers at random from the sample provided. Wash them free from soil and dry them with a cloth. Cut each tuber into four approximately equal segments and reject two opposite segments from each tuber.[1] Pass the remaining segments through a meat mincer and mix the pulp well. Weigh out a 100-g portion for the determination.

Place the 100-g sample into the macerator jar together with 60 ml of water, 3 ml of perchloric acid and 1 ml of acetic acid. Macerate for about 3 minutes, and transfer to a tall 400-ml beaker having an external diameter of about 65 mm.

Place five beakers into the household autoclave with 3 litres of water. Heat gently, keep at the boiling temperature for 1 hour, and then allow to cool slowly.

With vigorous stirring add slowly 5·0 ml of potassium carbonate solution to each of the beakers. Pour the suspensions into 250-ml centrifuge tubes and spin them in a centrifuge for 10 minutes at 2500 r.p.m. Decant the supernatant solutions into 500-ml measuring flasks. Put a wad of glass-wool into the upper end of the 9-mm part of each column to remove floating particles from the solution, and draw the solutions with gentle suction, by using the regulator (Fig. 1), through the columns. It is convenient to turn over the measuring flasks with their necks into the wide, upper parts of the columns. All columns can be connected to the same suction flask. Remove the measuring flasks when empty. Wash the wads with about 20 ml of water and remove them. Continue the washing with 100 ml of carbonate buffer and 100 ml of water by using measuring flasks as before.

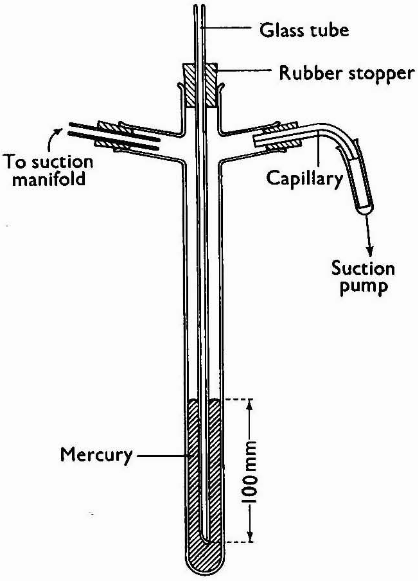

Fig. 1. Vacuum regulator for suction through ion-exchange columns

When all of the water has been drawn into the fillings of the tubes, remove the suction. Press down the upper layers of glass-wool with a thick, sharp-edged glass rod and allow all supernatant water to pass into the fillings under gravity. Add 0·5 ml of sodium chloride solution and place graduated test-tubes under the columns. Allow the solution to pass into the fillings, pressing at intervals with the glass rod upon the glass-wool to keep the shrinking fillings compact. When 1 ml of eluate has passed into the test-tubes add more sodium chloride solution. Collect a total of 6 ml of eluate in each tube. Add 1·0 ml of hydroxostannate(II) solution, mix, pour the solution into the cuvettes and scan 3 to 120 minutes after pouring the solution into the cuvettes, between 420 and 320 nm, by using sodium chloride solution as reference. Draw the common tangent to the branches of the curve on each side of the maximum, and measure the height of the peak above the point of the tangent at 379 nm. Call this height the absorbance of diquat, and take it as the measure for the amount of diquat in the sample. Prepare a standard curve by adding different amounts of diquat to 100-g portions of minced potatoes and taking them through the described procedure.

## DISCUSSION

During the investigation of the original procedure,[1] diquat was added to samples of potatoes at different stages of the procedure. The main losses were found to occur in the sorption step on the ion-exchange resin. Almost as high and irregular losses occurred there also when the procedure was run with only water solutions of diquat without potatoes. After neutralisation, filtration and washing, the sample solution contains dissolved carbon dioxide and calcium hydrogen carbonate. Figures for the solubility of calcium hydrogen carbonate in water under pressure of carbon dioxide were given by McCoy and Smith,[2] and we concluded from these that the amount of calcium in the filtrate might be a critical factor in the procedure. We tried, therefore, to replace calcium with barium and to increase the pH to 10·0 to obtain a sufficient concentration of carbonate ion and a quantitative precipitation of the bivalent cation. The sorption step was then satisfactory, but most of the diquat remained in the precipitate.

Hydrolysis with perchloric acid and precipitation with potassium was finally tried because potassium could not be expected to displace diquat from the resin. Acetic acid was added, and the amounts of potassium and of the acids were chosen so that an acetic acid - acetate buffer was obtained after the precipitation. About 19 per cent. of the diquat remained in the precipitate under the given conditions (Table III). Part of this could be recovered by washing the precipitate. However, as the amount lost is reproducible, it was not considered worthwhile lengthening the procedure by the introduction of a further washing step.

We learned later that the original procedure[1] gave good results in several laboratories. It appears probable, therefore, that some detail in the procedure must be carried out in a special manner to give good results, and that we have not observed this. An example of this was the method of adding solid calcium carbonate. We obtained different pH values in the final solution after this operation, and we found that this was caused by the occlusion of added solid calcium carbonate by the precipitated calcium sulphate. Irregular amounts of the precipitant were thus withdrawn from the reaction. As the new procedure with perchloric acid was so much faster and more convenient than that with sulphuric acid, the old procedure was not re-investigated after this discovery.

After the sorption the resin is washed with a buffer at pH 10·0 rather than with hydrochloric acid. This pH value is well beyond the isoelectric points of most amino-acids and coloured products from the potatoes, which are therefore efficiently washed out from the resin. This greatly reduces the background in the spectrophotometric measurement. Diquat, being a strong base, is not eluted by diluted sodium carbonate at this pH. Calcium from the sample, which would interfere in the spectrophotometric measurement, is eluted from the resin by the EDTA content of the buffer.

Diquat is not appreciably attacked at pH 10·0 in water solution. At pH 10·3 at room temperature about 2 per cent. of diquat is decomposed in 1 hour. At pH 10·5 about 30 per cent. and at 10·7 about 40 per cent. is decomposed under the same conditions. It might, however, be preferable not to interrupt the procedure between the alkaline washing and the washing with water.

It appears that a resin with a lower degree of cross-linking and with a smaller particle size should allow a faster sorption and elution. The Dowex product was therefore tried and found to give a satisfactory performance. When the elution is carried out according to the procedure described above, more than 98 per cent. of the diquat, all of which comes out with the sodium chloride, was eluted in the first fraction of 6 ml. Less than 2 per cent. is found in a second fraction and no discernible amount in a third. Recoveries from three fractions are shown in Fig. 2.

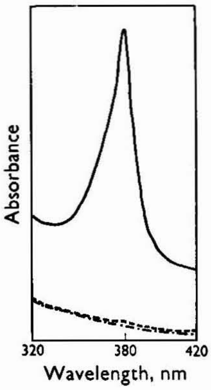

Fig. 2. Scanning curves obtained from three fractions of 6 ml eluted from resin according to described procedure: ——, first fraction; - - - -, second fraction; ·-·-·-·-, third fraction

In several series of experiments, small amounts of apparent diquat were obtained in samples of diquat-free potatoes. The cause was finally traced to the fact that centrifuge tubes of nylon instead of glass had been used. The blank disappeared completely when tubes of glass were used again. Not all of the diquat can be eluted from the ion-exchange resin. Even if the column is washed several times with large amounts of hydrochloric acid, sodium chloride and sodium hydroxide, a trace of diquat will still be eluted the next time the column is washed again with sodium chloride. The column cannot, therefore, be regenerated, but a new batch of resin must be used for every analysis, as prescribed by the original authors.[1]

TABLE I

RECOVERIES OF DIQUAT FROM DIFFERENT AMOUNTS OF RESIN

8·3 μg of diquat were added to samples of untreated potatoes and analysed according to the described procedure. Two 6-ml fractions were eluted.

| Weight of resin, g | Absorbance | |
|---|---|---|
| | First fraction | Second fraction |
| 4·0 | 0·010 | 0·470 |
| 2·5 | 0·450 | 0·015 |
| 2·0 | 0·500 | 0·015 |
| 1·5 | 0·525 | 0·005 |
| 1·5 | 0·530 | — |
| 1·2 | 0·460 | — |
| 1·2 | 0·480 | 0·005 |
| 0·9 | 0·390 | — |
| 0·6 | 0·250 | — |
| 0·4 | 0·140 | — |

The amount of resin used, 1·5 g, was found to be optimal under the conditions of the procedure. With both smaller and larger amounts the recoveries of diquat became lower, even if several fractions were eluted. Results of sorption and elution experiments of diquat from potato samples with different amounts of resin are given in Table 1. To investigate the influence of calcium, analyses were run without and with potatoes with the addition of different amounts of calcium chloride. The results are given in Table II. The largest amounts of calcium added have about the same order of magnitude as those that can be expected to occur in the sample.

TABLE II

RECOVERIES OF DIQUAT, ACCORDING TO DESCRIBED PROCEDURE, FROM WATER AND POTATO SAMPLES WITH DIFFERENT AMOUNTS OF CALCIUM ADDED AS CHLORIDE

| Calcium added to sample, mg | Absorbance of— Sample of water solution containing 5·1 μg of diquat | Absorbance of— Samples of untreated potatoes, 5·1 μg of diquat added |
|---|---|---|
| 0·0 | 0·40 | 0·39 |
| 26·5 | 0·42 | 0·44 |
| 53·0 | 0·47* | 0·40 |
| 106 | 0·43* | 0·34 |
| 212 | 0·38* | 0·37 |

* Precipitate after the addition of hydroxostannate(II) solution. Solution measured after spinning in a centrifuge.

Experiments showed that diquat can be reduced with hydroxostannate(II) solution. Unlike dithionite, this reducing agent and its oxidation product have no light absorption near 379 nm. The reagent can be used for a whole day's work, and it is not necessary to prepare a new batch for each analysis. The colour is fully developed 3 minutes after the addition of the reducing agent, and it is reasonably stable for about 2 hours. However, when the reduced solution is poured into the cuvettes, a small part of the diquat is oxidised by the admixed air, and the solution must stand again for a short time before the colour is fully re-developed. It is therefore more convenient to add the tin(II) chloride and pour the solution into the cuvette when the scanning of the preceding sample has already started. The effect of pouring out the solution into a beaker and back into the cuvette is shown in Fig. 3.

The volume of the finally reduced diquat solution is 7 ml. To obtain maximum sensitivity it is preferable to carry out the spectrophotometric measurement in long light-path micro

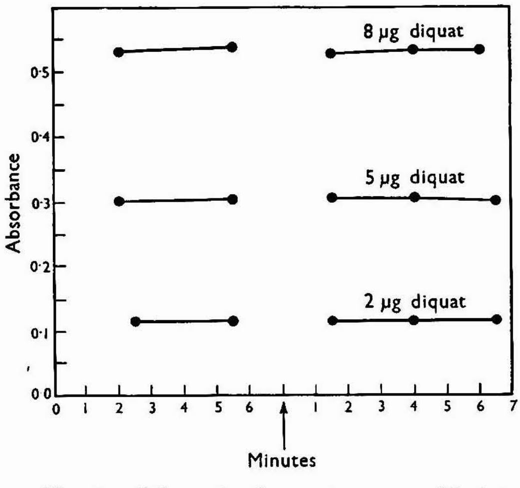

Fig. 3. Colour development curve with interruption. Sample was poured out from cuvette at break and poured back at the time indicated by arrow. Points mark time when recorder pen reached maximum. Reading with 2 μg of diquat before break 0·118, after break 0·118: with 5 μg of diquat before break 0·303, after break 0·302: with 8 μg of diquat before break 0·535, after break 0·525

TABLE III

LOSS OF DIQUAT ADDED AT DIFFERENT STAGES OF PROCEDURE

| | Loss, per cent. | |
|---|---|---|
| Stage of addition | 5 μg of diquat added | 5 μg of diquat added |
| Before hydrolysis . . . . | 28, 27 | 20 |
| Before precipitation . . . . | 25, 27 | 24 |
| Before sorption . . . . . . | 9, 8 | 3 |

cuvettes. The Hellma cuvette 104 QS with a 40-mm light path was found to be suitable. A black metal mask with two vertical 1-mm slits, one for the sample cuvette and one for the reference, is placed into the spectrophotometer or any other suitable instrument when this determination is carried out.

No changes were made in the sampling procedure.[1]

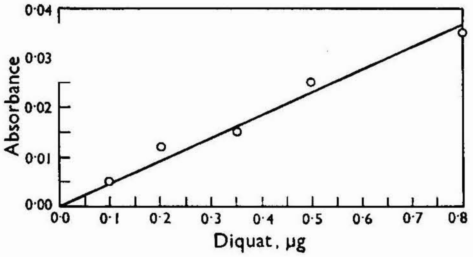

Fig. 4. Standard graph obtained with small amounts, 0 to 0·8 μg, of diquat added to samples of untreated potatoes

## RESULTS

In a series of experiments 10 μg of diquat were added to each of five diquat-free samples of potatoes at different stages of the procedure. The losses that occurred are reported in Table III.

Calibration curves obtained by the addition of known amounts of diquat to minced potatoes before the macerating step are shown in Figs. 4 and 5.

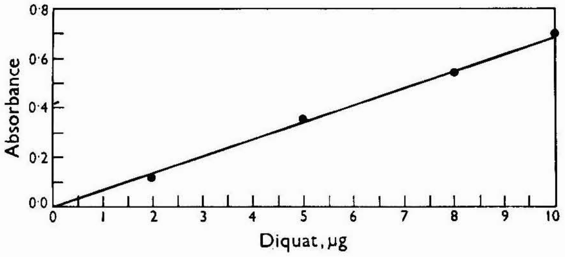

Fig. 5. Standard graph obtained with "large" amounts, 0 to 10 μg of diquat added to samples of untreated potatoes

To test the reproducibility of the chemical procedure, 2 kg of each of two different batches of field-treated potatoes were minced, mixed well and 10 samples of each mixture were weighed out and analysed according to the described procedure. The results are given in Table IV.

TABLE IV

ANALYSES OF TWO BATCHES OF FIELD-TREATED POTATOES

| Sample | Absorbance | Content of diquat, p.p.m. | Sample | Absorbance | Content of diquat, p.p.m. |
|---|---|---|---|---|---|
| Potatoes (Bintje) treated with 218 g of diquat per ha (88 g per acre) on June 14th, and with 435 g per ha (176 g per acre) on September 1st, 1965 | 0·120 | 0·02 | Potatoes (Bintje) treated with 435 g of diquat per ha (176 g per acre) on September 1st, 1965 | 0·090 | 0·015 |
| | 0·120 | | | 0·085 | |
| | 0·127 | | | 0·085 | |
| | 0·122 | | | 0·082 | |
| | 0·125 | | | 0·085 | |
| | 0·122 | | | 0·075 | |
| | 0·125 | | | 0·072 | |
| | 0·112 | | | 0·075 | |
| | 0·115 | | | 0·080 | |
| | 0·115 | | | 0·085 | |

Analyses run on November 16th to 19th, 1965.

A few scanned curves obtained with small amounts of diquat added to 100-g portions of macerated potatoes are shown in Fig. 6. They show that 0·1 to 0·3 μg of diquat in a sample can easily be detected.

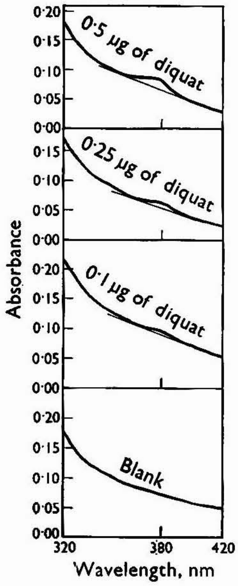

Fig. 6. Scanning curves obtained in sensitivity tests. Diquat added to samples of untreated potatoes

I thank Miss Linda Rask for skilled technical assistance. The work was made possible by a grant from the Swedish Agricultural Research Council.

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# The Use of 8-Hydroxyquinoline for the Separation of Yttrium-90 in the Determination of Strontium-90 in Biological Materials

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Homogeneous precipitation of yttrium carrier as the 8-hydroxyquinolinate has been used for the isolation and purification of yttrium-90 after the separation of the parent strontium-90 from biological materials. The technique has been compared with the generally used method of separating by hydroxide and oxalate precipitations and estimating the recovery by weighing as the oxide. The two methods are of similar accuracy but the new procedure is more direct and simple. Satisfactory decontamination from radioactive strontium is obtained by a single precipitation. The 8-hydroxyquinolinate can be weighed directly for the measurement of chemical yield, and it has a more favourable gravimetric factor than yttrium oxide.

IN the determination of strontium-90, the difficulty of unequivocally identifying this long-lived nuclide is usually obviated by isolating and measuring its radioactive daughter, yttrium-90, the short half-life (64 hours) of which facilitates decay measurements. For the determination of the chemical recovery, and to produce suitable counting sources, the yttrium carrier used in the isolation and purification of yttrium-90 is normally precipitated and mounted as the oxalate.[1,2] The fluoride has also been used, but the finely divided precipitate is often difficult to filter off and the gravimetric factor (the ratio of the weight of yttrium to the weight of precipitate) is unfavourably high. The use of yttrium oxalate also has several disadvantages—

(*a*) it is necessary to make a preliminary separation of yttrium as the hydroxide;

(*b*) it is difficult in routine analysis to obtain a precipitate of constant composition so that, in precise work, the oxalate must be ignited to oxide for the determination of yield, normally after counting is complete; and

(*c*) the gravimetric factor for the oxide is high. This is particularly disadvantageous because the amount of yttrium that can be added as carrier is limited by the self-absorption effects in the heavier oxalate counting source.

This paper describes the use of 8-hydroxyquinoline as an alternative precipitant for yttrium.

## EXPERIMENTAL

Two ml of a 1 per cent. w/v solution of 8-hydroxyquinoline in 2 M acetic acid, and 5 ml of a 20 per cent. w/v ammonium acetate solution were added to solutions containing amounts of yttrium varying from 2 to 4 mg; 6 M ammonia solution was added until the pH was about 9·5, and the solution was heated in a boiling water bath. After cooling, the precipitate was filtered off, washed with water, dried at 110° C and weighed. Somewhat variable values were obtained for the weight of 8-hydroxyquinolinate per unit weight of yttrium, and the precipitate weights were consistently high when an appreciable excess of 8-hydroxyquinoline was present. These difficulties were overcome when the experiment was repeated with a homogeneous precipitation technique, in which the pH of the solution was raised gradually by the hydrolysis of urea; the 8-hydroxyquinoline was added as a solution in methanol to avoid buffering effects owing to the presence of acetic acid.

The co-precipitation of strontium under these conditions was measured by precipitating 2 mg of yttrium in the presence of either 40 or 200 mg of strontium and an amount of strontium-85 sufficient to give about 1000 counts per minute in the 0·51-MeV photopeak, measured by using a 4 by 3-inch NaI(Tl) well-crystal. The precipitates were filtered off

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and washed, dissolved in nitric acid and counted in this way. Replicate experiments showed that less than 0·1 per cent. of the strontium was co-precipitated.

The 8-hydroxyquinolinate precipitation technique was compared with a separation method that involves hydroxide and oxalate precipitations, described by Bryant *et al.*[3] and hitherto in routine use in this laboratory. For this purpose the purified strontium solutions obtained in the analysis of 20 samples, comprising herbage, root mat and animal bone, were divided and separate aliquots treated by each method. The amounts of strontium-90 in the samples analysed ranged from about 200 to 1500 pC.

The sources of yttrium oxalate and yttrium 8-hydroxyquinolinate were counted three times, by end-window Geiger counters, over about two half-lives of yttrium-90; at least 1000 counts were recorded each time. Corrections were applied for background, dead-time losses, self-absorption and back-scattering, counter efficiency and radioactive decay.

The supernatant solutions from the 8-hydroxyquinolinate and hydroxide precipitations were analysed for strontium by flame photometry to determine the chemical recovery of strontium carrier in the earlier purification stages; the excess of 8-hydroxyquinoline was removed by extraction with chloroform. The chemical yield of yttrium was determined gravimetrically, either directly as the 8-hydroxyquinolinate or, for the oxalate, after ignition to oxide. The chemical yield factors were used to calculate, from the disintegration rates of the sources, the amounts of strontium-90 in the original samples.

### RESULTS—

The average ratio of the value for strontium-90 obtained by the 8-hydroxyquinolinate method to that by the oxalate method for the 20 samples was 0·97; the standard error of this mean was $\pm 0{\cdot}01$. The ratio was significantly different from unity at $P = 0{\cdot}01$.

### RECOMMENDED PROCEDURE—

This procedure was developed for application to solutions containing strontium-90 separated from biological materials.[2,3] Such solutions, usually in dilute nitric acid and containing up to 200 mg of strontium carrier, are kept for an appropriate period to allow the growth of yttrium-90 in the presence of yttrium carrier.

### REAGENTS—

*8-Hydroxyquinoline reagent*—Dissolve 1 g of analytical-reagent grade 8-hydroxyquinoline in about 80 ml of methanol. Dilute the filtered solution to 100 ml with methanol and store in an amber-glass bottle.

*Ammonia solution, sp.gr.* 0·88.

*Nitric acid*, 6 M.

*Chloroform.*

*Urea.*

### METHOD—

Add 3 ml of 8-hydroxyquinoline reagent to about 30 ml of solution containing from 1 to 3 mg of yttrium. Slowly add concentrated ammonia solution until precipitation begins, and then add sufficient 6 M nitric acid to dissolve the precipitate. Add 2 g of urea and heat on a boiling water bath, continuing for 30 minutes after the first re-appearance of a precipitate. Take the mid-time of the period of precipitation as the separation time of yttrium-90 for use in the subsequent calculation. After cooling, filter off the precipitate. Wash it with about 20 ml of water, dry to constant weight at 110° C and weigh to determine the recovery of yttrium. Count the precipitate for yttrium-90. Transfer the supernatant solutions to a separating funnel, acidify with 6 M nitric acid and remove the excess of 8-hydroxyquinoline by extracting twice with 25 ml of chloroform. Retain the aqueous phase for the measurement of the chemical yield of strontium in the earlier purification procedure and, if required, for the determination of strontium-89.

## CONCLUSIONS

Results for the concentration of strontium-90 in 20 samples, treated by the procedure involving 8-hydroxyquinoline as a precipitant for yttrium-90, were, on average, about 3 per cent. lower than those obtained by the method involving oxalate sources. There is no direct evidence as to which method gave the more accurate results. The procedure recommended here involves fewer manipulations and weighings, and hence fewer sources of experimental error, but the magnitude of the errors associated with these steps has not been separately assessed for either method. In the determination of strontium-90 in milk by a method similar to that of Bryant *et al.*,[3] the coefficient of variation has been found[4] to be about 7 per cent.; this refers to the over-all error of the analysis in which the final separation of yttrium-90 from strontium-90 is only a small, though important, part. There are also considerable sampling errors in surveys of strontium-90 in foods and in the environment. The accuracy of both separation procedures may therefore be considered adequate, but the technique of the precipitation of yttrium 8-hydroxyquinolinate affords several advantages over the generally used procedure of hydroxide and oxalate precipitations, followed by ignition to oxide. These are—

(*a*) a satisfactory decontamination from radioactive strontium is achieved in a single precipitation step;

(*b*) the measurement of recovery of yttrium can be made directly on the source at the time of preparation. No subsequent ignition is required; and

(*c*) the precipitate has a more satisfactory gravimetric factor than yttrium oxide (0·171 as against 0·787).

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# SHORT PAPERS

## Determination of Ethanol in Blood by Gas Chromatography

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Gas chromatography has been used for alcohol determinations for some years,[1 to 7] but it suffers from two main disadvantages when used directly on blood. First, it is difficult to make highly reproducible volume injections and the blood often coagulates, thereby blocking the syringe on entering the injection port; secondly, standard solutions have to be interspersed at frequent intervals to ensure that the column and detector response have remained linear. We report a system and technique, in which propanol is used as an internal standard, that have overcome these problems and have resulted in a method which is suitable for routine analysis of large numbers of blood samples.

### Method

A Pye 104 chromatograph is used with a 5-feet, 10 per cent. PEG400 on a 100 to 120-Celite column with a flame-ionisation detector, both at 85° C. The temperature of the injection port is the same as that of the column. This chromatograph is designed for use with a 4-inch Hamilton syringe, but we found it more convenient to use a 2¾-inch syringe, topping up the column with column filling for an extra 2 inches. After about 1000 injections the peaks begin to tail, but resolution can be restored by emptying the first 6 inches of the column and re-packing it with fresh filler. A Kent Chromalog integrator is fitted to the output of the amplifier, which is set at the 1-mV range on a "200" attenuator setting of the detector amplifier. In the experiments described below, the integrator was set at the 0·5 per cent. cut-off. Input pressures for the gases were set at argon, 5 lb; hydrogen, 5 lb; and air, 28 lb; these give flow-rates of 150, 100 and 600 ml per minute, respectively.

The blood sample is measured accurately by volume (0·1 ml) and diluted with exactly 1·0 ml of an aqueous propanol solution. In the experiments described below this has a concentration of 25 mg per 100 ml, and is suitable for blood alcohol concentrations in the range of 50 to 400 mg per 100 ml. (For measurement of lower concentrations of alcohol in blood the propanol concentration should be lowered and the amplifier attentuation reduced.)

The manual dilution error can be greater than the machine error, although with care and practice it may be reduced to the same order. By using 20 $\mu$l of blood diluted with 200 $\mu$l of aqueous propanol, with a Griffin and George type 221 haemoglobin-type diluspence, the combined machine and operator error for 10 dilutions has a standard deviation of 1·3 per cent. In the experiments described below, the manual method was used with a 0·1-ml wash-out pipette and a 1·0-ml, grade A, 11-second drain-time pipette.

Approximately 1 $\mu$l of the diluted blood sample is injected by means of a Hamilton syringe into the chromatograph. Ethanol has a retention time of 2 minutes, propanol of 3¼ minutes, and the "water" peak appears in 4½ minutes. We found that comparison of the peak heights of the ethanol with the propanol internal standard gave good results (±3 per cent.) when one experienced operator used the apparatus, but the operators varied between one another by as much as 20 per cent. on measuring the peak-height ratios on the same solution. Incorporation of the Chromolog removed this anomaly and provided a linear calibration graph. Calibration, and hence measurement of concentrations, is achieved by plotting the ratio of ethanol to propanol pulses from the integrator against the concentration of ethanol in the blood. This graph has been proved to be independent of the injected volume, of 50 per cent. changes in flow-rates of each gas, and of a +5° C or −10° C change in column temperature. The graph has remained unchanged for 3 months.

### Results

Ten separate dilutions of blood containing 50, 100, 200 and 400 mg per 100 ml of ethanol were prepared and injected into the apparatus. Ten similar dilutions of aqueous solutions containing the same concentrations of alcohol were similarly prepared and injected. The results obtained are given in Table I, which shows that the calibration is linear and that recovery of the alcohol from blood is 100 per cent.

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TABLE I

RATIOS OF ETHANOL TO PROPANOL PULSES

| | Blood | Standard deviation | Aqueous | Standard deviation |
|---|---|---|---|---|
| 50 mg per 100 ml | 0·1579 to 0·1677 | | 0·1568 to 0·1695 | |
| | mean—0·1611 | 0·00284 | mean—0·1637 | 0·00418 |
| 100 mg per 100 ml | 0·3120 to 0·3290 | | 0·3156 to 0·3333 | |
| | mean—0·3238 | 0·00458 | mean—0·3232 | 0·00473 |
| 200 mg per 100 ml | 0·6372 to 0·6446 | | 0·6333 to 0·6496 | |
| | mean—0·6409 | 0·00208 | mean—0·6417 | 0·00548 |
| 400 mg per 100 ml | 1·247 to 1·301 | | 1·252 to 1·283 | |
| | mean—1·280 | 0·0147 | mean—1·270 | 0·0113 |

Results of the machine error in which 20 injections of the same solution (about 250 mg per 100 ml) were injected are shown in Table II.

TABLE II

RESULTS OF ETHANOL-TO-PROPANOL RATIOS FOR 20 INJECTIONS OF THE SAME SOLUTION

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1. | 0·7925 | 6. | 0·7901 | 11. | 0·7959 | 16. | 0·7852 |
| 2. | 0·7937 | 7. | 0·7974 | 12. | 0·7914 | 17. | 0·7967 |
| 3. | 0·7927 | 8. | 0·7978 | 13. | 0·7968 | 18. | 0·7961 |
| 4. | 0·8008 | 9. | 0·7970 | 14. | 0·7923 | 19. | 0·7725 |
| 5. | 0·7952 | 10. | 0·7891 | 15. | 0·7831 | 20. | 0·7912 |

Mean = 0·7924. Standard deviation = 0·00580.

This column will easily resolve ether, acetaldehyde, acetone, ethyl methyl ketone and methanol from ethanol; isopropanol has only a slightly shorter retention time than ethanol and distorts the peak. Higher alcohols are also easily resolved. The detector is relatively insensitive to chlorinated compounds; of those tested, all except chloroform were easily separable from ethanol. The detector response was such that 100 mg per 100 ml of chloroform gave a response that was equivalent to only 15 mg per 100 ml of ethanol.

As "surgical" anaesthesia blood chloroform levels are only about 10 to 15 mg per 100 ml, it can be seen that this possible interference is of no practical significance.

The method is equally applicable to analyses of large numbers of urine samples, and its comparison with the usual dichromate method[8] has shown this gas-chromatographic method to be more precise and, of course, more specific.

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# The Detection of Nitrate in the Presence of Interfering Substances

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THE "brown ring" reaction that occurs between nitrates and iron(II) sulphate in the presence of sulphuric acid is an old and familiar test for nitrates, but suffers from limitations imposed by certain substances that either give masking reactions or prevent the coloured ring from forming.

Although hinted at by Mellor,[1] it does not seem to be generally known that if an excess of iron(II) sulphate is present in concentrated sulphuric acid medium, then small amounts of nitrates or nitrites give a pink to dark red colour (depending on the amount present) when added to this iron(II) - sulphuric acid reagent mixture. The addition of excess of nitrate or nitrite finally causes the red colour to fade, presumably because of the complete oxidation of all of the iron(II) in the mixture.

The iron(II) reagent was prepared by adding 5 volumes of concentrated sulphuric acid to 1 volume of a 10 per cent. w/v solution of iron(II) sulphate. At room temperature the mixture remained clear for a day or two, but after this time white crystals (presumably of one of the lower hydrates of iron(II) sulphate) were slowly deposited. Storage of the reagent at about 40° C retarded crystallisation (for 3 to 4 days), but the formation of crystals in no way impaired the reactions of the reagent with nitrate and nitrite.

In mixtures of potassium nitrate (2 mg) with an excess (300 mg) of potassium cyanide, sodium thiosulphate or ammonium persulphate, nitrate could be readily detected by the direct addition of about 0·1 g of the mixture to a few millilitres of the reagent. With the persulphate mixture the pink colour caused by the presence of nitrate was transient because of the oxidation of the iron(II).

Direct addition to the reagent could not be made to detect nitrate in mixtures containing chlorate, chloride, bromate, bromide, iodate or dichromate because of interference. With these mixtures it was necessary to diffuse out nitrate from them in the following way.

About 0·1 g of the mixture was placed in the glass cup attached to the stopper of a Cavett flask (obtained from Messrs. Fisons Scientific Apparatus Limited, Loughborough) and moistened with 3 to 4 drops of approximately 6 N sulphuric acid. Concentrated sulphuric acid (1 ml) was placed in the bottom of the flask, and the apparatus assembled and incubated for about 2 hours at between 75° and 80° C. After cooling, 1 ml of the iron(II) - sulphuric acid reagent was added to the acid in the flask, when the presence of nitrate was indicated by the development of the usual pink colour. Bromine was liberated from mixtures containing bromide or bromate, and chlorine from chlorates, and it was necessary to expel these halogens (especially bromine) by blowing air through the contents of the flask *at room temperature*, before adding the reagent.

The positive results obtained with nitrate in the presence of excess of chloride suggested that nitrosyl chloride would react directly with the iron(II) reagent to give a red colour, and subsequent experiments showed that this was correct.

Attempts to detect nitrate, when mixed with excess of potassium iodide, by diffusion met with failure, although the liberated iodine was removed from the contents of the Cavett flask by solvent extraction with benzene, carbon disulphide or carbon tetrachloride.

If the amount of sulphuric acid placed in the Cavett flask was reduced to 0·5 ml and the amount of reagent added after incubation was 3 to 4 drops, the limit of detection by diffusion was about 15 $\mu$g of nitrate.

Nitrate in weak solutions (*e.g.*, 0·1 g of potassium nitrate per 250 ml of water) could be detected by adding a few drops of the solution directly to a few millilitres of the reagent with cooling, whereas it was difficult to obtain a positive "brown ring" test with the same nitrate solution. This is probably because all of the nitrate present in the few drops of the solution that was added to the reagent reacted with the latter, whereas in the "brown ring" test it was only the nitrate present at the interface of the two liquids that was effective in producing the coloured ring.

The forensic chemist is sometimes asked to examine sweepings and debris for traces of industrial blasting explosives when it is thought that a suspect has used these explosives unlawfully, for instance to blow open a safe.

The method described above showed considerable promise when applied to this problem. Some sweepings taken from a garage floor were sifted free from large pieces of paper, leaves, sticks and so on, by using a coarse sieve (No. 7 mesh). Small amounts (0·25 to 0·50 g) of "Polar Ammon" gelignite were ground up in a mortar with about 50 g of sifted sweepings, and a small amount of the mixture was made into a paste with 6 N sulphuric acid.

The glass cup of the Cavett apparatus was filled to three quarters of its capacity with this paste, and the diffusion of nitrate carried out as already described. The addition of iron(II) reagent to the sulphuric acid in the Cavett flask produced a bright pink to dark red colour, representing total nitrate (*i.e.*, inorganic nitrates such as ammonium nitrate *plus* nitroglycerine) in the sample.

To detect organic nitrate (*e.g.*, nitroglycerine*) approximately 5 g of the dry sweepings were shaken with sodium-dried ether. The ether extract was filtered and the solution carefully evaporated, avoiding any heating of the residue.

* True nitro-compounds, *e.g.*, TNT give no colour with the iron(II) reagent.

This residue, which consisted chiefly of oil and grease from the garage floor, was placed in the Cavett cup, without any acid, and incubated directly as previously described. Addition of the iron(II) reagent to the acid in the flask after incubation produced a pink colour. Control samples of the garage sweepings, without the addition of explosive, gave no pink colour with the reagent after incubation for "total" and "organic" nitrate. The acid in the Cavett flask was sometimes pale brown in colour after incubation, possibly owing to traces of volatile hydrocarbon material passing into it, but this did not impair the production of the pink colour caused by nitrate.

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# Determination of Thiol Esters with *o*-Hydroxymercuribenzoic Acid

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RECENTLY, Cecil and Ferdinand[1] have shown that the thiol esters can be determined by reacting them with ammonia solution and titrating the resulting thiols amperometrically with mercury(II) chloride. The free thiols in the presence of thiol esters can be titrated at pH 3. This method has been claimed as being much more specific for thiol esters in comparison with the method based on the formation of hydroxamic acids.[2]

The present investigations are based on the titration of thiols with *o*-hydroxymercuribenzoic acid by using dithiofluorescein (thiofluorescein) indicator as suggested by the author,[3] which method has proved simple, selective and accurate. The actions of some compounds on thiol esters have been examined by this method and the following facts noted.

(*a*) The most reactive compounds in aqueous solutions are dimethylamine and primary amines such as methylamine, hexylamine, benzylamine and ethylenediamine. Other compounds, arranged in decreasing reactivity, are: piperidine, hydroxylamine, morpholine, glycine, diethylamine, ammonia and phenylhydrazine. The reaction results in the formation of thiol—

$$\mathrm{R.COS.R' + NH(CH_3)_2 \longrightarrow R.CON(CH_3)_2 + R'.SH}$$

(*b*) Compared to amines, sodium hydroxide in aqueous solution is not very reactive towards thiol esters, but the addition of alcohol, especially methanol, increases the reactivity of sodium hydroxide and decreases the reactivity of the amines. In alcoholic solution, sodium hydroxide has proved to be the most active agent. This phenomenon can be explained by the reactions—

$$\mathrm{R.CO.SR' + OH^- \longrightarrow R.COO^- + R'.SH}\ \text{(slow)}$$

$$\mathrm{R.CO.SR' + CH_3O^- \longrightarrow R.COOCH_3 + R'.S^-}\ \text{(rapid)}$$

(*c*) Thiol esters do not decompose by the action of tertiary amines. Free thiols can be simply titrated with *o*-hydroxymercuribenzoic acid in the presence of thiol esters without any interference, by using dithiofluorescein as the indicator, in a solution containing triethylamine at pH 8·5.

As it has been found difficult to obtain thiol esters of guaranteed purity, they were prepared directly in a solution of known concentration by the following procedure.

The alcoholic or aqueous solutions of thiol were treated with an excess of anhydride in the presence of triethylamine until the thiol was converted to thiol ester. The solutions were then diluted with water or alcohol to a known volume. The concentration of thiol ester can be assumed to be equal to the concentration of the thiol taken. The excess of anhydride readily decomposes, and the products do not interfere with the determination of thiol esters. Acetic anhydride, benzoyl anhydride, ethyl chlorocarbonate, glutaric anhydride, *p*-thiocresol, *n*-pentyl mercaptan, thioglycollic acid and cysteine were used for the synthesis of thiol esters.

A 0·01 N solution of *o*-hydroxymercuribenzoic acid was prepared by dissolving about 3·2 g of *o*-hydroxymercuribenzoic acid anhydride in 25 ml of N sodium hydroxide, and diluting to 1 litre with 20 per cent. v/v ethanol. The indicator was prepared by dissolving a small amount of dithiofluorescein in N triethylamine in the presence of EDTA.

Some thiol esters, *e.g.*, acetic acid esters, can be titrated directly with *o*-hydroxymercuribenzoic acid in the presence of dimethylamine and sodium hydroxide at room temperature, and some, *e.g.*, glutaric and benzoic acid esters, must be titrated at between 50° and 80° C. The others, *e.g.*, ethyl *S*-pentyl thiocarbonate, must be determined indirectly after heating with an excess of *o*-hydroxymercuribenzoic acid.

In general, two procedures can be suggested for the determination of thiol esters, and one or the determination of free thiols in the presence of thiol esters.

## METHODS

### PROCEDURE 1—

Dissolve 0·01 to 0·1 millimoles of thiol esters in 25 ml of water or alcohol. Add 2 ml of 40 per cent. w/w dimethylamine and 2 ml of N sodium hydroxide and titrate with 0·01 N *o*-hydroxymercuribenzoic acid in the presence of dithiofluorescein until the blue colour completely disappears. If necessary, titrate at an increased temperature.

### PROCEDURE 2—

Dissolve 0·01 to 0·1 millimoles of thiol ester in 10 ml of methanol, and add 5 ml of N sodium hydroxide and an excess of *o*-hydroxymercuribenzoic acid. Heat the solution in boiling water for 5 minutes, cool it, add the excess of thiol solution (cysteine can be used) and titrate to the dithiofluorescein end-point with *o*-hydroxymercuribenzoic acid. The amount of acid consumed by the added thiol should be subtracted from the result.

### PROCEDURE 3—

For the determination of thiols in the presence of thiol esters, add 1 ml of 3 N triethylamine and 1 ml of 0·5 N perchloric acid to the 25-ml solution (water or alcohol). Titrate the thiols with 0·001 to 0·01 N *o*-hydroxymercuribenzoic acid by using dithiofluorescein as indicator. A further titration corresponds, after the addition of sodium sulphite, to the disulphide content,[4] and after addition of dimethylamine and sodium hydroxide, to thiol esters.

With the above procedures it has been found that the recovery is about 100 per cent. with a mean deviation of ±0·3 per cent. for direct titration of thiol esters and ±1·0 per cent. for indirect determination.

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# The Polarographic Determination of Zinc in Plant Materials

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A POLAROGRAPHIC method for determining zinc in plant materials has been developed. The element, in acid solution from dry ashed plant tissues, is absorbed on a strongly basic anion-exchange resin in chloride form and is thus separated from other elements. It is eluted with a known volume of supporting electrolyte, and after additions of sodium sulphite and gelatin, the polarogram is recorded from an aliquot of this solution. The zinc content is determined by the method of standard addition. The method described is accurate, simple and rapid, and recovery experiments gave satisfactory results. The use of a limited number of reagents minimises the danger of contamination.

Because of the physiological importance of zinc a number of different methods for its determination in biological materials have been developed, several of which are polarographic, with or without preliminary separation of the element. Jones[1,2] used two methods for the polarographic determination of zinc simultaneously with copper and manganese, respectively. In both methods the elements were separated before the determination was made. Verdier[3] proposed a direct polarographic method for the determination of zinc in plant tissues and Sirois[4] described another simultaneous method for determining zinc, copper and manganese. Robertson[5] determined zinc polarographically after removing phosphate with zirconium nitrate.

In our experience, the best results are obtained when zinc is separated before the determination, independent of the method used. Maier and Bullock[6] used a strongly basic anion-exchange resin in the chloride form for separating zinc from an acid solution of ashed plant tissues. They eluted the zinc with a solution of sodium hydroxide and determined it colorimetrically with Zincon. Jackson and Brown[7] separated zinc similarly, by eluting it with 0·005 N hydrochloric acid and determining it with Zincon. In this method we have combined the ion-exchange method for the separation of zinc and the polarographic method for its determination, with the supporting electrolyte for elution of the element.

## EXPERIMENTAL

### APPARATUS—

A $PO_3$ Polarograph, Radiometer, Copenhagen, was used for this work.

### REAGENTS—

All reagents used were of analytical-reagent grade; water was de-ionised.

### PREPARATION OF COLUMN—

A slurry of Amberlite IRA-400 resin in water was introduced into a glass tube, 100 mm in length and 12 mm in diameter (wider at the top), so that a resin column about 80 mm high was obtained. During this treatment the water was allowed to flow from the column, and the resin settled on to the sintered-glass support. The column was treated with 50 ml of a solution 2·0 N with respect to ammonium hydroxide and ammonium chloride, and with 50 ml of 2·0 N hydrochloric acid. The resin was then ready for use. Water and all of the solutions used during this procedure were always maintained at a level above the resin.

### PROCEDURE—

Weigh from 1·0 to 2·0 g of oven-dried plant material, containing more than 10 p.p.m. of zinc, and ash by heating at 450° to 500° C overnight. Dissolve the ash in 15 ml of 2·0 N hydrochloric acid and warm to complete dissolution. Filter through a Whatman No. 40 filter-paper and wash the filter three times with 5-ml portions of the same acid, collecting the filtrate and washings in the top of the ion-exchange tube. Allow the solution to flow through the column at a flow-rate of about 1 ml per minute, wash with 40 ml of 0·5 N hydrochloric acid and discard the effluent solution and washings. Elute the zinc with 45 ml of a solution of 2·0 N ammonium chloride in 2·0 N ammonia solution, and collect the eluate in a 50-ml calibrated flask containing 0·5 g of sodium sulphite. Add gelatin solution to give a final concentration of 0·01 per cent., dilute to the mark with the 2·0 N ammonium chloride in 2·0 N ammonia solution, and mix. Record a polarogram from −1·1 to −1·6 volts with a 5-ml aliquot, and determine the concentration of zinc by the method of standard addition.

Pass 100 ml of de-ionised water through the column and maintain its level above the resin until the latter is again required for use. For the next determination treat the resin as described above; the same resin can be used up to ten times.

## RESULTS AND DISCUSSION

Many results have been obtained by the proposed metod; some of these are given in Table I.

TABLE I

ZINC CONTENT, P.P.M. ON DRY WEIGHT, SIX REPLICATE DETERMINATIONS

| Sample | Zinc, p.p.m. | Mean value | Standard deviation |
|---|---|---|---|
| Alfalfa hay .. .. | 21·2, 22·4, 22·5, 22·3, 21·8, 22·7 | 22·1 | 0·51 |
| Mixed hay .. .. | 32·7, 32·5, 31·0, 32·5, 31·4, 31·7 | 31·9 | 0·64 |
| Barley .. .. .. | 38·2, 38·9, 39·0, 38·3, 40·5, 39·5 | 39·0 | 0·78 |
| Maize .. .. .. | 29·4, 29·4, 31·5, 30·3, 29·8, 30·2 | 30·1 | 0·72 |
| Soya bean meal .. .. | 40·8, 41·6, 40·8, 41·5, 41·1, 39·8 | 40·9 | 0·59 |
| Wheat bran .. .. | 73·5, 74·3, 74·7, 72·3, 75·1, 74·0 | 73·8 | 1·23 |

Recovery tests were also conducted; known amounts of zinc were added as measured volumes of standard solutions to 1-g samples, whose zinc contents had previously been determined. These samples were then analysed as described above; the results are given in Table II. As the concentration of zinc in plants is sometimes much higher than in our samples, recovery was checked over a wide range of zinc contents. All the results are mean values for two determinations.

TABLE II

RECOVERY OF ADDED ZINC

| Zinc present, µg | Zinc added, µg | Zinc expected, µg | Zinc found, µg | Recovery, per cent. |
|---|---|---|---|---|
| 22 | 65 | 87 | 85 | 98 |
| 22 | 654 | 676 | 647 | 96 |
| 22 | 1308 | 1330 | 1290 | 97 |
| 32 | 65 | 97 | 91 | 94 |
| 32 | 654 | 686 | 717 | 105 |
| 32 | 1308 | 1340 | 1370 | 102 |
| 74 | 65 | 139 | 133 | 96 |
| 74 | 654 | 728 | 750 | 103 |
| 74 | 1308 | 1382 | 1310 | 95 |

The results obtained by the proposed method were compared with those obtained by the diphenylthiocarbazone colorimetric method.[8] As can be seen from Table III the agreement was good.

TABLE III

COMPARISON OF METHODS

| | Zinc content, p.p.m. | | | | | |
|---|---|---|---|---|---|---|
| Proposed method .. .. .. | 22 | 32 | 39 | 31 | 41 | 72 |
| Diphenylthiocarbazone method .. | 20 | 33 | 38 | 29 | 42 | 75 |

The proposed method has been successfully used for some time in our laboratory on a wide range of plant tissues. It is suitable for determining zinc in any type of biological sample or soil, when dissolved. Twenty micrograms of zinc in a final volume of 50 ml could be determined without difficulty; if a sample contains less than 20 µg of zinc a larger amount should be taken.

The method described is accurate, and the results obtained are in agreement with those given by the colorimetric diphenylthiocarbazone method. It is superior to the latter because of its simplicity and speed, and, as it involves the use of only a limited number of reagents, decreases the possibility of contamination. The whole procedure without ashing takes about 3 hours, and eight to ten samples can be analysed with ease in this time.

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# Book Reviews

AN APPROACH TO CHEMICAL ANALYSIS. ITS DEVELOPMENT AND PRACTICE. By H. N. WILSON. Pp. x + 373. Oxford, London, Edinburgh, New York, Paris and Frankfurt: Pergamon Press. 1966. Price 30s.

What is chemical analysis, and why do some chemists profess the title "analytical chemist"? The answers to these questions are contained in this excellent book by H. N. Wilson, the recipient of the Society's first Gold Medal. The author has set out with the purpose of providing chemists, who have little or no experience of chemical analysis, with an account of how the subject has developed and what its potentials are in terms of present and future problems.

With a wealth of experience to draw upon, over a period of great changes and developments in the subject, the author has presented a picture of chemical analysis that is factual yet philosophical, historical yet up to date, personal yet objective; the result is something unique in the literature of analytical chemistry.

The text is divided into two broad parts; the first, largely chemical in nature, deals more with the "classical" aspects of analytical chemistry, whilst the second part is concerned with the development and use of techniques based on physico-chemical principles. Although such a division of the subject is largely traditional and somewhat arbitrary it is, nevertheless, useful for some purposes. The distinction between classical and instrumental techniques can often be very real, and to the uninitiated it can blur the image of the analyst with his beaker and burette, his flask and his filter funnel. The present text ably demonstrates the complementary nature of these two main divisions of analytical chemistry. It illustrates well the need of an expanding industrial technology for more rapid methods of analysis, a need that has led in the past 2 decades to the development of highly sophisticated instrumental techniques, often empirical and often quite alien to the classical chemical approach. Although the value of these instrumental methods to routine analytical operations is beyond question, the real danger in an over-emphasis of their use is that the interests of analysts and chemists may diverge so widely as to preclude mutual understanding. Having fought so long for the better recognition of their subject as a distinct and separate branch of the science of chemistry, are analytical chemists now moving too fast and too far from their classical chemical origins and too quickly replacing the burette with the black box?

If this is so, then the publication of this book is indeed timely. Written with the experience of a lifetime's involvement in the subject, this book brings into true perspective the work and aims of the analytical chemist. It successfully bridges the philosophies that are tending to separate the chemists from the analysts, and even the analysts from each other.

Seldom has the reviewer had such a pleasant and rewarding task to perform; here is a book that is not only eminently readable, but also profoundly stimulating. Although not primarily directed to a readership of analytical chemists, there will be few who will not find this account of the development and practice of their subject, as seen through the eyes of one of its most able and distinguished exponents, very worthwhile reading. This book is a must for anyone contemplating a career in analytical chemistry.

WILLIAM I. STEPHEN

ZONE MELTING. By HERMANN SCHILDKNECHT. Pp. x + 222. Weinheim/Bergstrasse: Verlag Chemie GmbH; New York and London: Academic Press. 1966. Price DM 36; $9.00.

This volume is an English translation of the German original, the review of which (*Analyst*, 1965, **90**, 309) should be consulted for a summary of the contents of the present volume. As English-speaking readers may now be interested in the use of the new volume as a general textbook, attention should be drawn to some differences between Schildknecht's treatment and those of other authors.

It is regrettable that, in the present volume, a quantity, $Z$, called "number of passes," is defined as $xL/l$ where $L$ is the length of the column and $l$ is zone length, because all other workers on zone melting have taken the number of passes as being synonymous with the number of times the zone has passed.

Most writers have said that transport of matter in zone refining is due to the volume change on melting, but Schildknecht believes that it is due primarily to the interfacial forces of the melt - crystal system (and possibly also the melt - container system) and only to a small extent to the density differences between the liquid and solid phases. It is perhaps worth noting that all the diagrams in that section dealing with transport of matter show the behaviour of samples in horizontal boats.

On the vexed question of whether it is better to use horizontal boats or vertical tubes for the treatment of organic compounds, Schildknecht appears, on the whole, to prefer vertical tubes with the zone travelling downwards (see pages 106 to 107). However, much can be said in favour of the use of horizontal boats, and the book contains numerous drawings of apparatus devised by Schildknecht in which this method is used.

The translation has been efficiently carried out by Express Translation Service, London, but the spelling is American.

E. F. G. HERINGTON

ANALYTICAL MICROSCOPY. ITS AIMS AND METHODS IN RELATION TO FOODS, WATER, SPICES AND DRUGS. By T. E. WALLIS, D.Sc., F.R.I.C., F.P.S., F.I.Biol. Pp. viii + 226. London: J. & A. Churchill Ltd. 1965. Price 36s.

The third edition of this useful book is described as a revised issue, although the revision that has taken place is relatively slight. First, there has been some rearrangement in the text that has resulted everywhere in improvement. Secondly, it is stated that the information has been brought up to date, a claim that is hardly justified. For example, in the sections dealing with insects in food, no reference is made to the methods of isolation recorded in the A.O.A.C. or A.A.C.C. collected methods of analysis, or to the work of Harris and co-workers on the identification of insects from fragmentary material. Again, the section on the use of the microscope is in need of overhaul as is some of the nomenclature and bibliography.

Having said this, it must be stressed that in the major part of the book, *i.e.*, that dealing with the microscopy of vegetable foods and of water, Dr. Wallis has taken the opportunity to polish an already valuable text. Here the author writes with clarity and authority, although he is frequently too modest to indicate how much of the original work was his own.

Those "skilled in the art" will welcome a chance to replace their well worn copy of the second edition. To those new to the subject of analytical microscopy, this book can be recommended. Dr. Wallis writes from a life-time of study and experience; some of this experience must rub off on to any user of this valuable introduction to the subject. J. F. HERRINGSHAW

INVESTIGATIONS IN THE FIELD OF ORGANOLEAD CHEMISTRY. By L. C. WILLEMSENS and G. J. M. VAN DER KERK. Pp. x + 128. London: ILZRO. 1965.
*Free on request from the Lead Development Association, 34 Berkeley Square, London, W.1.*

This monograph published by the Institute for Organic Chemistry TNO, Utrecht, surveys in considerable detail the present state of knowledge of organolead chemistry. As such, it will be invaluable to any workers interested in this field, and may possibly result in further commercial developments of these interesting compounds. Apart from the ubiquitous T.E.L., whose annual tonnage is much greater than the combined figure for all the other organometallics, no industrial outlet has been found for any other organolead compound.

After an informative introductory section, the varied types of reaction encountered in this field are surveyed in 4 chapters, both from the standpoints of preparative organic chemistry and the study of reaction mechanisms. The final chapter describes the most effective preparative methods in greater detail, together with a brief account of the method used in the analysis of these compounds. The table of solubilities covering a variety of solvents is most welcome in a publication of this kind. There is a good index, which includes melting-points, and finally a list of almost 200 references to the original literature. F. G. ANGELL

CHEMICAL ANALYSIS IN PHOTOGRAPHY. By G. RUSSELL, A.R.P.S., F.R.I.C. Pp. 272. London and New York: The Focal Press. 1966. Price 90s.

This book is the first to be published on techniques and methods of chemical analysis specifically applied to photographic materials. The author has had wide experience as an analytical and research chemist in the photographic field, and has produced a valuable and comprehensive review.

When it is remembered that Fox Talbot first described his photographic process to the Royal Society in 1839, and when the volume of photographic literature published since that time is considered, it is incredible that the world has had to wait so long for a book of this nature. This volume is a valuable contribution to the analysis of photographic products, and should be an excellent laboratory manual for all analysts interested in the photographic field. The first chapter is devoted to "General Information," and will be considered later. Other chapters give detailed consideration to the sampling and analysis of gelatine, the analysis of silver nitrate and halides, the estimation of auxiliaries and additives (*e.g.*, sensitising and anti-halo backing dyes, stabilisers, gelatine hardeners, metal additives, solvents used in the photographic industry, humectants and anti-static additives). Later chapters deal with film base and paper, coated products, processing solutions, water and effluents and processed materials.

The chapters are well arranged, and analytical details are clearly stated, eliminating the need to refer to original papers. However, should the reader wish to do so, the individual chapters are fully documented with references—many of recent date. Where alternative methods of analysis are given, the method to be preferred is stated, and in view of the author's wide experience, this is a valuable aid to the analyst.

The only criticism relates to Chapter 1, and to the Appendices, and this in no way detracts from the value of the book for laboratory use. Chapter 1 is headed "General Information: Laboratory Requirements, Techniques, Methods, Instruments." It includes references to practically all modern and classical relevant methods, which have been summarised to such an extent as to be of doubtful value. Surely conventional text-books are better guides to specialised analytical techniques? Similar criticism can be made of the Appendices—20 in number. Most of the information can be found in standard chemical works of reference. In particular, it is difficult to justify the inclusion of logarithm and antilogarithm tables. Chapter 1, and the Appendices comprise one-fifth of the book; their omission would have permitted the sale of the book at a lower price, and the possibility of the wider sale that this volume so richly deserves.

This book is recommended as the first of its kind, and because it is indispensable to anyone concerned with the analysis of photographic products. G. W. G. MACLENNAN

VISUAL METHODS OF EMISSION SPECTROSCOPY. By N. S. SVENTITSKII. Pp. viii + 344. Jerusalem: Israel Program for Scientific Translations. Distributed in Great Britain and the Commonwealth, South Africa, Eire and Europe by the Oldbourne Press, London. 1965. Price 108s.

In his foreword, after referring to his earlier publication "Steelscope" (1948)—now largely obsolete—the author says: "The present book is a revised monograph on the subject of the steeloscope, supplemented by methods of quantitative spectroscopic analysis with the aid of steelometers and steeloscopes with a photometric eyepiece."

The treatment of the subject is comprehensive and authoritative, and the numerous practical hints are evidence of extensive personal experience of the analytical techniques that he describes. When dealing with his own significant contributions to the subject, the author modestly shuns publicity, so that one must consult the bibliography of 512 references (arranged under chapters) to discover a polarising photometer, his own version of the high-frequency initiated a.c. arc (the "Activated" a.c. arc), the determination of nickel, silicon and carbon in steels, the analysis of copper-base alloys and sampling by electric spark transfer, to quote his more important published work.

It seems that steeloscopes and steelometers are far more popular in the U.S.S.R. than they are in this country, which would account for the preponderance of references to Russian journals. However, in the remarkably informative sections on apparatus covering both spectroscopes and excitation sources, the equipment available from other countries is treated fairly.

A novel method of indicating literature references by the use of oblique strokes is adopted, thus: / 167, 171 / indicates two such references, while "electric sampling (82)" refers to the number of a section, of which there are 89 in all.

The half-tone reproductions of spectra, while adequate, tend to be rather indistinct. My sympathies are with the author as I know, from discussion on screening with the printers of my own publications, how very difficult the printing of reproductions of spectra can be! On the other hand, the text and the line drawings (particularly the latter) are very clear.

There are several spelling mistakes in the bibliography, *e.g.*, "Mavrodineanu" (page 271) is the correct name and, on pages 268 and 278 the German double "s" in "Schließmann" has become a "B."

The translators are to be congratulated on providing a very readable account and, for anyone using or contemplating using such visual methods, this book can be recommended as the best reference work yet published in this particular field. D. M. SMITH

FLUORESCENCE AND PHOSPHORESCENCE ANALYSIS: PRINCIPLES AND APPLICATIONS. Edited by DAVID M. HERCULES. Pp. xiv + 258. New York, London and Sydney: Interscience Publishers, a division of John Wiley & Sons. 1966. Price 90s.

This is a compilation of the expanded versions of 8 papers presented at a one-day symposium organised by the Analytical Division of the American Chemical Society. The first 4 chapters will probably be the most useful for the general reader. Chapter 1 (40 pages) reviews the theory of luminescence processes. It describes the most important types of electronic excited states, the methods of their formation and their properties. The second chapter (39 pages) deals with experimental methods. A variety of commercial instruments is described and experimental factors, briefly discussed, include inner filter effects, fluorescent reference compounds, interferences, sensitivity, correction of spectra, fluorescence efficiency, etc. Chapter 3 (69 pages) on organic compounds reviews the relationship between molecular structure and photo-luminescence, and discusses energy transfer, excimer formation, delayed fluorescence, dissociation in the excited state, solvent effects, and so on. The fourth chapter (17 pages) deals with the theory of the luminescence of metal chelate compounds and the structural factors involved. Comparatively little space is devoted to phosphorescence in Chapter 5 (17 pages), although a limited review of its applications is included. The remaining 3 chapters cover more specialised topics: chemiluminescence; some specific applications in biochemical research; and the theory of the polarisation of fluorescence of solutions.

The stated purpose of this book is to enable the novice or practising chemist to acquire a limited knowledge of fluorescence techniques. One might expect a text-book of this sort to leave the reader with a knowledge of the advantages and limitations of the technique as an analytical method, and a clear idea of how to apply it to a practical job of analysis. In this sense the book does not entirely achieve its objective, largely because of the difficulty of combining 8 papers by different authors into a unified whole. Many of the principles are adequately covered but some of the more advanced subject matter could have been replaced with advantage by more detailed discussion, with examples, of how to apply the techniques of fluorescence and phosphorescence measurement to analytical problems not easily solved by other methods. C. A. PARKER

KIRK-OTHMER ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY. Volume 8. Electron Tube Materials to Ferrites. Edited by HERMAN F. MARK, JOHN J. MCKETTA, jun., DONALD F. OTHMER and ANTHONY STANDEN. Second Edition. Pp. xiv + 901. New York, London and Sydney: Interscience Publishers, a division of John Wiley & Sons Inc. 1965. Price £16 18s.; price per volume for subscribers to the complete set of 18 volumes, £13.

Volume 8 of this series has now appeared, and it contains monographs ranging over a wide spectrum of subjects; all of interest or instructive, or both. As usual in these reviews (see *Analyst*, 1963, **88**, 899 *et seq.*) attention will be given primarily to the sections of analytical interest; and the list of Contents indicates that Fats and Fatty Oils (35 pages) should contain matter of this nature, as well as being of great general interest to analysts. The section that deals with analysis outlines the methods and summarises their functions without giving the experimental details. Nearly all of the methods mentioned are of the conventional type, although there is reference to the oxygen-bomb method for measuring stability. The reference to chromatography is brief, and the very useful application of gas - liquid chromatography to determining the degree of unsaturation of fatty acids is all too short. This method enables small amounts of fatty acids to be determined, thereby making obsolete many of the analyses reported by earlier methods. The following monograph on Fatty Acids is by a different author, and it also makes reference to this method, however, in equally brief terms. Both authors deal with physical methods of measurement and have compiled useful lists of oils or fatty acids, as the case may be, summarising details of their origins and properties.

The purely technical aspects of these 2 monographs deal mainly with extraction, processing and refining, the latter including an important section on deodorisation. For the fatty acids there is reference to industrially important reactions, such as esterification, oxidation and the production of surface-active agents. The continuous process for fat splitting, now in common use, is also well described, and there is a comprehensive section on the economic aspects of fatty acids, based on American statistical data. Certain individual fatty acids are of special interest, such as those from tall oil, which is now becoming of increasing importance as a by-product from the manufacture of wood pulp from coniferous wood by the sulphate process. Thus in 1963 (presumably in America), tall-oil fatty acid production totalled 240 million lb, and was used for many different purposes, *e.g.*, in coatings, detergents, driers and hard floor coverings.

The monograph on Feeds (Animal) consists chiefly of a list of the numerous products in use, principally derived from cereals, and their by-products, including brewers' and distillers' grains. A second section deals with oil-bearing seeds, and a third with forages (such as alfalfa) and dairy products (as casein); finally, marine products (as fish meal) are discussed. The monograph is almost entirely descriptive and has no analytical implications, but it is extremely useful in that it gives a comprehensive list of a wide variety of products of this kind, some of which are little known in this country.

Enzymes (Industrial) is another monograph (58 pages) with special analytical associations. After the origin, classification and isolation of the enzymes have been discussed, there is a section on the measurement of enzyme activity which follows the usual lines. A specially useful feature, however, is the list of definitions of a wide range of enzyme units, mostly empirical in nature. This is a complicated subject, and although some 23 units are defined, it is obvious that some must inevitably have been omitted; the whole system indeed is ripe for rationalisation.

The analyst having more academic interests will find the series of articles dealing with Esterification, Ester-Interchange, Esters (Organic), Ethane, Ethanoic acid, Ethanol, Ethers, Ethylene and Ethylene Oxide useful summaries of their respective subjects. It is a sign of our highly specialised times that ethylene oxide has a monograph of 36 pages to itself, including a short section on the distillation and chromatographic techniques used to determine the purity of this product. The relative merits of ethylene dioxide and methyl bromide as fumigants have recently come under notice, and although this use of the former is referred to in the monograph, a comparison of its efficiency in this respect with similar products would have been useful.

Analysts and others interested in the practical use of ethanol (in the industrial sense!) will find much of interest in the section on units in this monograph (48 pages). Tables relating U.S. Proof, British Proof and alcohol by weight are given, and there is a section on test methods in which attention is rightly drawn to the confusion that exists because of the different units accepted in different countries and even in the same country. Some of these differences arise from the temperature used for determining the specific gravity, and at times quite small differences in terms of °C are involved. Perhaps this is a chemical "Tower of Babel" that the universal adoption of the metric system will eventually eliminate. Reference is made to health and safety considerations in connection with ethanol, but the monograph is concerned with vapours rather than the liquid, and there is no reference to the important question of alcohol in blood and urine and its implications in drunkenness.

The monographs on Epoxidation, Epoxides and Epoxy Resins (75 pages in all) together form a comprehensive and up-to-date survey of this important series of reactions and compounds. They include a 5-page table of the reactions of the epoxides with literature references, and in another table, the properties of a large number of epoxides are summarised together with their infrared absorption data. These collations of widely spread information should be extremely useful to specialists in the subject.

Monographs of an engineering or other purely practical nature include Electron Tube Materials, Electroplating, Electrostatic Precipitation, Explosives, Evaporation and Extraction. Special mention should be made of the monograph on explosives as it contains descriptions of the manufacture and properties of a wide variety of such products. It comprises 138 pages in all and is divided into high explosives, low explosives, testing methods and propellants. The testing methods are of course functional rather than analytical.

There is the usual sprinkling of unexpected yet interesting monographs. That on Embedding is a case in point, and it is sub-divided into embedment, encapsulation, potting, casting, moulding and impregnation. Naturally the working materials to which reference is chiefly made are the plastics; methods, apparatus and technique are described but strangely enough, there is no mention of one of the most important recent applications of this technique, namely to the preservation of documents and, to some extent, of other museum exhibits.

Finally, among the unexpected monographs is that on Embalming Fluids; only 2½ pages it is true, but with a 20-item bibliography, all no doubt very useful in its time and place. Mortician readers, please note!

JULIUS GRANT

ENCYCLOPEDIA OF INDUSTRIAL CHEMICAL ANALYSIS. Volume 1. General Techniques A–E. Edited by FOSTER DEE SNELL and CLIFFORD L. HILTON. Pp. xvi + 763. New York, London and Sydney: Interscience Publishers, a division of John Wiley & Sons Inc. 1966. Price £17.

This is the first volume of a new encyclopedia to be devoted to industrial analytical chemistry, as contrasted with other multi-volume works that also treat methods of purely scientific interest. The first part on "general techniques" will be in three volumes, the topics being in alphabetical order. The second part, beginning with volume 4, will be devoted mostly to the analysis of specific materials.

There are 29 major articles in this volume and a few shorter ones, written by 34 contributors, most of them well known for their contributions to the analytical literature. A few of the authors are in institutes of technology or the National Bureau of Standards, but most are in important industrial laboratories in the United States. This is an American book; most of the references (a few are as recent as 1965) are to American journals or monographs, and most of the apparatus described is American. Nearly all of the articles are clearly written, a few are of outstanding merit and a real pleasure to read; those on "boiling point determination" and "colour designation and specification" are models of what such papers should be.

Having written that sentence, I am smitten by doubts. How can any one person fairly review a volume of this kind? It would need a syndicate of reviewers to do justice to such a wide variety of topics. Even to say "The article on A is obscure and complicated" could well mean "I don't know anything about A, and the subject is complex to start with." To award one star (interesting), two stars (worth perusal) or three stars (essential reading), like the Michelin "Guides," would be most arrogant and the best course seems to be to mention some of the more important articles so as to indicate the scope of the work. I would draw attention to the papers on "activation analysis" (25 pages), "amperometric titration" (19 pages), "atomic absorption spectroscopy" (25 pages), "capacity and dielectric constant" (38 pages), "complexation in aqueous media" (53 pages, almost entirely devoted to the chemistry of water-soluble chelate compounds), "conductometry and oscillometry" (60 pages), "countercurrent distribution" (28 pages), "distillation" (33 pages), "electron microscopy" (36 pages), "electron probe micro-analysis" (17 pages), "emission spectroscopy (44 pages) and "evaluation of analytical data" (17 pages). Not everybody will agree that the ration of the number of pages per article is properly correlated with the importance of the various subjects. I would have thought that Youden's contribution on "Evaluation of analytical data" was of such *fundamental* importance in industrial analysis, that it should have been twice as long, and the editors could have easily trimmed a few pages from some of the longer articles if they had need to do so.

This volume is well printed on good paper, and the quality of diagrams and photographs is very high. Misprints are very few. Readers may well think that at a price of 340 shillings, this is as it should be.

H. N. WILSON

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THE ANALYTICAL CHEMISTRY OF COBALT. By RONALD S. YOUNG. Pp. viii + 170. Oxford, London, Edinburgh, New York, Toronto, Paris and Braunschweig: Pergamon Press. 1966. Price 45s.

Until comparatively recently the use of cobalt was almost entirely confined to the ceramic and glass industries, but since the beginning of this century, cobalt has found use in a wide variety of materials such as heat-resistant alloys, catalysts, driers and cemented carbides. Its diverse fields of application now include radiography, electroplating, radioactive tracers and animal nutrition.

These developments have stimulated important advances in the analytical chemistry of cobalt, and the wealth of information that has been published on this subject is comprehensively reviewed in this monograph.

As well as providing an excellent coverage of the numerous chemical procedures and modern instrumental methods that have appeared in the literature, the author has increased the usefulness of this book by including practical details of several reliable classical methods. The chapters on Occurrence and Properties, Sampling, and Determination in Natural and Industrial Products are well covered.

The book is singularly free from typographical errors and obvious inconsistencies, and maintains the high standard set in previous monographs in this series.

The author has ably fulfilled the task of providing a book that all analysts engaged in this specialised field, as well as those who deal with the analysis of cobalt-bearing materials less frequently, will find most useful.

D. F. WOOD

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APPLIED INFRARED SPECTROSCOPY. Edited by DAVID R. KENDALL, Ph.D. Pp. xvi + 560. New York: Reinhold Publishing Corporation. London: Chapman & Hall Ltd. 1966. Price $23.00.

Applications of infrared spectroscopy are now so widespread that there is need for a comprehensive treatment to ensure competent use of the methods, and intelligent use of the information obtained. This book does much to meet this need.

It is primarily a compendium of practical know-how, of just the type required for those entering the field for the first time.

Sufficient theoretical background is included to explain the infrared spectra of molecules, but the most valuable chapters are those dealing with techniques of sample preparation, the principles of instrumentation and operation of spectrophotometers, and the requirements for setting up an infrared laboratory.

Particular industrial interests considered in detail include polymers, coal, pharmaceutical products, essential oils and cosmetics, while the rôle of infrared spectroscopy in industrial laboratories and in plant-stream analysis is comprehensively explored. Newer techniques such as micro-sampling and attenuated total reflectance are well covered, and there is an interesting anticipation of future developments in the use of computers in data handling.

This book will appeal principally to those with an industrial interest, but its wide scope and authenticity make it a useful reference source for a much wider public.

R. C. SEYMOUR