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Analytical Applications of a 0·5-MeV Cockroft - Walton Set based on the Measurement of Prompt γ-Radiation

Γ-Radiation Emitted during Proton Reactions

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Nuclear reactions are outlined which yield γ-rays when the elements from lithium to chlorine, with the exception of neon, are irradiated with protons of an energy of 0·5 MeV or less. Energies of the principal γ-rays are listed and analytical applications based on measurements of the γ-rays are discussed.

Analytical methods based on the measurement of radiation emitted during the decay of unstable nuclei are well known, and, in particular, radiative-capture reactions induced by thermal neutrons have enabled very sensitive activation techniques to be developed for many elements. Conventional activation analysis is usually concerned with the measurement of radiation associated with some relatively slow decay, which allows the sample to be removed from the place of irradiation and subsequently counted, but many nuclear transitions occur too rapidly to be detected by this technique. These rapid decays can provide much information of analytical interest, but determinations based on the measurement of this so-called "prompt radiation" have hitherto received little attention, as radiations from the samples must be counted *in situ*, often while irradiation is taking place, and chemical separation cannot be used to isolate the activity to be assayed from all others, before measurement.

Of particular interest is the measurement of the γ-radiation emitted during the de-excitation of excited nuclear states, because the energy and yield of the γ-rays provides information about the type and number of nuclei present in the sample without a radioactive nuclide being necessary as a product of the reaction, and measurement of γ-radiation enables the determination to be carried out on the intact sample. Advantages and disadvantages of prompt γ-radiation methods *vis-à-vis* conventional activation analysis have been discussed elsewhere[1] and will not be considered further here. Both penetrating radiation and charged particles can be used to produce excited nuclear states and the two techniques, when applied to analysis, are to some extent complementary, penetrating radiation being capable of providing information from a relatively large sample, while charged particles permit examination of a thin section of sample near to the surface. Low energy charged particles can be used with advantage to determine light elements in surfaces when suitable γ-lines are emitted from excited nuclei, and when limited penetration and heat dissipation in the sample do not preclude their use, for the coulomb barrier restricts reaction to elements of low atomic number, thus enabling the emitted γ-radiation to be measured relatively easily by simplifying spectral analysis.

Several analytical determinations, based on the measurement of prompt γ-radiation emitted during charged particle irradiation, have already been reported but these have been largely concerned with the measurement of γ-lines excited by particles accelerated by Van de Graaff electrostatic generators.[1,2,3,4,5] The use of an 0·5-MeV Cockcroft - Walton set for exciting prompt γ-spectra that may be used for analytical determination is considered in this paper. Although the sensitivity attainable with this machine is lower at these lower particle energies, the cost of the accelerator is also less (under £20,000). The use of proton irradiations to produce excited nuclear states in the elements from lithium to chlorine, with the exception of neon, is discussed.

Even when targets are bombarded with particles of 0·5 MeV or lower energy, highly excited states of residual nuclei are frequently formed by virtue of the large positive energy balance of many reactions, and decay of the resulting bound or virtual levels can often be

complex. Fortunately many transitions occur in relatively low yield, thus simplifying analysis of the prompt γ-spectra. A great deal of information is available in nuclear physics literature that describes reactions of the light elements with protons, and the results have been summarised.[6,7] Consequently, nuclear processes occurring during reaction of light elements with protons will not be discussed in detail here; only salient aspects will be mentioned.

Experimental

The arrangement of equipment used for the measurement of prompt γ-radiation emitted during charged particle irradiation has been outlined elsewhere.[3] The proton beam from the Cockcroft - Walton set was analysed by means of a 90° bending-magnet, and was subsequently passed through a series of slits, lenses and stops to produce a well defined beam on target. If necessary, the area of sample irradiated could be increased by "wobbling" the target (oscillating it in the beam). Secondary electron suppressors were inserted in the line if required.

Targets were irradiated in single or multiple target holders, the latter being remotely controlled and capable of holding up to 40 samples. An air-tight valve on the beam tube of the largest target changer allowed samples to be transferred to the accelerator, after preparation in an inert atmosphere, or at reduced pressure if necessary.

γ-Rays emitted during the irradiation were detected with either a sodium iodide scintillator or a lithium-drift germanium diode, and the output from the detector, after amplification, was fed to an analysing system; single, 100, 512 or 1024-channel analysers were used as required and as available. When a sample was to be irradiated to a known particle dose, the current falling on the target was fed to a current integrator and the integrator used to control the analyser. Real and live times were always recorded when multi-channel analysers were in use.

Targets of a variety of shapes and sizes could be accepted by target holders, but for convenience, discs of 20-mm diameter, about 2 to 3 mm thick, were usually irradiated. These discs were either cut from solid metal, or, when this was not possible, made by compressing powder or turnings with a 30-ton hydraulic press.

γ-Rays emitted during reaction of protons with light elements—

Reactions of light elements which yield γ-rays with protons of an energy of 0·5 MeV or less are discussed in this section, and the energies of the emitted γ-rays are summarised.

The excitation functions for these reactions frequently exhibit sharp resonances, and when several resonances occur at proton energies of less than 0·5 MeV, for brevity only the γ-yield from one or two of the most intense resonances is considered. Moreover, when the γ-yield from a reaction is particularly complex, the weakest γ-lines have not been included.

A list of energies at which (p,γ) resonances occur has already been compiled.[8]

Lithium—γ-Rays may be emitted by lithium-6 during proton irradiation by decay of the broad 6·35-MeV level of beryllium-7 to ground or by cascade through the first excited level at 0·431 MeV.[9]

Two high energy γ-rays are emitted as a result of radiative proton capture by lithium-7 at the 0·441-MeV resonance, one with an energy of 17·6 MeV, the other less intense with an energy of 14·8 MeV.[10] γ-Rays from the reaction of natural lithium (7·4 per cent. of lithium-6; 92·6 per cent. of lithium-7) with protons are dominated by the yield from lithium-7.

Beryllium—The reaction ^{9}Be (p,γ) ^{10}B shows a resonance at 0·33 MeV, feeding the 6·88-MeV level in boron-10.

Decay occurs by cascade through levels of 0·717, 1·74 and 2·15 MeV. The most prominent γ-rays occur at energies of 0·41, 0·72, 1·02, 4·71, 5·12, 6·14 and 6·86 MeV.[11,12]

Boron—The γ-radiation from irradiation of natural boron with low energy protons is dominated by the reaction ^{11}B (p,γ) ^{12}C (Q = 15·958), and a resonance at 0·16 MeV feeds the capture state of carbon-12 at 16·11 MeV. Decay is to ground or by cascade through the 4·4-MeV level. Thus γ-rays having energies of 16·1, 11·7 and 4·4 MeV[13] are emitted.

Carbon—Although a resonance for the reaction ^{13}C (p,γ) ^{14}N is reported at 0·448 MeV, the γ-ray spectrum from the reaction of natural carbon with low energy protons is dominated by the yield from the reaction ^{12}C + p. A resonance for capture radiation is observed at a proton energy of E_p = 0·459 MeV, and decay of the 2·36-MeV capture level in nitrogen-13 is to the ground state.[14]

Nitrogen—A resonance for radiative capture of protons by nitrogen-14 is observed at a proton energy of $E_p = 0{\cdot}28$ MeV feeding the 7·56-MeV level in oxygen-15. Decay occurs by cascade through levels at 5·2, 6·1 and 6·7 MeV, and γ-ray energies have been reported as being 0·75, 1·39, 2·38, 5·29, 6·21 and 6·84 MeV.[15] A weak resonance for proton capture by nitrogen-15 occurs at $E_p = 0{\cdot}338$ MeV, and at the same proton energy a resonance is observed for the reaction ^{15}N (p,α) ^{12}C, producing the 4·4-MeV level in carbon-12.

However, a more intense resonance is observed at 0·429 MeV,[16] but even at this energy the total γ-yield from natural nitrogen (99·6 per cent. of nitrogen-14; 0·4 per cent. of nitrogen-15) is low.

Oxygen—The cross-section for the reaction ^{16}O (p,γ) ^{17}F is low up to 0·5-MeV proton energy, although radiative capture of protons has been reported.[17] The first resonance in the reaction ^{18}O + p is found to be at $E_p = 0{\cdot}560$ MeV.[6]

Fluorine—Reaction of fluorine with protons is dominated by the reaction ^{19}F (p,α) ^{16}O, for which three resonances are observed for proton energies at 0·222, 0·340 and 0·486 MeV. The resonance at 0·340 MeV is the most intense (cross-section = 160 mb) and the oxygen-16 de-excites largely by emission of γ-rays of an energy of 6·14 MeV (96 per cent.) and 7·12 MeV (4 per cent.).[18]

Sodium—The most intense resonance for the reaction of sodium with protons occurs at 0·308 MeV. More than 20 γ-rays have been detected from the reaction ^{23}Na + p at this energy, of which the most intense from proton capture have energies of 1·37, 2·86, 3·83, 4·23, 6·77, 7·75 and 10·61 MeV. In addition, a 1·63-MeV γ-ray is observed from the reaction ^{23}Na (p,α) ^{20}Ne.[19]

Magnesium—Two resonances in the reaction ^{24}Mg (p,γ) ^{25}Al are observed at $E_p < 0{\cdot}5$ MeV, at $E_p = 0{\cdot}22$ and 0·42 MeV, corresponding to excitation energies of aluminium-25 of 2·50 and 2·69 MeV. De-excitation of aluminium-25 occurs by a number of different modes, giving γ-rays of 0·46, 0·95, 1·54 and 2·04 MeV at the lower resonance and 0·45, 0·85, 0·88, 0·95, 1·33, 1·80, 2·24 and 2·69 MeV at the higher resonance.[20,21]

Resonances in the reaction ^{25}Mg (p,γ) ^{26}Al occur at 0·316, 0·392, 0·437 and 0·496 MeV.[7] γ-Rays at the resonance at 0·436 MeV are observed with energies of 0·415, 1·33, 1·84, 3·82, 4·70, 6·28 and 6·77 MeV.[22]

Three resonances for the reaction ^{26}Mg (p,γ) ^{27}Al are found at $E_p < 0{\cdot}5$ MeV, at $E_p =$ 0·292, 0·338 and 0·454 MeV;[7] γ-rays emitted at the 0·454-MeV resonance have energies of 0·84, 1·01, 2·92, 3·18, 4·65, 5·79, 7·73 and 7·87 MeV.[23]

The most intense resonance for reaction of protons with natural magnesium (78·6 per cent. of magnesium-24, 10·11 per cent. of magnesium-25 and 11·29 per cent. of magnesium-26) at proton energies of less than 0·5 MeV is the one at $E_p = 0{\cdot}454$ MeV,[24] from the reaction ^{26}Mg (p,γ) ^{27}Al.

Aluminium—Five resonances occur for the reaction ^{27}Al (p,γ) ^{28}Si at proton energies of $E_p = 0{\cdot}225$, 0·294, 0·326, 0·405 and 0·442 MeV.[7] The most intense resonance is at $E_p = 0{\cdot}405$ MeV,[24] and emitted γ-rays have energies of 1·79, 2·84, 3·40, 4·60, 5·10, 6·80, 7·36 and 10·2 MeV.[25]

Silicon—The γ-yield from the reaction of natural silicon with protons is not high. Resonances for the reaction ^{28}Si (p,γ) ^{29}P occur at $E_p = 0{\cdot}369$ MeV, for the reaction ^{29}Si (p,γ) ^{30}P at $E_p = 0{\cdot}326$ and 0·414 MeV, and for the reaction ^{30}Si (p,γ) ^{31}P at $E_p = 0{\cdot}5$ MeV.

The ^{28}Si (p,γ) ^{29}P reaction at the 0·369-MeV resonance yields γ-rays with energies of 1·14, 1·37, 1·72 and 1·95 MeV,[26] while at the 0·414-MeV resonance the ^{29}Si (p,γ) ^{30}P gives γ-rays at $E\gamma = 0{\cdot}67$, 1·46, 2·28, 2·99, 4·50, 5·30 and 5·94 MeV.[27] When a thick target of natural silicon is irradiated with protons of an energy greater than 0·414 MeV, the 5·30 and 0·67-MeV γ-rays are found to be the most intense.

Phosphorus—Resonances in the ^{31}P (p,γ) ^{32}S are observed at a proton energy of $E_p = 0{\cdot}355$ and 0·440 MeV. γ-Rays emitted include those with energies of $E\gamma = 2{\cdot}23$, 2·24, 4·47, 4·80, 7·03 and 9·27 MeV.[28]

Sulphur—A resonance for the reaction of protons with naturally occurring sulphur is found at 0·446 MeV, and is ascribed to the reaction ^{33}S (p,γ) ^{34}Cl. The three most intense γ-lines from this reaction have energies of 2·02, 3·41 and 5·41 MeV.[29]

Chlorine—Irradiation of natural chlorine with protons provides one resonance below 0·5 MeV, at 0·446 MeV, which is ascribed to the reaction $^{35}Cl + p$. De-excitation of the residual argon-36 nucleus occurs primarily through the first excited state giving γ-lines at 1·95 and 7·09 MeV.[30]

The γ-lines mentioned above are collected together in Table I in the order of increasing energy, but it should be noted that many of the γ-rays are emitted in low yield and are only observed after irradiation of a sample containing a large proportion of the target nuclides, to a high particle dose. Table I does not include γ-rays emitted after decay of the ground state of the nuclide produced by the (p,γ) or (p,α) reaction [*e.g.*, ^{13}N (β^+) ^{13}C produced by the reaction ^{12}C (p,γ) ^{13}N] and first and second escape peaks have not been included where pair production is possible. Examples of two of the more complex spectra excited by low energy protons in thick targets are shown in Figs. 1 and 2 and are in general accord with results already published for thin targets.

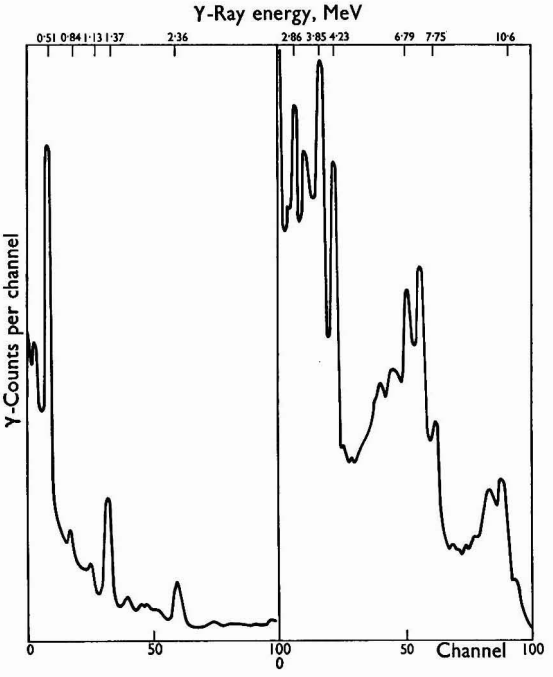

Fig. 1. Prompt spectrum from sodium irradiated with 0·48-MeV protons. Angle of observation 0°, target 7·5 per cent. sodium as sodium bromide in iron powder, dose 100,000 μC

APPLICATIONS—

Analytical methods may be based on the quantitative measurement of the yield of prompt γ-rays emitted during irradiation of a sample with charged particles, with beam current integration or some other form of standardisation to monitor the particle dose falling on the target. Interference with the method will be caused by the same excited levels being populated by reaction with nuclei of elements other than the one to be determined, or by γ-rays from other elements being of an energy that is so similar to the one being measured that they cannot be distinguished by analysis of the γ-spectra. In certain cases it is possible to calculate the magnitude of a particular interfering γ-peak from others in the spectrum, and when a sharp resonance is observed in the excitation function for the reaction upon which the analytical method is based, the γ-yield from that specific resonance may be obtained by irradiating the sample at energies above and below the resonance and calculating the difference. However, from Table I it can be seen that the reactions induced by 0·5-MeV

protons are usually radiative capture and only rarely is the same nuclide produced from different target elements. One of the exceptions is the 4·43-MeV level in carbon-12 which is formed both by the (p,γ) reaction on boron-11 and the (p,α) reaction on nitrogen-15. When boron is the target element the 4·43-MeV line is accompanied by high energy γ-rays at 11·7 and 16·1 MeV.

TABLE I

ENERGIES OF γ-RAYS EMITTED BY LIGHT ELEMENTS IRRADIATED WITH PROTONS OF ENERGY LESS THAN 0·5 MeV

$E\gamma$, MeV	Reaction	$E\gamma$, MeV	Reaction	$E\gamma$, MeV	Reaction
0·41	^{9}Be (p,γ) ^{10}B	2·04	^{24}Mg (p,γ) ^{25}Al	5·29	^{14}N (p,γ) ^{15}O
0·42	^{25}Mg (p,γ) ^{26}Al	2·23	^{31}P (p,γ) ^{32}S	5·30	^{29}Si (p,γ) ^{30}P
0·45	^{24}Mg (p,γ) ^{25}Al	2·24	^{24}Mg (p,γ) ^{25}Al	5·41	^{33}S (p,γ) ^{34}Cl
0·46	^{24}Mg (p,γ) ^{25}Al	2·24	^{31}P (p,γ) ^{32}S	5·79	^{26}Mg (p,γ) ^{27}Al
0·67	^{29}Si (p,γ) ^{30}P	2·28	^{29}Si (p,γ) ^{30}P	5·94	^{29}Si (p,γ) ^{30}P
0·72	^{9}Be (p,γ) ^{10}B	2·36	^{12}C (p,γ) ^{13}N	6·14	^{9}Be (p,γ) ^{10}B
0·75	^{14}N (p,γ) ^{15}O	2·38	^{14}N (p,γ) ^{15}O	6·14	^{19}F (p,α) ^{16}O
0·84	^{26}Mg (p,γ) ^{27}Al	2·69	^{24}Mg (p,γ) ^{25}Al	6·21	^{14}N (p,γ) ^{15}O
0·85	^{24}Mg (p,γ) ^{25}Al	2·84	^{27}Al (p,γ) ^{28}Si	6·28	^{25}Mg (p,γ) ^{26}Al
0·88	^{24}Mg (p,γ) ^{25}Al	2·86	^{23}Na (p,γ) ^{24}Mg	6·77	^{23}Na (p,γ) ^{24}Mg
0·95	^{24}Mg (p,γ) ^{25}Al	2·92	^{26}Mg (p,γ) ^{27}Al	6·77	^{25}Mg (p,γ) ^{26}Al
1·01	^{26}Mg (p,γ) ^{27}Al	2·99	^{29}Si (p,γ) ^{30}P	6·80	^{27}Al (p,γ) ^{28}Si
1·02	^{9}Be (p,γ) ^{10}B	3·18	^{26}Mg (p,γ) ^{27}Al	6·84	^{14}N (p,γ) ^{15}O
1·14	^{28}Si (p,γ) ^{29}P	3·40	^{27}Al (p,γ) ^{28}Si	6·86	^{9}Be (p,γ) ^{10}B
1·33	^{24}Mg (p,γ) ^{25}Al	3·41	^{33}S (p,γ) ^{34}Cl	7·03	^{31}P (p,γ) ^{32}S
1·33	^{25}Mg (p,γ) ^{26}Al	3·82	^{25}Mg (p,γ) ^{26}Al	7·07	^{35}Cl (p,γ) ^{36}Ar
1·37	^{23}Na (p,γ) ^{24}Mg	3·83	^{23}Na (p,γ) ^{24}Mg	7·12	^{19}F (p,α) ^{16}O
1·37	^{28}Si (p,γ) ^{29}P	4·23	^{23}Na (p,γ) ^{24}Mg	7·36	^{27}Al (p,γ) ^{28}Si
1·39	^{14}N (p,γ) ^{15}O	4·43	^{11}B (p,γ) ^{12}C	7·73	^{26}Mg (p,γ) ^{27}Al
1·46	^{29}Si (p,γ) ^{30}P	4·43	^{15}N (p,α) ^{12}C	7·75	^{23}Na (p,γ) ^{24}Mg
1·54	^{24}Mg (p,γ) ^{25}Al	4·47	^{31}P (p,γ) ^{32}S	7·87	^{26}Mg (p,γ) ^{27}Al
1·63	^{23}Na (p,α) ^{20}Ne	4·50	^{29}Si (p,γ) ^{30}P	9·27	^{31}P (p,γ) ^{32}S
1·72	^{28}Si (p,γ) ^{29}P	4·60	^{27}Al (p,γ) ^{28}Si	10·2	^{27}Al (p,γ) ^{28}Si
1·79	^{27}Al (p,γ) ^{28}Si	4·65	^{26}Mg (p,γ) ^{27}Al	10·61	^{23}Na (p,γ) ^{24}Mg
1·80	^{24}Mg (p,γ) ^{25}Al	4·70	^{25}Mg (p,γ) ^{26}Al	11·7	^{11}B (p,γ) ^{12}C
1·84	^{25}Mg (p,γ) ^{26}Al	4·71	^{9}Be (p,γ) ^{10}B	14·8	^{7}Li (p,γ) ^{8}Be
1·95	^{28}Si (p,γ) ^{29}P	4·80	^{31}P (p,γ) ^{32}S	16·1	^{11}B (p,γ) ^{12}C
1·95	^{35}Cl (p,γ) ^{36}Ar	5·10	^{27}Al (p,γ) ^{28}Si	17·6	^{7}Li (p,γ) ^{8}Be
2·02	^{33}S (p,γ) ^{34}Cl	5·12	^{9}Be (p,γ) ^{10}B	—	—

The depth of penetration that can be achieved with charged particles accelerated by an 0·5-MeV Cockcroft - Walton set is low and, in addition, the variation in cross-section that often occurs as the energy of the particles is degraded in a thick target may result in the γ-yield being emitted from only a small proportion of this depth. Therefore, any analytical method based on the measurement of prompt γ-radiation emitted during charged particle irradiation will be governed by these characteristics and will only yield information about the composition of a thin section of a thick target near to the surface. If the sample is homogeneous, this yield may be considered to be representative of the sample as a whole; if the sample is inhomogeneous the distribution of certain elements through the sample may be investigated, either by scanning the surface with a finely collimated particle beam, or by irradiating separate sections of the sample that have been prepared mechanically.

Specific analytical applications of the measurement of prompt γ-radiation emitted during charged particle irradiation will not be considered in any detail here. However, to illustrate the uses of the technique three examples are given in Fig. 3, none of which requires any chemical pre-separation of the constituents of the sample. Each time the γ-yield from a particular reaction is plotted against the known amount of target element present in the sample. Results obtained for the determination of carbon in steel, based on measurement of the 2·3-MeV γ-ray emitted during decay of excited states of nitrogen-13 formed by the reaction ^{12}C (p,γ) ^{13}N, are shown in Fig. 3 (*a*). Determinations based on this reaction have already been described with 0·8-MeV protons,[2] but as the resonance feeding the 2·3-MeV state of nitrogen-13 occurs at $E_p = 0{\cdot}459$ MeV, it should be possible to use an 0·5-MeV Cockcroft - Walton set for similar determinations. Results presented in Fig. 3 (*a*) were obtained by irradiating samples with 0·48-MeV protons. Fig. 3 (*b*) shows results obtained from the

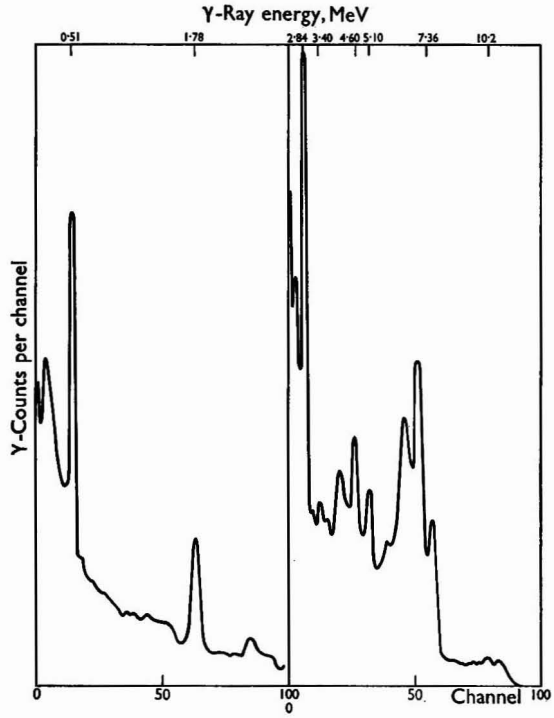

Fig. 2. Prompt spectrum from aluminium metal irradiated with 0·48-MeV protons. Angle of observation 90°, dose 50,000 μC

irradiation of magnesium - aluminium alloys with 0·48-MeV protons, measuring the 0·84-MeV aluminium-27 line emitted as a result of the reaction $^{26}Mg\ (p,\gamma)\ ^{27}Al$. Fig. 3 (*c*) is a plot of the yield of 6·1-MeV γ-rays emitted during irradiation of mixtures of iron and calcium fluoride.

In the absence of previous chemical processing of the sample, prompt-radiation techniques must rely on purely instrumental methods to isolate the activity to be measured from all others emitted by the sample. Under these conditions, the smallest amount of any element that can be determined quantitatively is governed by a number of factors, including the

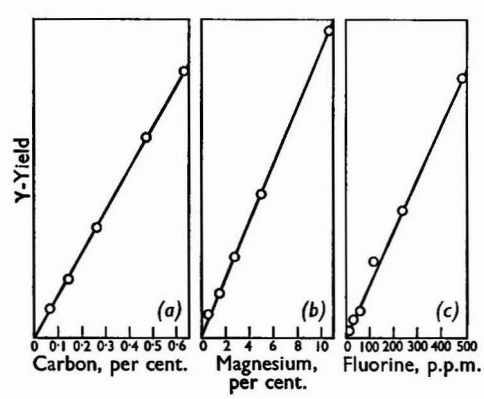

Fig. 3. Plot of γ-line yield against the content of emitting element for a number of samples: (*a*), carbon in plain carbon steels; (*b*), magnesium in magnesium - aluminium alloys; (*c*), fluorine in calcium fluoride - iron mixtures

dose to which the sample can be irradiated, the efficiency of γ-ray detection, the method of spectral analysis and the intensity of interfering γ-radiation. Consequently, the approximate sensitivities, given in Table II, are recorded as γ-yields of targets containing a single reacting element, as detected by a 3 × 3-inch thallium-activated sodium iodide scintillator, 3·5 cm from the target at 90° angle of observation.

The total dose to which samples could conveniently be irradiated depended on the rate at which the dose could be given, that is, the beam current during the irradiation. For samples that were easily damaged by heating, the beam current was usually limited to 1 μA or less, but many metallic samples were subjected to beam currents of 100 μA. The dose of 10^5 microcoulombs given in Table II corresponds to an irradiation approaching 17 minutes at a beam current of 100 μA.

Where γ-ray energies were sufficiently high for pair-production to occur, counts in the first and second escape peaks were totalled together with the photopeak. As sensitivity depends on stopping power, the type of target used is also recorded in Table II.

TABLE II

γ-YIELDS FROM THICK TARGETS OF SOME LIGHT ELEMENTS BOMBARDED WITH 0·475-MeV PROTONS

Element	Target	Reaction	γ-Ray energy, $E\gamma$, MeV	Sensitivity, c per p.p.m. per 10^5 μC
Beryllium ..	.. 2 per cent. Be - Cu alloy	^{9}Be (p,γ) ^{10}B	0·72	2·4
Boron ..	.. Be - Fe	^{11}B (p,γ) ^{12}C	4·43	4·2
Carbon ..	.. C - Fe	^{12}C (p,γ) ^{13}N	2·36	6·1
Fluorine ..	.. CaF_2 - Fe	^{19}F (p,α) ^{16}O	6·14	950
Sodium ..	.. NaBr - Fe	^{23}Na (p,γ) ^{24}Mg	1·37	2·2
Magnesium ..	.. Mg - Fe	^{26}Mg (p,γ) ^{27}Al	0·84 + 1·01	2·5
Aluminium ..	.. Al - Fe	^{27}Al (p,γ) ^{28}Si	1·79	0·3

Prompt γ-rays must be measured in the presence of two types of background; that from any natural or artificially formed radioisotope in the vicinity of the target and prompt radiation produced in the machine. The intensity of the γ-yield from radioisotopes will depend on the previous history of the irradiation position, which, for example, may have been used for neutron generation. Energies of γ-rays emitted by long-lived radioisotopes are of a lower energy than much of the radiation from proton capture, and interference occurs only when prompt γ-rays of low energy are being measured. The contribution of delayed radiation can be assessed by counting before or after irradiation, or eliminated by using a pulsed beam, and subtracting counts detected between pulses from counts detected during pulses.[5] The most troublesome form of machine background has been found to arise from contaminants in the target assembly or accelerator flight-tube. In particular, γ-contributions from carbon and fluorine are difficult to remove when low energy protons are used to irradiate the samples. By careful cleaning of flight-tube, stops and target assembly, the fluorine background could be reduced to about 1 p.p.m. for these experiments.

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The Determination of Fluorine in Fluorite Ores and Concentrates by Isotope-source Fast-neutron Activation Analysis

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On irradiation with fast neutrons, fluorine-19 is converted to nitrogen-16 by the (n,α) reaction. The fluorine content of fluorite ores and concentrates can be simply and rapidly determined by measurement of the γ-activity of this nitrogen-16 product. No sample preparation, other than crushing and grinding, is required.

The introduction of pyrohydrolysis for the recovery of fluorine from ores and minerals has done much to increase the speed and reliability of fluorine determinations. Even so, the rate at which replicate analyses can be made is still insufficient for modern industrial practice. In a preliminary communication[1] we have proposed neutron-activation analysis with an isotope neutron source as a means of rapidly and accurately determining fluorine in fluorite ores and concentrates. The determination is based upon the use of a thorium - beryllium source, giving neutrons with energies in the range 3 to 5 MeV. On exposure to this source, fluorine-19 is converted to nitrogen-16 by the (n,α) reaction. The γ-activity produced, of energy 5 to 7 MeV and half-life 7·2 seconds, is measured with a thallium-activated sodium iodide crystal, photomultiplier and single-channel γ-spectrometer.

Experimental

Isotope neutron source—

To undertake this work, use was made of an available thorium - beryllium source of 1·5 C, giving about $2{\cdot}8 \times 10^7$ neutrons per second. The sensitivity of the reaction to fluorine is such that with this particular source, in a single sequence of one irradiation and count, the total number of counts accumulated is insufficient to give the required degree of statistical accuracy on the final results.

A source of 5 C giving 10^8 neutrons per second would be barely adequate for this, and a 10-C source giving 2×10^8 neutrons per second desirable. All these sources are intensely γ-active and pose considerable problems in handling and shielding, especially at the higher neutron levels.

Americium - beryllium neutron sources, with only low energy γ-activity, are much easier and safer to handle, but for a given neutron output a more active source is required. Thus a 5-C americium - beryllium source produces only $1{\cdot}25 \times 10^7$ neutrons per second, equivalent to a 625-mC thorium - beryllium source. While this work was in progress, a 5-C americium - beryllium source became available for a period of a few days. In this time it was observed that, because of the improved design of this source, it was possible to use the neutron flux more efficiently, and to obtain a higher sensitivity to fluorine than the nominal neutron output would indicate.

To increase the statistical accuracy of the results the irradiation and counting sequence was repeated a number of times ("re-cycled") in a similar way to that described by Anders.[2] This was necessary for both the americium - beryllium and the thorium - beryllium sources.

Neutron-source housing—

The size and design of the housing for the neutron source was determined by the necessity of shielding the operator from both the n-activity and the γ-activity. The source itself (supplied by the Radiochemical Centre and sealed in a stainless-steel can) was mounted in an aluminium block at the centre of a 10-inch cube of lead. This cube was surrounded by paraffin wax, cast in a single block inside a wooden box (of dimensions $2 \times 2 \times 2$ feet). Additional shielding was provided on the sides remote from the operator by dense concrete blocks, and between the operator and the source by an additional wall built from lead bricks and paraffin wax.

The top portion of the wax block and the lead cube were cut away to permit access to the source as shown in Fig. 1. Additional lead bricks were placed in position above the lead cube, and between the wax block and the lead castle containing the crystal and photomultiplier.

The source was emplaced by dropping it down a steel tube located with one end in the aluminium block, the other protruding above the level of the top of the wax block.

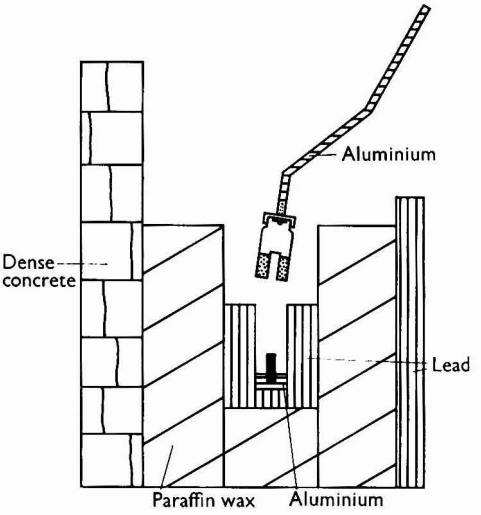

Fig. 1. Apparatus for the fast-neutron irradiation of fluorite ores

SAMPLE TRANSFER SYSTEM—

Special containers are necessary to irradiate samples of fluorite ore. These were made by cutting away the bottom portion of several 125-ml polythene reagent bottles, and welding into place "top hats" machined from polythene rod. The screw caps of these bottles were drilled, and then fastened to aluminium-alloy rod (of the type commonly used for laboratory scaffolding) to make suitable handles. These bottles could then be inserted manually into the box, with the sample material surrounding the neutron source. To obtain maximum sensitivity (counts per g of fluorine), the whole of the fluorite ore sample should be subjected to the maximum neutron flux. In practical terms this means restricting the weight of the sample to operate on the linear part of the calibration curve (Fig. 2). Within this limitation, the counting statistics can be improved by using the largest sample that can be accommodated to give the greatest total count.

After irradiation, the sample containers are lifted out of the source housing, inserted through a hole cut in the top of a lead castle, and allowed to rest over and around a thallium-activated sodium iodide crystal. For this work a crystal (length 1 inch, diameter $\frac{13}{16}$ inch) was selected with the same diameter as the source, so that with the container in the counting position, the crystal was located inside the cavity.

COUNTING SYSTEM—

Standard electronic units were used in the form of a single-channel γ-spectrometer and counter. In addition a laboratory-built 2-second timer was used to actuate the counter. This timer was itself set in action by the release of a micro switch fitted to the aluminium block holding the source. This ensured that the counting period for each sequence was started exactly 2 seconds after the removal of the sample from the source.

The γ-spectrometer was set to count all γ-activity of energy greater than about 4 MeV, including the 6·1-MeV energy of nitrogen-16 and the associated escape peaks, in the same way that nitrogen-16 is counted in the determination of oxygen.[3]

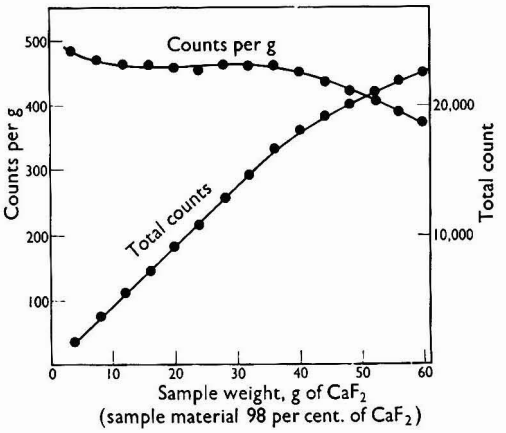

Fig. 2. Ratio of count to sample weight

The irradiation time was fixed at 35 seconds, permitting the growth of over 95 per cent. of the maximum possible activity. The counting time was fixed experimentally at 30 seconds, beyond which the additional count became increasingly comparable to the background count.

PROCEDURE—

The sample material, fluorite ore, concentrate or mill product is weighed into the sample container, which is then assembled as in Fig. 1 and transferred to the box, where the sample is irradiated for 35 $\pm$ 1 seconds. Precise timing is, therefore, not essential at this stage. After irradiation the sample and container are transferred to the lead castle, and the activity counted for 30 seconds. Both the transfer time and the counting period must be accurately controlled. After counting, the sample and sample container are allowed to cool for 15 seconds and are then returned to the box for further sequences of irradiation followed by counting, as necessary to accumulate the required total count.

As the plot of counts per gram of material against fluorine content has been shown to be a straight line passing through the origin (Fig. 2), the fluorine content of any sample is obtained by a simple calculation or by reference to the calibration graph.

RESULTS

This neutron-activation procedure for determining fluorine has been applied to fluorite ores, mill products and concentrates, as well as to several miscellaneous fluorine-containing products. A selection of results showing the extent of agreement that is obtained with a pyrohydrolytic method in normal routine use is given in Table I.

TABLE I

COMPARISON OF RESULTS OBTAINED BY NEUTRON ACTIVATION WITH THOSE OBTAINED BY PYROHYDROLYSIS

Expressed as a percentage of calcium fluoride

Neutron activation ..	91·4	81·6	67·7	55·9	54·8	36·8	15·4	10·9	7·8	7·4	7·3
Pyrohydrolysis ..	91·9	81·2	65·0	57·1	52·7	36·1	14·9	10·9	7·9	7·3	7·9

PARTICLE-SIZE EFFECTS—

Samples of pure crystalline fluorite were roughly crushed and then sieved to give size fractions in the range −5 to −240 mesh B.S.S. Each of these was examined in turn, with the procedure given above. Although the total number of counts varied for each fraction taken, no difference could be detected in the counts per gram. Fine grinding is, therefore, not essential, and sample materials can be examined after roughly crushing and grinding.

BULK DENSITY EFFECT—

Ten grams of a standard fluorite ore containing 98 per cent. of calcium fluoride were weighed into a container and diluted to a fixed volume with a series of rock and mineral samples covering a density range. After mixing, the total count for the 10-g aliquot was determined by the procedure given above. The results are given in Table II.

TABLE II

EFFECT OF BULK DENSITY ON TOTAL COUNT

Rock or mineral mixed		
Description	Specific gravity	Total count of 10 g of calcium fluoride
—	—	3840
Limestone	2·7	3930
Sandstone	2·7	3840
Granite	2·6	3831
Barytocalcite	3·6	3795
Zinc blende	4·1	3656
Barytes	4·5	3586
Ilmenite	4·8	3543
Arsenopyrite	6·0	3485
Galena	7·5	3214

It is clear from these results that, as expected, increasing the bulk density does have an appreciable effect giving rise to a lower count from a given amount of fluorine. A separate calibration graph or factor is therefore required for operation with each particular material, for example with fluorite-containing lead or barytes concentrates. The commonly occurring host rocks, limestone, sandstone and granite have no apparent effect upon the observed total count.

TEMPERATURE EFFECTS—

In calculating the results of fluorine determination by neutron activation, the effect of temperature variation upon the photomultiplier must be considered. The results given in Table I were all obtained by noting the temperature of the detector unit, and applying a correction based upon the slope of the graph (Fig. 3).

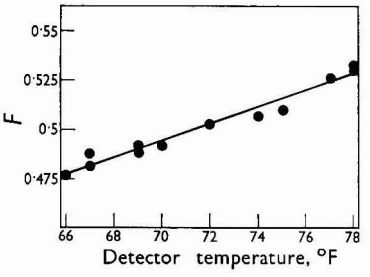

Fig. 3. Effect of detector temperature on count, where

$$F = \frac{\text{CaF}_2 \text{ content} \times \text{Weight of sample}}{\text{Total count in six cycles}}$$

INTERFERENCES—

Appreciable amounts of fast-neutron absorbers could give rise to low results by attenuation of the neutron flux, but their presence is unlikely. However, apart from the temperature and bulk density effects, no interferences have been observed in determining fluorine in a large number of fluorite ores and other fluorine-containing products. No other radioactive isotope with gamma energy of sufficiently high level to be recorded has been noted with either the thorium - beryllium or the americium - beryllium source. The reactions ^{16}O (n,p) ^{16}N and ^{11}B (n,p) ^{11}Be do not occur, as the threshold neutron-energy levels for these reactions are above the neutron energies of the two sources used.

ACCURACY AND LIMIT OF DETECTION—

In fluorite ores (30 to 40 per cent. of calcium fluoride) and concentrates (75 to 100 per cent. of calcium fluoride), the accuracy of the results depends only on the accuracy of the result for the standard used and upon the statistical error involved in the counting of nitrogen-16. For fluorite concentrates a total count in excess of 10,000 was accumulated, giving a statistical error of ± 1 per cent. of calcium fluoride.

The procedure described above was intended for ores and similar products containing fluorine as a major component. It is not suitable for the determination of trace amounts. Fluorine has been detected in certain rocks from a "fluorite province" containing less than 1 per cent. of calcium fluoride, and it appears that the limit of detection is about 0·5 per cent. of calcium fluoride.

CONCLUSIONS

The determination of fluorine has long been regarded as most difficult, tedious and time consuming. On an industrial scale, the determination has proved to be expensive and not infrequently subject to systematic error. Neutron-activation analysis with an isotope source has now been shown to be a rapid, accurate and acceptable alternative, at least for the industrial control of fluorite production.

Disadvantages of the apparatus described in this paper include the lack of sensitivity, resulting in the need to re-cycle the irradiation-counting sequence, and the difficulty of timing the manual transfer operation. Improvements in design include provision for pneumatic sample transfer and an increase in sensitivity to the point at which re-cycling can be avoided. The time for a single determination will then be reduced to just over 1 minute.

We are grateful to the Radiochemical Centre, Amersham, Services Electronics Research Laboratory and Dynatron Electronics Ltd., for the loan of equipment, and to Glebe Mines Ltd., for their co-operation in a field trial of the apparatus.

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The Importance of Fuel Gas Composition in the Atomic-absorption Spectrophotometric Determination of Magnesium

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The specifications for commonly used "low temperature" fuel gases permit wide variations in composition. The effect, on the determination of magnesium in nickel, of using two samples of "propane" of differing compositions is considerable, and the use of acetylene is advocated. The results emphasise the need for a complete specification of flame conditions to be given when reporting sensitivities and interference susceptibilities in atomic-absorption procedures when using flame atomisation.

Flames used for atomic-absorption spectrophotometry can be loosely classified as "cool" (<2000° C) or "hot." Examples of cool flames are air - town gas, air - butane and air - propane, while the most commonly used hot flame is air - acetylene, although nitrous oxide - acetylene is coming into use.

Most of the metallic elements can be determined with more than one flame, but often there is a considerable difference in sensitivity between flames.[1] The difference in sensitivity of detection of elements in these flames and the extent of interference by other elements are usually attributed to the different temperatures reached in the reaction zone of the flame.

In an earlier publication[2] we reported the determination of low concentrations of magnesium in nickel by atomic-absorption spectrophotometry. In this work we used an air - town gas flame and found no interference from 500 p.p.m. of nickel in the determination of up to 0·50 p.p.m. of magnesium. After several months' satisfactory application of this procedure, occasional runs showed clear evidence of slight interference by nickel. When all other variables had been studied and found to be adequately controlled, suspicion fell on the town gas supply.

Although town gas is supplied at a constant calorific value, its composition varies widely from place to place and also from day to day at the same place, depending on the local gas producers' requirements. Two typical analyses, not from the same supply, are shown in Table I.

Table I

Composition of two samples of town gas

	Sample A, per cent.	Sample B, per cent.
Carbon monoxide	2·7	9·1
Hydrogen	50	44·9
Nitrogen	8·0	18·2
Carbon dioxide	12·3	2·7
Oxygen	0·5	0·4
Methane and ethane	23·5	19·3
Other hydrocarbons	3·0	5·4

This variation could well explain the occasional interference of nickel encountered in the determination of magnesium and, for other determinations, could lead to variations in sensitivity and amount of interference encountered. We decided, therefore, to reject town gas as a standard fuel and turned our attention to other fuels. Air - acetylene was the most commonly used hot flame and air - butane or air - propane seemed a reasonable choice as a cool flame. Before proceeding to examine these, however, it seemed prudent to investigate the stated purity and constancy of composition of these three commonly used fuels.

Acetylene is readily available at a purity of higher than 98 per cent. with the sole proviso that the last 5 to 10 per cent. of the cylinder contents may be contaminated with acetone.

Butane as supplied commercially conforms to existing specifications, compiled without consideration of possible analytical applications, which require only that it consists principally of butane or butene, or both. The composition is dependent on the refinery from which it is obtained. Typical compositions are shown in Table II.

TABLE II

COMPOSITION OF COMMERCIAL BUTANE

Component, mol. per cent.	Refinery A	B	C	D	E
Ethane and ethene	0·1	Nil	Nil	0·2	Nil
Propene	1·3	Nil	Nil	3·4	3·1
Propane	9·2	11·5	0·6	8·4	6·2
Butenes	12·3	Nil	Nil	31·9	46·5
Iso-butane	76·9	19·8	3·9	15·6	36·2
Butane		68·7	95·5	30·5	8·0

Propane is available at higher than 99 per cent. purity, but the cost of the pure material is such as to preclude its use as a fuel. Commercial propane is again a by-product of oil refineries and its composition is also a function of the particular refinery. Typical values for the composition of propane from various refineries are given in Table III.

TABLE III

COMPOSITION OF COMMERCIAL PROPANE

Component, mol. per cent.	Refinery A	B	C	D	E
Propane	91·1	72·5	89·1	57·4	95·2
Propylene	Nil	24·5	Nil	39·5	Nil
Methane	Nil	Nil	Nil	Nil	Nil
Ethane	2·3	2·4	4·0	0·7	1·8
Ethylene		Nil	Nil	0·1	Nil
Butane	6·6	0·3	6·9	2·3	3·0
Butylene	Nil	0·1		Nil	Nil

Consideration of Tables II and III shows that propane is available from three out of five sources at about 90 per cent. purity, whereas only one source produced butane of a comparable purity. Accordingly, propane was considered to be a more appropriate subject for study than butane. The information given in Tables II and III was supplied by Shell Oil Company from whom we obtained small amounts of propane from refineries D and E, which were selected as providing the two extremes of composition given in Table III. Their effects on the determination of magnesium in nickel were compared.

EXPERIMENTAL

To study the behaviour of magnesium in both air - acetylene and air - propane flames we constructed a burner having two separate interchangeable burner heads. This burner could then use the same atomiser conditions, and stable flames could be produced merely by altering the fuel-inlet jet. The basic design of the burner is shown in Fig. 1.

The acetylene burner head was supplied by Messrs. Hilger and Watts; it has a slot 0·5 mm wide and 120 mm long, and it is a sliding fit on the main burner tube. The propane burner-head top-plate was made from 1·5-mm stainless steel carrying five rows of 1·32-mm holes on 3-mm centres. This top-plate was attached to the brass casting, as supplied with the early Hilger and Watts town gas burner, the stem of which had to be reamed out to be a sliding fit on the new burner tube.

The sample spray and fuel enter the main burner tube through a single side-tube just above the base. To avoid any possible encrustation of the fuel-inlet jet with evaporated sample solution it is set back at an angle of 45°. The base of the burner tube has a removable cap to facilitate cleaning.

The pressure of air for maximum efficiency of the E.E.L. atomiser used in this work was 30 lb per sq. inch ($2 \times 10^5 N/m^2$) and this therefore represented the amount of air to be admitted to the burner. The air-to-fuel ratio for stable flames with the two fuels was expected to be different, so provision was made for the use of fuel-inlet jets of different sizes. This was done by making the jet compartment removable (see Fig. 1). A series of jets, designed for the Amal Maximus burner, was turned down so that the jets readily slid into the jet compartment tube, the bases being slotted to permit insertion of a screwdriver for fixing.

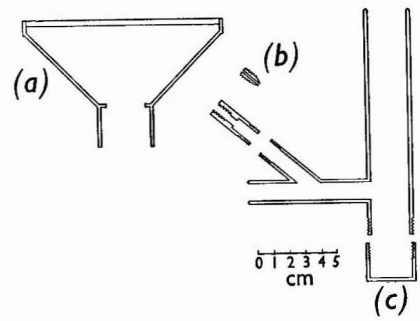

Fig. 1. Burner assembly: (*a*) interchangeable burner head; (*b*) interchangeable fuel-inlet jet; (*c*) main burner

The main burner assembly was made of brass, for ease of machining and ready availability. Stainless steel could have been used, but at a considerably higher fabrication cost, and was hardly justified as no contamination by brass burners has so far been detected by us.

The remainder of the apparatus used in this work was as previously reported,[2] with the exception of the scale expansion unit which has been modified to permit a 10-fold increase in sensitivity. The circuit diagram of the scale expansion unit is shown in Fig. 2.

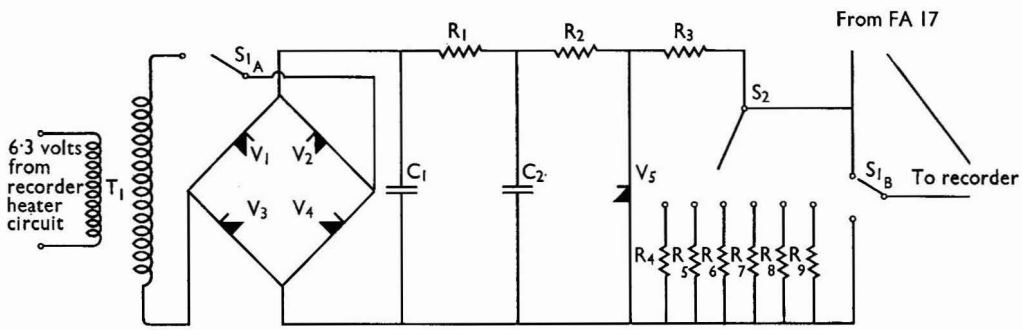

Fig. 2. Scale expansion unit

Experiments were carried out with the two burner heads to determine optimum conditions for apparently stable flame formation at air flow-rates of 7 litres per minute through the E.E.L. atomiser. These conditions are shown in Table IV.

TABLE IV

CONDITIONS FOR STABLE AIR - PROPANE AND AIR - ACETYLENE FLAMES

Fuel gas	Inlet-jet diameter, mm	Fuel gas flow-rate, ml per minute	Fuel gas pressure, inches (water gauge)
Propane	0·55	300	4
Acetylene	0·76	700	4

Study of the air - propane flames showed that the sensitivity of the two flames towards magnesium when using propane D and E, under otherwise identical conditions, differed widely as also did the effect of nickel. To obtain the maximum information from this study, the variation of absorption with the position of the optical path in the flame was examined with a wide range of air-to-fuel ratios. The results are presented in Figs. 3 and 4.

Discussion

Consideration of the several graphs in Figs. 3 and 4 show that, except under a limited set of conditions, the presence of nickel has a marked effect on the profile of magnesium absorption in the flame and also that the composition of the propane fuel is of importance. It is worthy of note that the degree to which the presence of nickel affects the magnesium absorption and the variation of absorption through the flame is very different for the two compositions of propane, and conditions which might be established for any one supply of propane could well need re-investigation when a fresh supply was obtained.

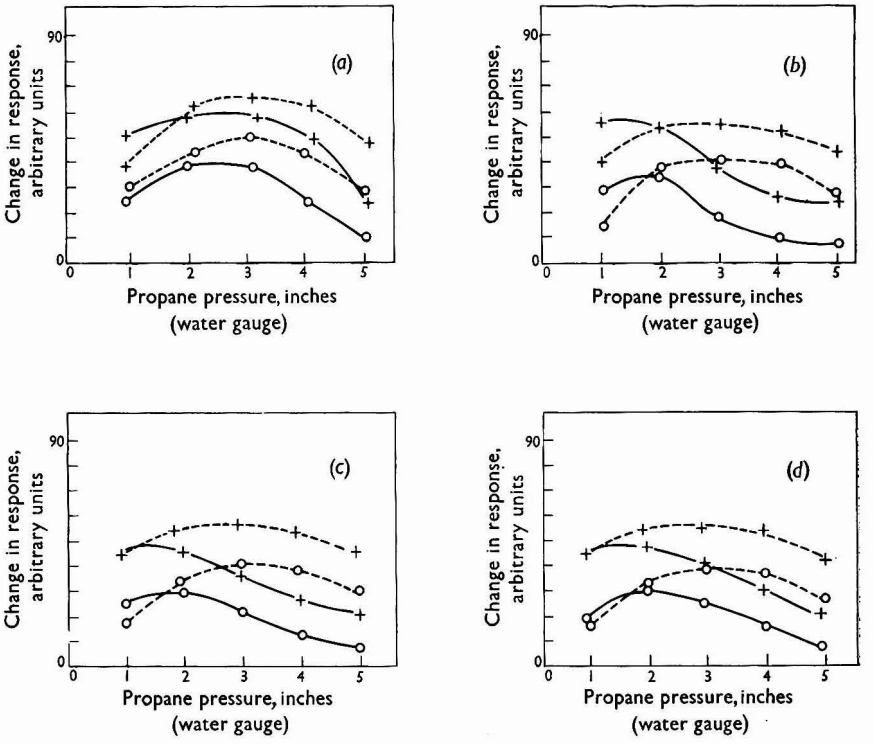

Fig. 3. Variation of instrumentresponse with propane pressure for magnesium and for magnesium *plus* nickel at different settings of burner position below optic axis: (*a*) 0·40; (*b*) 0·55; (*c*) 0·60; (*d*) 0·65 inches. Propane from refinery E represented by ——; from refinery D by - - - - -; curves (○) obtained with 0·13 p.p.m. of magnesium; curves (+) with 0·13 p.p.m. of magnesium *plus* 250 p.p.m. of nickel

While it is possible to use an air - propane flame for the determination of magnesium in nickel, the need for close control of conditions and for the regular provision of standards renders the procedure less than satisfactory.

When air - acetylene was used with the slot-type burner head, the results given in Fig. 5 were obtained. It is clear that the air - acetylene flame is less sensitive to operating conditions than air - propane and that the use of air - acetylene is to be preferred for the determination of magnesium in nickel as it gives enhanced sensitivity, and the presence of nickel is without influence on the determination.

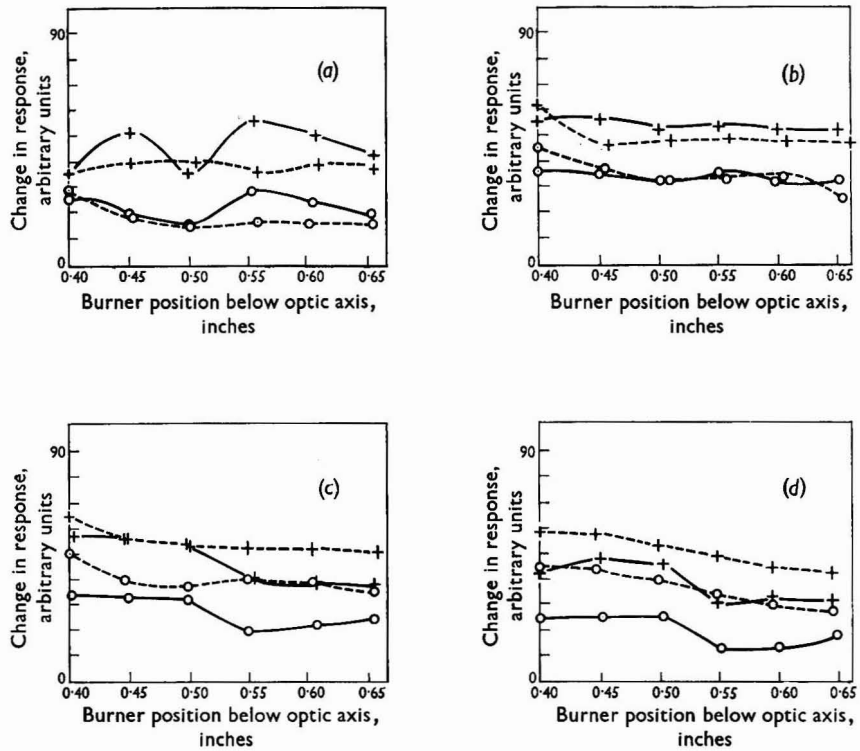

Fig. 4. Variation of instrument response with burner position for magnesium and for magnesium *plus* nickel at different propane pressures measured in inches (water gauge): (*a*) 1; (*b*) 2; (*c*) 3; (*d*) 4. Propane from refinery E represented by ——; from refinery D by - - - - -; curves (○) obtained with 0·13 p.p.m. of magnesium; curves (+) with 0·13 p.p.m. of magnesium *plus* 250 p.p.m. of nickel

This work has been confined to the study of one element, magnesium, but it seems to us probable that some of the differences of opinion expressed in the atomic-absorption spectrophotometric literature may well be a result of differences in composition of nominally identical fuels. It is also apparent that when using propane fuel it should not be assumed that the sensitivity and degree of interference obtained with one cylinder of propane will necessarily be the same with another cylinder.

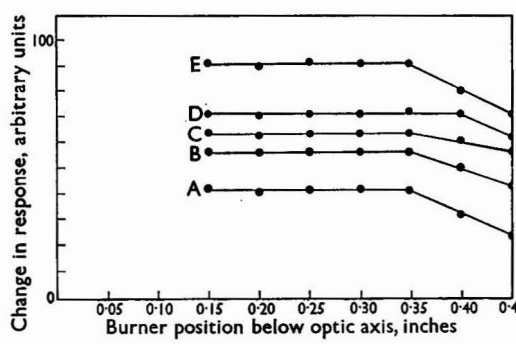

Fig. 5. Variation of instrument response with burner position for magnesium and magnesium *plus* nickel at different acetylene pressures measured in inches (water gauge): curve A, 1; curve B, 2; curve C, 3; curve D, 4; curve E, 5. The curves are the same for 0·13 p.p.m. of magnesium and 0·13 p.p.m. of magnesium *plus* 250 p.p.m. of nickel

We are grateful to Mr. C. H. R. Gentry, Head of the Central Materials Laboratory, and the Directors of the Mullard Radio Valve Company for permission to publish this work, and to the Shell Oil Company for provision of information on the composition of propane and butane.

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Appendix

Components list for the scale expansion unit (Fig. 2)

R_1	=	500-ohm, 1-watt resistor
R_2	=	75,000-ohm, 0·5-watt resistor
R_3	=	2000-ohm, 2-watt variable resistor with a tolerance of 5 per cent.
R_4	=	100-ohm, 0·25-watt resistor with a tolerance of 5 per cent.
R_5	=	200-ohm, 0·25-watt resistor with a tolerance of 5 per cent.
R_6	=	300-ohm, 0·25-watt resistor with a tolerance of 5 per cent.
R_7	=	510-ohm, 0·25-watt resistor with a tolerance of 5 per cent.
R_8	=	680-ohm, 0·25-watt resistor with a tolerance of 5 per cent.
R_9	=	900-ohm, 0·25-watt resistor with a tolerance of 5 per cent.
C_1, C_2	=	4-μF capacitors, 50-volt working
S_1	=	Double-pole, double-throw switch
S_2	=	Single-pole, 6-way switch
V_1, V_2, V_3, V_4	=	Mullard OA5
V_5	=	Mullard OAZ203
T_1	=	Transformer, ratio of input to output, 1 : 2·5

The Use of 2-Selenophene Aldoxime for the Gravimetric Determination of Palladium

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The use of 2-selenophene aldoxime as a gravimetric reagent for palladium is described. The optimum analytical conditions for precipitation of the palladium complex and the effect of possible interferences have been investigated.

Among the many different types of organic reagents that have been proposed for the determination of palladium are 2-furan aldoxime[1] and its sulphur analogue, 2-thiophene aldoxime[2]; the replacement of the heterocyclic oxygen atom by the heavier sulphur atom leads to a more sensitive reagent. It was decided to investigate the effect of replacing the sulphur by selenium and so give an increased weighting effect to the reagent. The effect of foreign ions on the precipitation of the palladium(II) ions has been investigated, and the optimum analytical conditions were determined.

Experimental

Preparation of the reagent—

Selenophene, prepared from selenium and acetylene by a slight modification of the method of Briscoe,[3] was converted to 2-selenophene carboxaldehyde[4] and hence to 2-selenophene aldoxime[5] by previously reported methods. The spectra, melting or boiling-points were determined and necessary elemental analysis was made at appropriate stages to confirm the course of the synthesis. The analysis gave selenium, 45·4 per cent.; nitrogen, 8·05 per cent. 2-Selenophene aldoxime requires: selenium, 45·3 per cent.; nitrogen, 8·05 per cent.

An ethanolic solution (0·5 per cent. w/v) of the aldoxime was used in all subsequent work.

Preparation of palladium(II) solution—

A stock solution was prepared from palladium(II) chloride supplied by Johnson Matthey, London. The palladium(II) content of the solution was determined gravimetrically with indane 1,2-dione dioxime[6] and 4-methyl cyclohexane 1,2-dione dioxime.[7]

Qualitative tests—

A fixed amount of the metal-ion solution (about 3 ml containing 500 μg of the metal at an appropriate pH) was mixed with the reagent (0·2 ml of a 0·5 per cent. w/v ethanolic solution of 2-selenophene aldoxime). The reactions at room temperature and after boiling for 30 minutes were noted.

The pH values chosen for investigation were pH 2, 7 and 9. The 43 metals containing ionic species tested were—

Li(I), Na(I), K(I), Rb(I), Cu(II), Ag(I), Au(III), Be(III), Mg(II), Ca(II), Sr(II), Ba(II), Zn(II), Cd(II), Hg(II), Al(III), La(III), Ce(IV), Tl(I), Ti(IV), Zr(IV), Th(IV), Pb(II), As(III), Sb(III), Bi(III), V(III), Cr(III), Mn(II), Fe(II), Fe(III), Co(II), Ni(II), Ru(III), Rh(III), Pd(II), Os(IV), Pt(II), Pt(IV), Ir(IV), MoO_4^{2-}, WO_4^{2-} and UO_2^{2+}.

Of these, only eight species gave precipitates at any of the pH values considered. Palladium(II) and cerium(IV) gave yellow precipitates that were stable between pH 2 and 7; the palladium(II) precipitate decomposed on boiling at pH 9·0. The other six species platinum(II), platinum(IV), gold(III), rhodium(III), ruthenium(III) and osmium(IV) gave brown precipitates at each of the pH values studied, and all of these precipitates decomposed on warming. These latter ions must be regarded as possible interferences in any method for the determination of palladium with this reagent. Ions such as thallium(I), silver(I), lead(II), mercury(II) and tungstate (WO_4^{2-}) that gave precipitates with hydrochloric acid also interfere, but are removed before adding the reagent; the amount of thallium(I) and lead(II) left in solution after removal of the chloride precipitate did not interfere.

PRECIPITATION OF THE PALLADIUM CHLORIDE COMPLEX OF 2-SELENOPHENE ALDOXIME—

An aqueous solution of palladium(II) chloride containing 6·00 mg of palladium in 150 to 200 ml was acidified with hydrochloric acid to between pH 1 and 2 and then warmed to 60° C. A solution of 2-selenophene aldoxime was slowly added with constant stirring until no further precipitation occurred. A 20 per cent. excess of the reagent solution was then added and the solution allowed to digest at 60° C for 30 minutes, and then for 4 hours at room temperature. The precipitate was collected in a No. 4 porosity sintered-glass crucible, washed with about 20 ml of 0·1 N hydrochloric acid, and then with distilled water until the washings were free from chloride. The precipitate was finally air-dried at room temperature.

INVESTIGATION OF SUITABLE DRYING CONDITIONS FOR THE COMPLEX—

A weighed amount of the complex was heated for three successive 2-hour periods at 105° C, constant weight being then achieved. It was then heated for further 2-hour periods at 120° and 130° C. No significant weight change was recorded at 120° C, but a decrease in weight accompanied by visual evidence of decomposition was apparent at 130° C.

Future drying of the complex was always carried out at 105° to 110° C.

DETERMINATION OF THE FORMULA OF THE COMPLEX—

A known weight of the complex was decomposed by wet oxidation with a nitric acid - perchloric acid mixture and the resulting solution analysed for palladium by atomic-absorption spectrophotometry.

A further sample was combusted in an oxygen flask and an aqueous solution of the combustion products was analysed for chloride by coulometric titration, and for selenium iodimetrically.

The compound was analysed for carbon, hydrogen and nitrogen by using a Perkin-Elmer Automatic C–H–N Analyzer. The following results indicate an empirical formula of $Pd(C_5H_5ONSe)_2Cl_2$—

	Palladium	Selenium	Chlorine	Carbon	Hydrogen	Nitrogen
Percentage found	20·97	30·18	13·66	23·02	1·82	5·24
Percentage calculated for $Pd(C_5H_5ONSe)_2Cl_2$ ..	20·25	30·05	13·50	22·86	1·93	5·32

DETERMINATION OF THE OPTIMUM pH FOR PRECIPITATION—

The complex was precipitated from solutions of various pH values by using the method previously outlined. The pH values of the solutions were adjusted to the requisite values with dilute hydrochloric acid or sodium hydroxide solutions.

pH of solution	0·5	1·0	1·5	2·0	3·0	5·0	3·0	5·0
Palladium taken, mg ..	6·70	6·70	6·70	6·70	6·70	6·70	6·70	6·70
					(*a*)	(*a*)	(*b*)	(*b*)
Palladium recovered, mg ..	6·70	6·69	6·74	6·70	6·66	6·38	6·69	6·70

(*a*) At pH 3·0 and above, a much lighter coloured precipitate was formed and lower recovery values were obtained. Analysis of the complexes formed at pH 3·0 and 5·0 showed a deficiency of chloride compared to that required by theory.

(*b*) When extra chloride ions were added (*viz.*, 1 g of sodium chloride added to the solution before precipitation) quantitative recoveries were again recorded, and the chloride analysis of the complex agreed with theory.

In practice, a pH of between 1·0 and 2·0 was considered convenient and all subsequent work was done in this pH range.

THE EFFECT OF INCREASING THE AMOUNT OF 2-SELENOPHENE ALDOXIME USED—

By using the above method at a pH of between 1·0 and 2·0, the various amounts of 2-selenophene aldoxime were added up to 100 per cent. excess. The results given below show that even at 100 per cent. excess no co-precipitation occurs.

Percentage excess of reagent added ..	10	30	50	100
Palladium recovered, mg	6·29	6·25	6·30	6·30

6·28 mg of palladium were taken in all determinations.

THE DETERMINATION OF PALLADIUM IN THE PRESENCE OF FOREIGN IONS—

Cations—The pH of a solution containing 6·40 mg of palladium and 10 equivalents of one of the following cations, Al(III), Be(II), Bi(II), Cd(II), Co(II), Cr(III), Cs(I), Cu(II), Fe(III), Fe(II), Hg(II), Ir(IV), In(II), Mg(II), Mn(II), Ni(II), Os(VIII), Sb(II), Th(IV), UO_2^{2+}, VO^{2+} and Zn(II) was adjusted with hydrochloric acid to between 1·0 and 2·0, and the precipitation method previously outlined followed. The results obtained were all within the standard deviation of the values obtained with palladium alone.

With antimony present, tartaric acid (0·5 g) was added to keep it in solution.

Anions—As an excess of chloride ions was needed to effect complete precipitation, the effect of the presence of other ions was investigated. A solution containing 50 mg of one of the foreign anions, fluoride, bromide, molybdate, nitrate, phosphate, sulphate, thiosulphate, selenate, borate, acetate, benzoate, succinate and tartrate, was added to an aqueous solution of palladium(II) chloride containing 6·40 mg of palladium. The pH was adjusted to between 1·0 and 2·0 with hydrochloric acid and the method outlined followed. The results were again within the standard deviation of the values obtained with palladium alone.

INTERFERENCES—

The following metal ions were shown to interfere: platinum(II), platinum(IV), gold(III), rhodium(III), ruthenium(III), osmium(IV) and cerium(IV).

These metals must therefore be previously removed, or be present in a state in which they do not interfere.

Ruthenium(III) and osmium(IV) can be removed by previous distillation of their quadrivalent oxides,[8] while milligram amounts of rhodium(III) may be removed by ion exchange.[9] Gold(III) can be reduced to the metal by previous addition of hydroxylammonium chloride to hydrochloric acid solution of pH 1·0, if the solution is then left to stand on a steam-bath for half an hour; gold is precipitated whereas palladium is not. Cerium(IV) can be reduced to cerium(III), which does not interfere, by the addition of hydrogen peroxide and boiling off the excess. Although with the sulphur analogue it is stated[2] that interferences by platinum(IV) may be obviated by adding ammonium oxalate and precipitating the complex at room temperature, with 2-selenophene aldoxime we found that consistently high results were still obtained, and therefore platinum must be absent.

RECOMMENDED PROCEDURE FOR THE DETERMINATION OF PALLADIUM(II)—

After removing interfering elements, adjust to pH between 1·0 and 2·0 the acidity of a palladium solution containing about 5 mg of palladium(II) for each determination. Warm the solution to about 60° C and add, slowly with stirring, a 0·5 per cent. w/v ethanolic solution of 2-selenophene aldoxime until about 20 per cent. excess is present. Allow the solution to stand at 60° C for 30 minutes, and then for 4 hours at room temperature. Collect on a No. 4 porosity sintered-glass crucible, wash with 0·1 M hydrochloric acid (about 20 ml) and then with distilled water until the washings are free from chloride. Dry to constant weight at 110° C.

DISCUSSION

2-Selenophene aldoxime is a useful and selective reagent for the determination of palladium. As the compound is a stable, crystalline solid, giving a stable solution, it is useful as a laboratory reagent. It is quite soluble in hot water and appreciably soluble in cold water; there is therefore little tendency for co-precipitation of the reagent with the palladium complex. The precipitate formed is granular, easy to filter and stable, both in suspension and when dry at temperatures below 130° C. The complex has a low solubility and its large molecular weight gives appreciable increases in sensitivity when compared with the more classical reagents, *viz.*, an increase of 57·2 per cent. compared to dimethylglyoxime, and 21·7 per cent. compared to 2-thiophene aldoxime.

Although the freshly precipitated complex is soluble to some extent in a range of organic solvents, the absorption spectrum of the palladium complex is essentially a broad peak with a maximum in the region of 330 mμ. It is not considered suitable for use in a colorimetric method for the determination of palladium.

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An Oxidimetric Determination of Molybdenum

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The use of silver, mercury, tin(II) and amalgamated zinc as reducing agents in the oxidimetric determination of molybdenum was investigated. Cerium(IV), dichromate and metavanadate solutions were used for the titration of the molybdenum(V) solutions. All of the methods, except when molybdenum(V) prepared by reduction with silver was titrated with dichromate, gave satisfactory results. With the Jones reductor three redox systems were used for determining molybdenum(III) and gave equal, satisfactory results.

SOLUTIONS of sexavalent molybdenum are reduced to the quinquevalent state by silver, mercury and tin(II), and to the tervalent state by amalgamated zinc. These reductions can be used for the oxidimetric determination of molybdenum.[1 to 5] The degree of reduction for the first three, however, depends on the hydrochloric acid concentration of the solution. During the course of this work the conditions under which reduction is quantitative were standardised, as there are some discrepancies in the literature over the precise procedures to be followed.

For silver, mercury and tin(II), the degree of reduction was studied as a function of the hydrochloric acid concentration of the sample. Standard cerium(IV) sulphate solutions were used as oxidant for the determination of the reduced molybdenum. The use of sodium metavanadate and potassium dichromate as oxidants was also studied.

Molybdenum(VI) is reduced to molybdenum(III) by the Jones reductor. Because of the sensitivity of molybdenum(III) to oxidation by atmospheric oxygen, it is necessary to collect the reduced solution in a known excess of standard oxidising agent, which is then titrated with a reducing agent. The following redox systems were used: permanganate - iron(II); cerium(IV) - iron(II); and iron(III) as oxidising agent for molybdenum(III), the resulting iron(II) being titrated with permanganate.

EXPERIMENTAL

Blanks were run in all determinations. The mean results reported are the average of at least five determinations for each.

REAGENTS—

Standard molybdate solutions—These are prepared from a standardised sample of ammonium paramolybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$ (obtained from Merck *pro analysi*) which was standardised gravimetrically as lead molybdate and molybdenum 8-hydroxyquinolinate.

Standard hydrochloric acid solutions, ranging between 2 and 8 N.

Cerium(IV) sulphate solution, 0·1 N—Prepare and standardise.

Potassium dichromate solution, 0·1 N—Prepare and standardise.

Sodium metavanadate solution, 0·1 N—Prepare and standardise.

INDICATOR SOLUTIONS—

Ferroin—Use 0·025 M solution of 1,10-phenanthroline - iron(II) sulphate complex solution (Merck) reagent.

N-*Phenylanthranilic acid*—Prepare a 0·2 per cent. solution by dissolving 1 g of the compound in 20 ml of a 5 per cent. sodium hydrogen carbonate solution. Dilute the solution to 500 ml with distilled water.

REDUCTION AND TITRATION PROCEDURES—

Silver reductor—The column was prepared as described by Kolthoff and Belcher.[6] The usual reduction procedure was followed with various concentrations of hydrochloric acid. After cooling, the acidity of the mixture was made 2 N and the sample was titrated with

a standard solution of cerium(IV) sulphate, about 0·1 N, with ferroin as indicator. The results are shown in Table I.

TABLE I

REDUCTION OF MOLYBDENUM BY A SILVER REDUCTOR AND TITRATION OF THE PRODUCTS

Hydrochloric acid, N	Weight of molybdenum taken	Weight of molybdenum found	Molybdenum found, as percentage of that taken
1·0	—	—	96·31 ± 0·06
1·5	—	—	99·00 ± 0·08
2·0	0·1260	0·1258*	99·82
		0·1258*	99·82
		0·1260	100·0
		0·1258	99·82
		0·1259*	99·91
		0·1260	100·0
2·25	0·1260	0·1260	100·0
		0·1261	100·1
		0·1262	100·2
		0·1261	100·1
		0·1260	100·0
2·50	0·1365	0·1374	100·7
		0·1377	100·9
		0·1374	100·7
		0·1375	100·7
		0·1375	100·7
3·0	—	—	108·1 ± 0·5
4·0	—	—	238·8 ± 0·7

* Reduced in the presence of 10 ml of orthophosphoric acid.

When the molybdenum(V) solution (prepared by reduction with silver in 2 N hydrochloric acid) was titrated with potassium dichromate the molybdenum found, as a percentage of that taken, was 98·98 ± 0·01; with sodium metavanadate as oxidising agent it was 99·97 ± 0·02. The titrations were carried out in the presence of 10 ml of 85 per cent. orthophosphoric acid. Ferroin and *N*-phenylanthranilic acid were used as indicators in the dichromate and metavanadate titrations, respectively.

Mercury—The sample solution was shaken with 25 ml of mercury in a 250-ml separating funnel for 10 minutes. The greater part of the mercury was drained off; the reduced molybdenum solution, remaining mercury and mercury(I) salts were then filtered on to a filter-paper. The mercury was again shaken with two 50-ml portions of hydrochloric acid (of the same concentration as the sample) and the mixture was added to the molybdenum solution. The precipitate of mercury(I) salts was washed with three 30-ml portions of the acid and the filtrate again added to the molybdate solution. After addition of the indicator the sample was titrated with a cerium(IV) sulphate solution.

The results are given in Table II.

TABLE II

REDUCTION OF MOLYBDENUM BY MERCURY AND TITRATION OF THE PRODUCTS

Hydrochloric acid concentration, N	Molybdenum found, as percentage of that taken with: Cerium(IV) sulphate	Potassium dichromate	Sodium metavanadate
1·5	99·76 ± 0·04	—	—
2·0	99·92 ± 0·08	—	—
3·0	99·93 ± 0·06	100·0 ± 0·1	99·92 ± 0·07
4·0	99·95 ± 0·07	—	—
5·0	105·2 ± 0·7	—	—
6·0	No reproducible values.		

Tin(II)—Gottlieb and Lang[7] published a method in which molybdenum(VI) is reduced by excess of tin(II) chloride, which was then removed by oxidation with bromine. The excess of bromine was removed with arsenite. This procedure is tedious and inconvenient. In our

work the excess of tin(II) was removed with a mercury(II) chloride solution, as in the well known iron(III) determination.

The acidity of the sample was adjusted with hydrochloric acid and the solution heated to 70° C. A slight excess of tin(II) chloride solution was added to the mixture from a burette. The excess of tin(II) was removed by adding 10 ml of a 5 per cent. mercury(II) chloride solution.

After cooling to room temperature, the sample was titrated. A slight adsorption of indicator on the mercury(I) chloride precipitate occurred but had no influence on the colour change at the end-point.

The results are given in Table III.

TABLE III

TITRATION OF MOLYBDENUM(V) SOLUTIONS PREPARED BY REDUCTION WITH TIN(II)

Hydrochloric acid, concentration, N	Molybdenum found, as percentage of that taken with		
	Cerium(IV) sulphate	Potassium dichromate	Sodium metavanadate
1·0	98·84 ± 0·37	—	—
2·0	100·0 ± 0·1	—	—
2·5	100·1 ± 0·1	99·93 ± 0·05	99·96 ± 0·05
3·0	99·85 ± 0·18	—	—
4·0	100·01 ± 0·1	—	—
6·0	99·94 ± 0·04	—	—

The Jones reductor—The column was prepared as described by Vogel,[8] and the usual reduction procedure in a 2 N sulphuric acid medium followed.

The permanganate - iron(II) system—A sharper end-point resulted when the permanganate was over-titrated with the iron(II) solution, and the end-point was reached with the permanganate solution. This method was accepted as standard procedure.

The cerium(IV) - iron(II) system—After addition of ferroin indicator the cerium(IV) was over-titrated with the iron(II) solution and the end-point reached by titrating with the same cerium(IV) solution. This method gave a sharper colour change at equivalence-point.

The iron(III) - iron(II) - permanganate system—The procedure is based on a method by Döring,[9] who added orthophosphoric acid to the iron(II) solution in which the molybdenum(III) was to be collected. We tried this method without success. A possible reason may be that iron(III) forms a more stable phosphate complex than iron(II). Iron(II) is, therefore, a weaker oxidising agent in the presence of orthophosphoric acid than in its absence. The oxidation of molybdenum(III) by iron(III) must have been incomplete under the above mentioned conditions. When orthophosphoric acid was omitted altogether quantitative values were obtained.

The results are summarised in Table IV.

TABLE IV

THE DETERMINATION OF MOLYBDENUM(III) PREPARED WITH A JONES REDUCTOR

Redox system	Molybdenum found, as percentage of that taken
Permanganate - iron(II)	99·99 ± 0·01
Cerium(IV) - iron(II)	99·97 ± 0·03
Iron(III) - iron(II) - permanganate ..	99·95 ± 0·04

DISCUSSION

The reduction of molybdenum(VI) to molybdenum(V) with the silver reductor is quantitative only if the hydrochloric acid concentration, at the time of reduction, lies between 2·0 and 2·25 N (Table I). The presence of orthophosphoric acid has no influence on the reduction of molybdenum(VI) by silver, nor has it any significant effect on the reaction rate of the molybdenum(V) - cerium(IV) titration and may be omitted.

Titration of molybdenum(V) solutions with potassium dichromate gave a constant negative error of 1 per cent., as shown by results on p. 167. This was also reported by Wenier and Boriss[10] and Grubitsch, Halvorsen and Schindler,[5] who gave the following explanation.

Traces of copper catalyse the atmospheric oxidation of molybdenum(V),[9] therefore, if the silver reductor was prepared by reducing a silver solution with copper, traces of copper may always be found in the column. It must be pointed out that no such errors occur when molybdenum(V) solutions prepared with the same reductor are titrated with cerium(IV) and metavanadate solutions. Part of the dichromate may perhaps be reduced by the fine silver particles, which are inevitably washed out of the reductor column during reduction.

The reduction of molybdenum(VI) by mercury is complete within the hydrochloric acid concentration range of 2 to 4 N (Table II). At higher concentrations partial reduction to a lower oxidation state, probably molybdenum(III), occur. Because of the difficult reduction technique and the ease with which molybdenum(III) is oxidised by atmospheric oxygen, we did not try to obtain a quantitative reduction of molybdenum(VI) to molybdenum(III) with mercury. All three oxidants used may be equally recommended for the titration of molybdenum(V) solutions.

In hydrochloric acid concentrations lower than N, a molybdenum-blue compound is formed with tin(II) as reducing agent. In acid concentrations higher than 2 N quantitative reduction of molybdenum(VI) to molybdenum(V) was found. It is important to note that only a small excess of tin(II) chloride is to be used, as the following reaction may take place—

$$Sn^{2+} + HgCl_2 \longrightarrow Sn^{4+} + Hg + 2Cl^-.$$

Quantitative values for the oxidimetric determination of molybdenum were found with the reduction carried out in the acid concentration range 2 to 6 N (Table III). Any one of the three oxidants may be used with confidence. The procedure is fairly simple and the method has the advantage that the acid concentration is not too critical.

The Jones reductor is most suitable for the quantitative reduction of molybdenum(VI) to molybdenum(III). The process is fast and the acid concentration is not critical. All three methods may be used with equal confidence. The iron(III) - iron(II) - permanganate system has the advantages that only one standard solution and no indicator is needed for the determination.

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A Thin-layer Chromatographic Screening Test for Organophosphorus Pesticide Residues

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A procedure is proposed for use as a screening test for the presence of traces of organophosphorus pesticides in vegetable tissue. The compounds are extracted with dichloromethane and the extracts are cleaned-up on silica-gel chromatoplates developed with hexane - acetone solution, 5 + 1. Eluted compounds are then oxidised with ammonium persulphate or a nitric acid - perchloric acid mixture for phosphorus determinations by molybdenum-blue procedures. Good recoveries are reported from a range of crop samples. Mobile solvents required for the clean-up of some polar pesticides and metabolites on multi-band chromatoplates are also listed.

THE procedure recently proposed[1] for the detection, determination and identification of residues of organophosphorus pesticides in vegetable tissue combines thin-layer and gas - liquid chromatography with infrared spectrometry, and consequently gives a maximum amount of information regarding the sample under examination. However, the exercise takes at least 6 hours to complete and some expensive apparatus is required. A simple and comparatively rapid screening test was needed which could be applied to sort out, for this more detailed examination, samples that might contain appreciable residues.

The paper-chromatographic procedure described by Bates[2] offers simplicity of approach and possibilities of simultaneous identification and determination. Each analysis, however, requires 20 hours for completion, although several samples may be examined at the same time provided sufficient staff and apparatus are available. This procedure involves a freezing-filtration stage to remove fats and waxes, followed by further columnar clean-up steps before total-phosphorus determinations are made.

The clean-up properties of silica-gel chromatoplates, together with the shorter development times required as compared to paper chromatograms, seemed likely to provide a more suitable method of achieving this. Steller and Curry[3] have used such a procedure in a determination of dimethoate residues, but their wet-combustion step alone took up to 2 hours.

EXPERIMENTAL

By using small chromatoplates (15 × 7·5 cm) in place of the more usual size (20 × 20 cm), development time is cut from the normal 30 to 40 minutes to 6 to 7 minutes. Application of an ammonium persulphate oxidation to organophosphorus residues eluted from the layer adsorbent with hexane - acetone solution, 3 + 1, has made it possible to propose a screening method that can be completed in 1½ to 2 hours for a single sample. Up to 3 sample extracts can be applied to each chromatoplate for simultaneous examination, and about 12 samples can be examined per man-day.

The procedure described here is most suitable for organophosphorus pesticides with R_F values in the system used greater than that of dimethoate; these R_F values are shown in Table I. Dimethoate is only partially included in the detailed procedure, but the bulk of it, together with such polar compounds as menazon, oxydemeton-methyl, phorate oxygen-analogue, etc., can also be determined on the same chromatoplate by elution from the base-line area with a more polar solvent (hexane - acetone, 1 + 1). Inorganic phosphorus is not eluted unless the acetone content of the mixed solvent is greater than 70 per cent. v/v. To cope with the additional co-extractives also eluted by this solvent a more vigorous oxidation procedure is required, the nitric acid - perchloric acid treatment described by Laws and Webley[4] being suitable. However, by using the multi-band chromatoplates previously described[5] for the spot-area determination of dimethoate, all of these compounds can be

obtained in a clean state for the persulphate oxidation procedure. By use of the mobile solvents listed in Table II the pesticidal compounds concerned are cleanly caught on the silica-gel band, the bulk of the extractives migrating to the solvent front.

TABLE I

R_F VALUES OF SOME ORGANOPHOSPHORUS COMPOUNDS

Silica-gel chromatoplates, 250-μ thick, (15 × 7·5 cm) developed with hexane - acetone solution, 5 + 1, as described in the proposed procedure

Compound	R_F value
Azinphos-methyl	0·18
Carbophenothion	0·65
Chlorthion [*O*-(3-chloro-4-nitrophenyl) *OO*-dimethyl phosphorothioate]	0·34
Demeton-O-methyl	0·50
Demeton-S-methyl	0·13
Diazinon	0·49
Dimethoate	0·03
Disulfoton	0·65
Fenchlorphos	0·60
Malathion	0·33
Menazon	b
Oxydemeton-methyl	b
Paraoxon (diethyl 4-nitrophenyl phosphate)	0·11
Parathion	0·45
Phenkapton	0·62
Phorate	0·65
Phorate oxygen-analogue	0·02
Phorate oxygen-analogue sulphone	0·01
Phosphamidon	0·37

b = remains on base-line.

All of the compounds examined showed total recoveries of upwards of 80 per cent. of pesticides added at the 0·2 p.p.m. level to various samples of vegetable tissue. Crop blank values were generally below 0·2 p.p.m.; this figure is taken as a reasonable working level, samples showing above this amount being worthy of further examination by the fuller procedure.[1]

The oxidation procedure of Getz[6] has been modified slightly to give greater ease of operation; by reading optical densities at 820 mμ (maximum absorption is given at this wavelength) instead of 660 mμ, a useful increase in sensitivity is observed. Still greater sensitivity has been obtained by using the multiplication factor given by determining the molybdenum content of the molybdophosphate complex, as described by Umland and Wünsch,[7] and by Djurkin, Kirkbright and West,[8] but the elapsed time is necessarily increased. These procedures may prove valuable when clean-up difficulties are experienced, as smaller sample sizes can be used.

The method described is designed as a general screening procedure. When only specified single substances are sought, *e.g.*, in following the decay of residues in field trials, then it is preferable to elute that area of the chromatoplate corresponding to the likely position of the pesticide, as shown by its known R_F value. In this way blank values can be lowered.

TABLE II

MOBILE SOLVENTS FOR POLAR COMPOUNDS ON MULTI-BAND CHROMATOPLATES[5]

Composition of chromatoplate: (*a*) 5-cm silica gel - kieselguhr, 1 + 1; (*b*) 3-cm silica gel; (*c*) 12-cm kieselguhr. Developed for 45 minutes: tank size 22 × 21 × 9 cm

Compound	Mobile solvent
Dimethoate	Chloroform - acetone, 9 + 1
Menazon	Chloroform - acetone, 2 + 3
Oxydemeton-methyl	Acetone
Phorate oxygen-analogue	Chloroform
Phorate oxygen-analogue sulphone	Chloroform - acetone, 19 + 1

Similar procedures have also been applied with the more usual 20 × 20-cm chromatoplates. Development times are longer, but these plates may be preferable when separation of individual compounds or their metabolites is required.

APPARATUS—

Thin-layer chromatography equipment—Suitable for the preparation of 250-μ thick silica-gel chromatoplates, 15 × 7·5 cm. (The demonstration kit available from Quickfit and Quartz Ltd. was used.)

Activation oven—Air-oven set at 120° C.

Development chamber—Glass tank, 22 × 21 × 9 cm, with well fitting lid.

Top-drive macerator.

Danish-Kuderna evaporator—This is fitted with a 10-ml pear-shaped flask.

Graduated test-tubes—10-ml capacity.

Spectrophotometer—Complete with 2-cm cells.

Water-bath.

REAGENTS—

Reagents should be of recognised analytical grade whenever possible.

Dichloromethane.

Hexane.

Acetone.

Silica gel G—For thin-layer chromatography (obtainable from E. Merck, Darmstadt).

Sodium sulphate—Granular, anhydrous.

Ammonium persulphate solution, 0·25 M—Prepare daily.

Urea solution, 0·25 M.

Ammonium molybdate solution—A 2·5 per cent. w/v solution of ammonium molybdate in 10 N sulphuric acid.

Ascorbic acid solution, 2 *per cent.*—Prepare daily.

Potassium dihydrogen phosphate.

PROCEDURE—

(*a*) *Extraction*—Macerate 50 g of finely chopped or shredded vegetable tissue with 50 ml of dichloromethane for 1 minute. Decant off the solvent phase and repeat with two 25-ml portions of dichloromethane. Combine the extracts and, if necessary, spin the mixture in a centrifuge to obtain a clear liquor. Run the extracts through a 10 × 1-cm column of anhydrous sodium sulphate into a Danish-Kuderna evaporator fitted with a 10-ml pear-shaped flask. Wash the flask through with 15 ml of dichloromethane and evaporate the solution to about 0·5 ml.

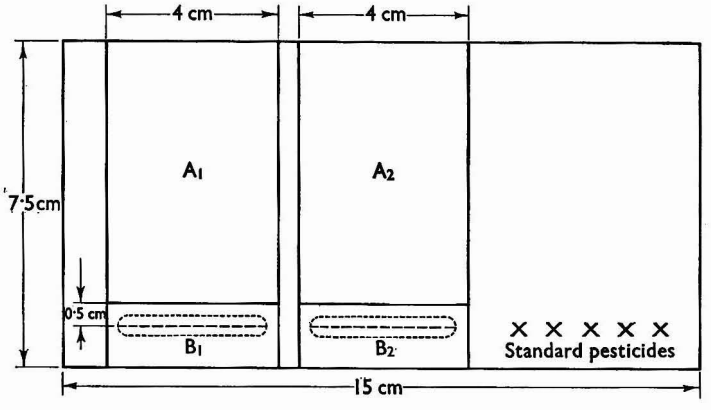

Fig. 1. Areas A_1 and A_2 removed for persulphate oxidation procedure (*c*); areas B_1 and B_2 removed for wet-combustion procedure (*e*). Dotted areas show applied extract streaks

(*b*) *Thin-layer chromatographic clean-up*—Prepare 250-μ thick layers of silica gel G on 15 × 7·5-cm glass carrier plates and activate them by heating at 120° C for at least 2 hours. Apply the extract obtained above as a 3-cm long streak parallel to one of the longer edges of the plate and about 1 cm from it. Develop by ascending chromatography with hexane - acetone solution, 5 + 1, until the mobile solvent just reaches the upper edge of the layer (this takes about 7 minutes), remove the plate from the tank and allow the solvent to evaporate. Scribe a line along the plate parallel to the applied streak and 0·5 cm above it; discard all adsorbent below this line or treat it as described in (*e*) below. Scribe two lines across the plate, perpendicular to the first line, in such a way as to enclose the area containing the developed chromatogram and slightly wider than the applied streak (about 4 cm). Carefully remove all of the adsorbent contained within the area so marked (Fig. 1) from the carrier plate, and transfer it to a small funnel fitted with a small cotton-wool plug. Elute with five 2-ml portions of hexane - acetone solution, 3 + 1, collecting the solution in a 10-ml graduated test-tube. Evaporate the solution carefully to dryness on a warm water-bath.

TABLE III

RECOVERIES OF ADDED PESTICIDES [PERSULPHATE OXIDATION (*c*)]

Compound	Factor*	Crop	Pesticide, p.p.m. Initial level†	Pesticide, p.p.m. Added level	Mean recovery, per cent.
—	—	Reagent blank	0·04	—	—
Azinphos-methyl	10·2	Apple	0·21	0·5	83
Demeton-methyl	7·4	Brussels sprouts	0·08	0·2	89
		Peas	0·15	0·2	90
		Apple	0·14	0·2	86
		Carrot	0·14	0·5	87
Demeton-S-methyl	7·4	Cabbage	0·10	0·2	90
		Pear	0·15	0·2	96
		Potato	0·06	0·2	94
		Tomato	0·08	0·2	83
Diazinon	9·8	Brussels sprouts	0·46	0·5	88
		Carrot	0·17	0·2	88
Dimethoate	7·4	Apple	0·17	0·5	37
		Cabbage	0·15	0·2	48
		Peas	0·15	0·5	27
		Potato	0·08	0·2	36
		Tomato	0·10	0·2	44
Malathion	10·7	Cabbage	0·19	0·2	90
		Peas	0·19	0·2	87
		Potato	0·12	0·2	93
		Tomato	0·13	0·2	100
Parathion	9·4	Lettuce	0·04	0·2	90
		Potato	0·05	0·2	98
		Strawberry	0·03	0·2	78
		Sugar beet	0·02	0·2	95
		Tomato	0·04	0·2	83
Phenkapton	12·2	Apple	0·16	0·2	87
Phorate	8·4	Cabbage	0·17	0·2	92
		Peas	0·17	0·5	92
		Potato	0·09	0·2	90
		Runner beans	0·58	0·5	88
		Tomato	0·11	0·2	93
Phosphamidon	9·7	Apple	0·20	0·5	81
		Brussels sprouts	0·46	0·5	85
		Runner beans	0·62	0·5	92

* Factor to convert μg of phosphorus to μg of pesticide.

† The initial level of pesticide on a crop free from residue would be the normal blank value (theoretically 0·0). In practice, however, small amounts of organophosphorus residues were found on some of the crops used.

(*c*) *Wet oxidation and phosphorus determination*—Add 2 ml of ammonium persulphate solution to the residue in the tube obtained as described above, and heat it in a boiling water bath for 10 minutes. Cool rapidly, add 3 ml of urea solution to the mixture and replace the

tube in the boiling water for 5 minutes. Cool, add 1 ml of ammonium molybdate solution, mix the solutions well and add 1 ml of ascorbic acid solution. Mix and place the tube in boiling water for 1 minute. Cool rapidly, dilute the solution to 7 ml with water and determine the optical density of the resultant solution at 820 mμ in 2-cm cells against water as reference material. Determine the amount of phosphorus in the extract by reference to the standard graph prepared as described below.

TABLE IV

RECOVERIES OF ADDED PESTICIDES [OXIDATION METHOD (*e*)]

Compound	Factor*	Crop	Pesticide, p.p.m. Initial level†	Pesticide, p.p.m. Added level	Mean recovery, per cent.
—	—	Reagent blank ..	0·06	—	—
Dimethoate	7·4	Cabbage	0·10	0·5	64
		Carrot	0·14	0·2	59
			0·14	0·5	63
		Potato	0·08	0·2	56
			0·08	0·5	61
Menazon	9·1	Apple	0·07	0·2	98
			0·07	0·5	94
		Broad beans ..	0·01	0·2	96
			0·01	0·5	96
		Potato	0·05	0·2	96
			0·05	0·5	93
Oxydemeton-methyl ..	7·9	Cabbage	0·15	0·2	81
			0·15	0·5	84
		Carrot	0·15	0·2	87
			0·15	0·5	88
		Potato	0·08	0·2	82
			0·08	0·5	84
Phorate oxygen-analogue ..	7·9	Cabbage	0·11	0·5	93
		Carrot	0·15	0·2	82
			0·15	0·5	86
		Potato	0·08	0·2	94
			0·08	0·5	95
Phorate oxygen-analogue sulphone	8·9	Cabbage	0·12	0·5	88
		Carrot	0·17	0·2	82
			0·17	0·5	84
		Potato	0·09	0·2	87
			0·09	0·5	85

* Factor to convert μg of phosphorus to μg of pesticide.

† The initial level of pesticide on a crop free from residue would be the normal blank value (theoretically 0·0). In practice, however, small amounts of organophosphorus residues were found on some of the crops used.

(*d*) *Preparation of standard graph*—Evaporate various amounts of a standard potassium dihydrogen phosphate solution (from 0 to 2 μg of phosphorus) to dryness in a 10-ml graduated tube and continue as described above in (*c*). Alternatively, when the pesticide sought is known, use standard amounts of the compound over the range 0 to 10 μg. Report results as p.p.m. of pesticide when its identity is known, or as p.p.m. of organophosphorus when its identity is unknown or mixtures of pesticides are present.

(*e*) *Polar compounds—wet oxidation and phosphorus determination*—Transfer the discarded adsorbent material lying below the scribed line in (*b*) above to a small funnel plugged with cotton-wool, and elute with 5 portions each of 2 ml of hexane - acetone solution, 1 + 1. Carry out the oxidation and phosphorus determined as described by Laws and Webley.[4]

RESULTS

Recoveries of pesticides added to various crops are listed in Tables III and IV. The compounds included in the described procedure are given in Table III; Table IV gives similar results obtained from some polar compounds and metabolites, by using the acidic wet-combustion procedure. Blank values are quoted in terms of the respective pesticide in each instance. The samples used in this study were all of unknown spray-treatment history.

Permission to publish this paper has been given by the Government Chemist, Ministry of Technology.

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The Detection of Adulteration of Fruit Juices by Thin-layer Chromatography

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The technique of thin-layer chromatography has been applied to extracts of citrus and non-citrus juices in order to detect adulteration.

Procedures for preparing suitable extracts of the juices are given.

For non-citrus juices, 10 per cent. adulteration with apple juice, or 25 per cent. of another foreign juice can be detected, as can 0·1 μg of glycine in 5 μl of citrus juice extract.

NON-CITRUS JUICES

Several workers[1,2,3] have developed chromatographic procedures for the identification and evaluation of non-citrus juices, based on the analysis of anthocyanin colouring matters. The method outlined below enables one juice to be detected and identified in the presence of another, and is based on differences in the composition of the juices investigated that are revealed by the techniques of thin-layer chromatography.

Method

Apparatus—

A small chromatographic column—The lower half of a 10-ml pipette with a glass bead in the tip is satisfactory.

Glass thin-layer chromatographic plates—Size according to the number of samples to be investigated.

Reagents—

Ion-exchange resin—Permutit Zeo-Karb 225, chromatographic grade SRC9. Shake the resin with analytical-reagent grade concentrated hydrochloric acid and wash it with distilled water until free from chloride.

Eluting solvent—Prepare a 2 per cent. solution of analytical-reagent grade hydrochloric acid in general-purpose reagent grade methanol.

Developing solvent for thin-layer chromatography—Use a mixture of general-purpose reagent grade propanol and distilled water (70 + 30 v/v).

Cellulose powder—Whatman CC41 for thin-layer chromatographic plates, spreader set at 400 μ. Heat the plates at 60° C until apparently dry and store without desiccant.

Spray reagent for thin-layer chromatography—Prepare freshly a solution of 1 per cent. of vanillin in 96 per cent. ethanol containing 1 per cent. of sulphuric acid.

Procedure—

Shake 20 ml of natural juice, or a smaller volume of a concentrated juice diluted to 20 ml, for 1 minute with about 5 g of the prepared resin. Allow it to stand for a few minutes, decant the juice, and then wash the resin by decantation with water until the washings are colourless. Transfer the resin to the small column and elute the coloured compounds with the acidified methanol. Collect the coloured fraction (about 5 ml). Treat all the juices under examination similarly, together with samples from pure fruit. Spot these on to the cellulose plates; 4 drops of each extract from a glass capillary tube dried after each addition is adequate. Run at least two spots for every extract to obtain a reliable pattern for each.

Develop the chromatogram in a tank saturated with aqueous propanol for 1 hour. Dry in a current of warm air, view under ultraviolet light and compare the fluorescent patterns. Spray the plate with the vanillin reagent and heat in an oven at 100° C until coloured patterns develop, and compare these also.

Results and discussion

As can be seen from Fig. 1, ultraviolet light reveals numerous characteristic spots by means of which it is generally possible to detect 25 per cent. of one juice in another. After spraying, the most important spot is the larger green one in the apple-juice chromatogram. This allows as little as 10 per cent. of apple juice to be detected in another juice. The spot may vary in colour from green to grey - green, according to the heating time of the chromatogram.

The juices used for this work were commercial products of unknown origin and variety, etc., and chromatograms of twelve samples of each juice showed no significant variations, although Nybohm[1] reported some differences between varieties. Variations in colours produced on thin-layer chromatograms sometimes occur inexplicably with this spray reagent, and also positions of spots can vary somewhat in relation to the amounts applied. Hence it is desirable, and good practice, always to run genuine juices alongside suspect ones, rather than to rely solely on reported patterns and colours, etc. The age of juices does not affect the chromatogram unduly, although the appearance of the chromatogram in visible light before spraying may be modified by the presence of brown colours, rather than the bright red colour of fresh juices.

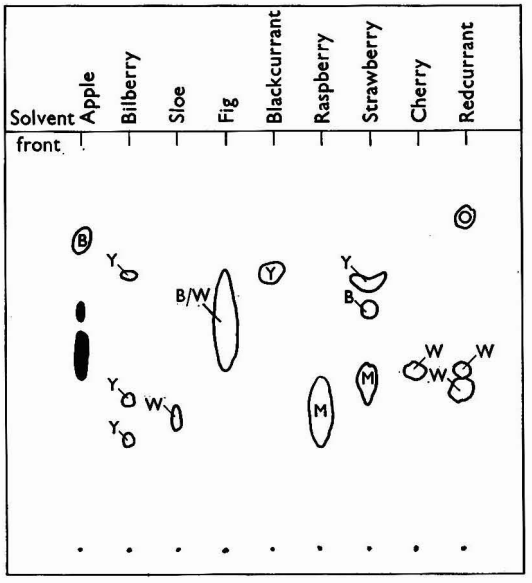


Fig. 1. Appearance of chromatogram on a cellulose chromatoplate. Fluorescent spots under ultraviolet light

CITRUS JUICES

The more common forms of adulteration of orange juices involve either dilution of the juice with peel extracts, etc., or dilution with water, followed by the addition of sugar, glycine, potassium salts and phosphates to bring the usual analytical results into the range of natural juices.

The former method still eludes detection with certainty by thin-layer chromatography.[4] Chloramine values[4] and ultraviolet absorption measurements on extracts[5] give valuable evidence for the presence of peel extracts. The latter method is definitely detected by the thin-layer chromatographic technique. Many workers[6,7,8] use general values, *e.g.*, for phosphate and nitrogen content, and for sugars, etc., to evaluate juices and detect adulteration.

The procedures involved in their determination are, however, lengthy and may give misleading figures, owing to the natural variations of juices.[9] Glycine, used to bring the nitrogen content of diluted juices into the normal range, is not reported in orange juices, or else is reported as being present to a very small extent.[10,11] The method described below is rapid and sensitive, and is applicable to orange, lemon, lime and grapefruit juices.

Method

Apparatus—

Glass thin-layer chromatographic plates—As previously used.

Reagents—

Ethanol, 96 per cent.

Developing solvent for thin-layer chromatography—Use a mixture of propanol and distilled water (70 + 30 v/v).

Silica gel for thin-layer chromatography—Containing 13 per cent. of calcium sulphate as binder, the spreader set at 250 μ. Activate the plates for 1 hour at 100° C and store at 40° C.

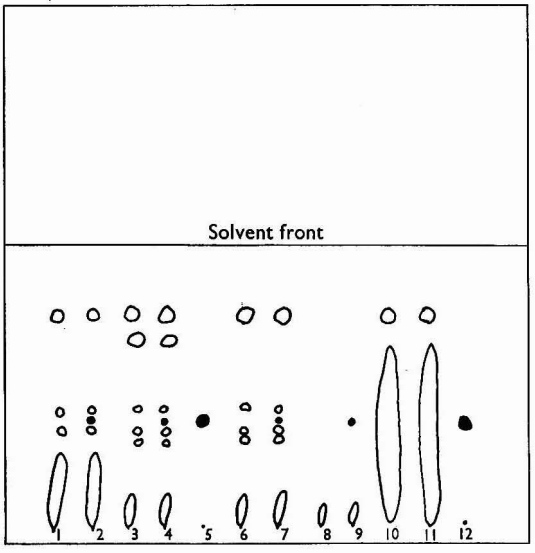
Spray reagent for thin-layer chromatography—Prepare a 0·5 per cent. solution of ninhydrin in butanol.

Procedure—

To 1 ml of each juice of natural strength, or 1 ml of concentrated juices after dilution to natural strength, add 6 ml of the ethanol. Shake the solutions for 1 minute and spin them in a centrifuge. Spot on a plate (in 1-μl drops) 5 μl of each of the supernatant liquors, drying after each addition.

Prepare similar extracts of pure juices and spot them on the plate as controls. To locate the glycine spot position exactly, apply also a 1-μl spot of a 0·1 per cent. solution of glycine.

Develop the chromatogram in the tank saturated with aqueous propanol until the solvent front has advanced 8 to 10 cm. Dry in a current of warm air. Spray with the ninhydrin solution and heat at 110° C for about 5 minutes, or until the glycine spot is well developed.



● = Glycine spots
1 = Lemon juice
2 = Lemon juice with added glycine
3 = Orange juice
4 = Orange juice with added glycine
5 and 12 = Glycine
6 = Grapefruit juice
7 = Grapefruit juice with added glycine
8 = Lime juice
9 = Lime juice with added glycine
10 = Lemon juice, plate overloaded
11 = Lemon juice, added glycine masked by overloading of plate

Fig. 2. Appearance of chromatogram on a silica-gel chromatoplate

Results and discussion

Fig. 2 shows the pattern obtained for amino-acids for these four citrus juices. In every instance when glycine had been added to the juice it showed as a pink spot just ahead of the yellow proline spot. No proline spot was observed for the lime juice, but the pink spot was separate and easily discernible. No glycine was detected in any natural juice. The lower limit of detection was below 0·1 μg of glycine in the 5-μl spot, which is about equivalent to the amount of glycine that would require to be added to compensate for a 5 per cent. dilution of the juice. Gross adulteration of the juice with peel extract can sometimes be detected by viewing the chromatogram under ultraviolet light. The fluorescent spots will be much stronger in the adulterated juice, owing to the presence of peel oil.

Overheating of the chromatograms must be avoided as the whole plate may become coloured, thus masking the small pink glycine spot.

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The Assay of Certain Organic Bases in Aqueous Eye-drops

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Methods have been devised for the assay of medicaments in eye-drop solutions containing benzalkonium chloride and chlorhexidine diacetate in which interference caused by these substances is eliminated.

The 1966 Supplement to the British Pharmaceutical Codex 1963 has specified some marked changes in the monographs for eye-drops. These changes have introduced the use of chlorhexidine diacetate as a bactericidal and fungicidal agent and extended the use of benzalkonium chloride. Also, to meet the wider needs of hospital practice, most monographs on eye-drops now deal with solutions of a range of strengths instead of a single concentration, as previously. Before these changes were made the assay of organic nitrogenous bases depended upon precipitation of the base with a measured excess of sodium tetraphenylboron solution, and subsequent titration of the residual excess with a solution of cetylpyridinium chloride. The fact that this method, had its use been continued, would have caused bactericidal agents to be precipitated with medicaments, with consequent determination of the former as the latter, would not have mattered greatly had the concentration ranges for the medicaments not been extended. The level of bactericidal agent was formerly extremely low in relation to the level of medicament, and any interference was correspondingly small. The new monographs in the B.P.C. Supplement, however, include much lower concentrations of medicaments, and interference caused by chlorhexidine diacetate and benzalkonium chloride becomes relatively larger as levels are reduced.

At the time of publication of the 1966 Supplement suitable methods of assay were not available to meet this situation, and for this reason, there are at present no standards given under eye-drops in most of the monographs in the B.P.C. The B.P.C. Formulary Standards Sub-committee A, which is responsible for the provision of standards for these formulations, has recognised that this is an unsatisfactory situation, and the work now described has been undertaken at the request of that committee. The methods described are modifications of the original tetraphenylboron assay by Johnson and King[1]; and they are intended for use with aqueous eye-drops containing nitrogenous bases with chlorhexidine diacetate or benzalkonium chloride as a bactericidal agent.

The use of sodium tetraphenylboron for the assay of quaternary ammonium salts and organic bases, singly and in mixtures, has been widely investigated.[2 to 8] Direct and indirect titrimetric procedures and gravimetric methods have been described. Patel and Anderson[2] reported the assay of benzalkonium chloride by titration with sodium tetraphenylboron in a two-phase system under alkaline conditions with bromophenol blue indicator. They showed that under these conditions only quaternary ammonium salts could be titrated; non-quaternary salts were not titratable. Uno, Miyajaima and Tsukatoni[3] reported that quaternary ammonium salts could be titrated with sodium tetraphenylboron under acidic conditions with methyl orange as indicator. The acidic colour of methyl orange was not observed, except in the presence of an excess of sodium tetraphenylboron, when a pink colour was produced. The end-point in the titration was marked by the change from yellow to pink. Kaito and Kobayashi[4] determined organic bases in a two-phase system by direct titration with Nile blue as indicator, which they claimed was superior to bromophenol blue. Boden[5] described the direct titration of quaternary ammonium salts with sodium tetraphenylboron and he, too, used a cationic indicator. In this instance the indicator, neutral red, marked the end-point by its appearance in the organic solvent layer. Cross[6] combined a number of features from some of the methods mentioned to provide a neat and convenient method for the assay of mixtures of cationic surfactants. By titrating with sodium tetraphenylboron at pH 3, 10 and 13, he was able to resolve mixtures of quaternary and non-quaternary ammonium salts, and nitrogenous bases of the pyridinium and guanidinium type. He used methyl orange and bromophenol blue as indicators in a two-phase chloroform - water system.

In general, two-phase titration techniques are based on the transfer of indicator, with or without an associated colour change, from one phase to the other at the end-point. Whether a cationic or an anionic indicator is used, the requirements are the same for both, namely, that the indicator salt should be almost wholly soluble in one phase before the end-point, and almost wholly soluble in the other phase after it. It is also necessary that the substituted ammonium tetraphenylboron salt formed should be stable, and that the indicator should not be permanently precipitated by any of the components of the mixture being titrated. Solutions for eye-drops were found to fall short of almost all of these requirements, so that the methods described for direct titration, despite their obvious attractions, could not be applied. Chlorhexidine formed precipitates with the anionic indicators and these precipitates were insoluble in both chloroform and water. Other chlorinated solvents were no more satisfactory than chloroform in their ability to dissolve these chlorhexidine - indicator salts, and the use of solvents such as ethanol or acetone, either alone or in admixture with other solvents, simply caused a distribution of colour between the phases. Further, the medicaments themselves did not form tetraphenylboron salts that were of sufficient stability to enable a direct titration procedure to be used. It was necessary, therefore, to retain the precipitation stage in the method described for eye-drops in the B.P.C. 1963, and it was possible to apply the diphasic titration technique only to the preliminary titration of benzalkonium chloride.

No satisfactory method for the direct titration of chlorhexidine diacetate could be devised and, as it displayed a considerable readiness to precipitate with a variety of reagents under various conditions, it was decided to remove it in this way. Accordingly, a method was devised based on the precipitation of chlorhexidine as sulphate. The methods for assay of eye-drop solutions are described below.

Assay of some nitrogenous bases in eye-drops in the presence of benzalkonium chloride—

The method is based on titration at pH 10 and 3·7 to determine benzalkonium chloride and medicament, respectively. The titre at pH 10 is determined in a two-phase chloroform - water system, with bromophenol blue as indicator. At the start of the titration the colour is concentrated in the chloroform layer, and the end-point is marked by the change from blue to colourless. Titration at pH 3·7 follows precipitation of the medicament and bactericidal agent with excess of sodium tetraphenylboron solution.

The method described has been applied to aqueous solutions containing amethocaine, atropine, carbachol, cocaine, homatropine, physostigmine and pilocarpine at concentrations of 0·5 per cent. w/v, and hyoscine at a concentration of 0·25 per cent. w/v. Table I lists results that show the absence of interference by medicaments at pH 10, and Table II the results obtained with prepared eye-drop solutions.

Table I

Titration of benzalkonium chloride (0·02 per cent.) at pH 10 in presence of nitrogenous bases

Medicament, 0·1 per cent. w/v (4-ml samples)	Titre, ml of 0·01 M sodium tetraphenylboron	
	Without benzalkonium chloride	With benzalkonium chloride
Amethocaine	0·0	0·20
Atropine	0·0	0·23
Carbachol	0·0	—
Cocaine	0·0	0·22
Homatropine	0·0	0·21
Hyoscine	0·0	0·21
Physostigmine	0·0	0·21
Pilocarpine	0·0	0·21

Five millilitres of a 1 per cent. w/v solution of cocaine containing 0·5 per cent. w/v of benzalkonium chloride gave a titre of 6·55 ml of 0·01 M sodium tetraphenylboron solution at pH 10; and 5 ml of 0·5 per cent. w/v benzalkonium chloride solution gave a titre of 6·6 ml at pH 10. No titre was obtained at pH 10 with 5 ml of 1 per cent. w/v cocaine solution.

TABLE II

RECOVERY OF MEDICAMENTS FROM EYE-DROP SOLUTIONS CONTAINING 0·02 PER CENT. W/V OF BENZALKONIUM CHLORIDE

Medicament (2-ml samples)	Titre at pH 10, ml of 0·01 M sodium tetraphenylboron	Concentration determined, per cent. w/v: (*i*) Without benzalkonium chloride	Concentration determined, per cent. w/v: (*ii*) With benzalkonium chloride	Recovery, (*ii*) as percentage of (*i*)
Amethocaine ..	0·12 0·11	0·52	0·51 0·52	99
Atropine	0·11 0·11	0·50	0·50 0·50	100
Carbachol	0·13 0·12	0·50	0·46 0·47	93
Cocaine	0·11 0·11	0·50	0·47 0·47	94
Homatropine ..	0·11 0·12	0·50	0·50 0·50	100
Hyoscine	0·11 0·11	0·25	0·28 0·26 0·27	110
Physostigmine ..	0·12 0·10	0·53	0·52 0·52	98
Pilocarpine ..	0·11 0·11	0·50	0·50 0·50	100

METHOD

REAGENTS—

Bromophenol-blue solution—Prepare as described in the British Pharmacopoeia 1963, Appendix IIB.

Acetate buffer solution, pH 3·7—Prepare as described in the British Pharmaceutical Codex 1963, Appendix 8.

Buffer solution, pH 10—Mix 100 ml of 0·2 M disodium hydrogen orthophosphate solution and 6 ml of 0·25 M trisodium orthophosphate solution.

Cetylpyridinium chloride, 0·005 M—Prepare as directed in the British Pharmaceutical Codex, Appendix 8; Volumetric Solutions. Store in an amber-coloured bottle.

Sodium tetraphenylboron, 0·01 M—Dissolve 3·422 g of sodium tetraphenylboron in 1 litre of water, and adjust the pH to between 8·0 and 9·0 with sodium hydroxide. Store in an amber-coloured bottle. Standardise with analytical-reagent grade potassium chloride.

Chloroform—Analytical-reagent grade.

PROCEDURE—

Transfer by pipette 2 ml of eye-drop solution into a 100-ml glass-stoppered conical flask. Add 5 ml of pH 10 buffer solution, 5 ml of chloroform and 2 drops of bromophenol blue indicator. Shake the mixture well and titrate slowly with 0·01 M sodium tetraphenylboron solution, shaking it well between successive small additions, until the chloroform layer changes from blue to colourless (the chloroform layer may not turn blue until the first drop of 0·01 M sodium tetraphenylboron solution is added).

To a further 2 ml of eye-drop solution in a beaker, add 5 ml of pH 3·7 buffer solution and 5 ml of 0·01 M sodium tetraphenylboron solution. Allow the solution to stand for 10 minutes and then filter it through a dry, No. 4 porosity, sintered-glass crucible. Rinse the beaker and the crucible with 5 ml of water and titrate the combined filtrate and washings with 0·005 M cetylpyridinium chloride solution, with 0·5 ml of bromophenol-blue solution as indicator. Repeat the operation, omitting the sample and the filtration stage. The difference between the titres is equivalent to the total medicament and benzalkonium chloride present. Calculate the amount of medicament from the difference between the blank titre and the sum of the titres at pH 3·7 and 10, expressed in terms of 0·01 M sodium tetraphenylboron solution.

$$\text{Percentage w/v of medicament} = x - \frac{(y + 2z)}{2} \cdot \frac{100f}{2}$$

where x is the blank titre in millilitres of 0·005 M cetylpyridinium chloride,
y is the titre at pH 3·7 in millilitres of 0·005 M cetylpyridinium chloride,
z is the titre at pH 10 in millilitres of 0·01 M sodium tetraphenylboron, and
f is the weight of medicament equivalent to 1 ml of 0·01 M sodium tetraphenylboron.

ASSAY OF SOME NITROGENOUS BASES IN EYE-DROPS IN THE PRESENCE OF CHLORHEXIDINE DIACETATE—

The method is based on the precipitation of chlorhexidine as sulphate at pH 3·7, with subsequent precipitation of medicament by using a measured excess of sodium tetraphenylboron and titration of the excess of reagent with cetylpyridinium chloride solution. Initially, saturated nickel sulphate solution was used as a precipitant, but while this was satisfactory when the concentration of chlorhexidine was high, it was not suitable at low concentration. The results in Table III were obtained by using nickel sulphate and they demonstrate that, even in the presence of a large amount of chlorhexidine diacetate, interference following sulphate precipitation is small. Chlorhexidine at the 0·25 per cent. w/v level would interfere to the extent of about 0·2 per cent. w/v, expressed as medicament, if it were not removed before precipitation with sodium tetraphenylboron.

TABLE III

ASSAY OF MEDICAMENTS IN EYE-DROP SOLUTIONS IN THE PRESENCE OF 0·25 PER CENT W/V CHLORHEXIDINE DIACETATE

Medicament (5-ml samples)	Concentration determined, per cent. w/v
Cocaine (0·5 per cent. w/v)	0·51, 0·50, 0·53, 0·51
Homatropine (0·5 per cent. w/v)	0·51, 0·54
Hyoscine (0·2 per cent. w/v)	0·22, 0·20
Pilocarpine (0·5 per cent. w/v)	0·52, 0·52

To avoid masking the bromophenol-blue indicator solution change at the end-point of the sodium tetraphenylboron - cetylpyridinium chloride titration, sodium sulphate was substituted for nickel sulphate in the final method. The results obtained by the method described are set out in Table IV.

The results in Table V indicate that chlorhexidine interferes at about the 0·01 per cent. level if it is not removed.

TABLE IV

RECOVERY OF MEDICAMENTS FROM EYE-DROP SOLUTIONS CONTAINING 0·01 PER CENT. W/V OF CHLORHEXIDINE DIACETATE

Medicament (2-ml samples)	Concentration determined, per cent. w/v: (*i*) Without chlorhexidine diacetate	(*ii*) With chlorhexidine diacetate	Recovery, (*ii*) as percentage of (*i*)
Cocaine	0·10	0·11	110
		0·11	
	0·50	0·49	98
		0·49	
		0·48	
Homatropine	0·10	0·10	100
		0·10	
	0·50	0·49	98
		0·49	
Hyoscine..	0·10	0·09	90
		0·09	
	0·25	0·26	104
		0·26	
Pilocarpine	0·10	0·10	100
		0·10	
		0·10	
		0·10	
	0·50	0·49	98
		0·49	

TABLE V

ASSAY OF MEDICAMENTS IN EYE-DROP SOLUTIONS CONTAINING 0·01 PER CENT. W/V OF CHLORHEXIDINE DIACETATE WITH AND WITHOUT SULPHATE PRECIPITATION

Medicament (2-ml samples)	Concentration determined, per cent. w/v	
	With sulphate precipitation	Without sulphate precipitation
Cocaine	0·49	0·50
Homatropine	0·49	0·51
Hyoscine	0·26	0·27
Pilocarpine	0·49	0·51

METHOD

REAGENTS—

Those listed under Method for assay of some nitrogenous bases in eye-drops containing benzalkonium chloride.

Sodium sulphate, anhydrous, granular—Analytical-reagent grade.

PROCEDURE—

Transfer by pipette 2 ml of eye-drops into a 50-ml beaker, add between 0·3 and 0·5 g of anhydrous sodium sulphate, dissolve it by swirling, and allow the mixture to stand for 10 minutes. Add 5 ml of pH 3·7 buffer solution and 5 ml of 0·01 M sodium tetraphenylboron, and allow it to stand for a further 5 minutes. Filter the solution through a dry, No. 4 porosity, sintered-glass crucible and wash the beaker twice with 1 ml of water, adding the washings to the solution in the crucible before applying suction. Titrate the solution as described in the method for eye-drops containing benzalkonium chloride. Repeat the procedure, omitting the sample and the filtration stage. The difference between the two titres, expressed in terms of 0·01 M sodium tetraphenylboron solution, is equivalent to the concentration of medicament present.

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Field Methods for Determining Certain Organomercurial Vapours in Air

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Two methods are proposed for determining the vapours of certain organomercury compounds in air, at concentrations in the region of 10 μg of mercury per cu.m. The mercurial vapours are collected either on a glass-fibre pad treated with cadmium sulphide, or on a fluidised bed of active carbon. Mercury vapour is released by heating, and is determined by comparing the colour produced on selenium sulphide test-papers with a range of standard colours. The cadmium sulphide method is applicable to the determination of ethylmercury chloride, ethylmercury phosphate, diphenylmercury and methylmercury dicyandiamide; the fluidised-bed method is also applicable to this range of compounds and, in addition, to diethyl mercury. Mercurial dusts can be determined by the cadmium sulphide method, and mercury vapour by a slight modification of the fluidised-bed technique. In both methods the apparatus used is simple to manipulate and the time needed for a complete determination is less than 30 minutes.

The use of organomercury compounds as fungicides, both as a seed dressing and in the treatment of bulbs, has increased considerably during recent years. In 1955, a tentative threshold limit value was recommended for these compounds and it is now generally agreed that their concentration in air should not exceed 10 μg of mercury per cu. m.[1] There is, therefore, a need for a rapid field test to determine traces of organomercurial vapours in atmospheres in which these compounds are manufactured or used. A method that has been widely used as a field test for this class of compound was proposed by Sergeant, Dixon and Lidzey[2] in 1957. It consists in collecting mercury and its compounds on iodised active carbon and mineral-wool, heating under controlled conditions and determining the mercury liberated by the colours produced on selenium sulphide test-papers. The method works well at concentrations of 100 μg of mercury per cu. m of air, but would require a sampling time of 100 minutes to reach the present limit for mercurials of 10 μg per cu. m. Such a time is excessive for field work and a method of increasing the sampling rate was sought so that a determination could be completed within 30 minutes. Three approaches were considered.

The first consisted in collecting the organomercurial vapour in acid permanganate solution at a high air flow-rate by means of a Greenburg - Smith impinger, and determining the mercury by a dithizone method. Procedures based on this principle are most useful in the laboratory and, although not applicable to all mercurial vapours, have been used successfully in our investigations as a means of calibrating standard atmospheres of several mercurials. Such methods are less suitable for field use on account of the manipulative difficulties associated with handling large cumbersome impingers for the collection of the sample, and with making dithizone determinations in factory conditions. This technique was, therefore, not considered further as a field method.

In the second method collection of the vapour was on a fluidised bed of active carbon at a high air flow-rate in Lidzey and Longmaid's apparatus,[3] with completion of the determination by an ignition technique similar to that of Sergeant, Dixon and Lidzey.[2]

The third method consisted in collecting the organomercury compound in a liquid medium and filtering it through a glass-fibre pad treated with cadmium sulphide to retain the mercurial vapours by the method of Monkman, Maffett and Doherty.[4] Elimination of the liquid trapping medium, and collection of the mercurial vapour directly from air on a cadmium sulphide pad, was considered as the basis of a field method, followed by the ignition procedure mentioned above[2] to complete the determination.

At a concentration of 10 μg of mercury per cu. m of air, the time required to collect 5 μg of mercury would be 10 minutes by the second method and 15 minutes by the third,

assuming air flow-rates of 50 and 33·3 litres per minute, respectively. Both methods appeared to be possible field tests for organomercurial vapours in factory and laboratory atmospheres, and were further investigated.

Experimental

Purity of organomercury compounds—

Specimens of the following compounds were purchased and assayed for total mercury content by the methods of Sporek[5]: diethylmercury (DEM), diphenylmercury (DPM), ethylmercury chloride (EMC), ethylmercury phosphate (EMP) and methylmercury dicyandiamide (MMDD).

(*a*) *DPM and EMP*—The mercurial was refluxed with nitric acid, diluted and cooled, and permanganate added in slight excess; the pink colour was just discharged with iron(II) sulphate solution and mercury titrated with standard thiocyanate solution.

(*b*) *DEM*—The liquid was weighed into a gelatin capsule containing cotton-wool, and combusted by the oxygen-flask technique in presence of nitric acid (1 + 1).[6] The mercury was then determined as in (*a*). Infrared examination of the liquid indicated that the impurity present was ethyl acetate.

(*c*) *EMC*—The mercurial was refluxed with nitric acid, cooled and diluted with water. Urea was added and the solution was neutralised with sodium hydroxide solution. Potassium iodide was then added and the liberated alkali titrated with standard acid.

(*d*) *EMP*—The mercurial was dissolved in a mixture of acetone and water (1 + 1), urea was added and the solution made just pink to phenolphthalein. After addition of potassium iodide the liberated alkali was titrated with standard acid.

(*e*) *MMDD*—The mercurial was refluxed with a mixture of perchloric and nitric acids and the analysis was completed as under (*a*).

The results of the above analyses are shown in Table I.

Table I

Purity of organomercury compounds, per cent.

Substance	Method	Mercurial	Mean value
DPM	*a*	99·6 99·6 100·0	99·7
EMP	*a*	115 (98·0)*	115
	d	115 (97·6) 115 (97·8)	(97·8)
DEM	*b*	60·5 59·0	59·8
EMC	*c*	97·0 94·8 96·2	96·0
MMDD	*e*	103 104	103

* Figures in brackets relate to EMP calculated as the bis-ethyl compound.

The compounds examined are reasonably pure with the exception of diethylmercury, which contained only 60 per cent. of the active compound.

Preparation and calibration of standard atmospheres—

Atmospheres containing known concentrations of organomercury compounds were required to assess the efficiency of sampling techniques and to develop suitable field tests. Several methods for preparing and calibrating atmospheres of 5, 10 and 20 μg of mercury per cu. m of air were used, and these are summarised below.

Preparation—Solutions of ethylmercury chloride in water were readily vaporised by means of a fluid-feed atomiser described by Gage,[7] and modified by Marshall.[8] In this

method the liquid is injected from a syringe at a known rate into a metered air stream and further diluted with air to the required concentration. Atmospheres of methylmercury dicyandiamide were prepared in a similar manner. Vapour saturation techniques were used for other mercurials. A slow stream of air was passed through diethylmercury and the vapour diluted to the required concentration with a secondary air supply. For ethylmercury phosphate, heated air was passed through the powder sandwiched between two glass-fibre pads and the vapour diluted with air. Atmospheres of diphenylmercury were generated by passing air through a suspension of the solid on kieselguhr, maintained at a constant temperature, and diluting with air to the required concentration.

Calibration—The atmospheres of ethylmercury chloride, ethylmercury phosphate and diphenylmercury were calibrated by collecting 5 μg of mercurial as mercury in a high rate Greenburg - Smith impinger containing acid permanganate solution,[3] and determining the mercury by an absorptiometric dithizone method based on that described by Sandell.[9] It was necessary to allow ethylmercury phosphate to remain in contact with the acid permanganate solution for half an hour after collection to obtain complete recovery of mercury. Atmospheres of methylmercury dicyandiamide failed to react with acid permanganate solution to any significant extent. The mercurial was therefore collected in water, in which it is soluble, and extracted by passing the aqueous solution through a glass-fibre pad impregnated with cadmium sulphide.[3] The pad was then dried with ethanol and pyrolised in a silica tube in a current of air. The mercury vapour thus produced was collected in acid permanganate solution and the mercury determined absorptiometrically as before. Atmospheres of diethylmercury also failed to react with acid permanganate solution; they were calibrated by pyrolysis in a silica tube and the mercury vapour produced was determined by means of an ultraviolet mercury-vapour detector.

RECOVERY OF MERCURIALS AT THE IGNITION STAGE—

In both of the proposed methods an ignition stage is used in which the mercurial is decomposed to mercury and subsequently determined by the colour produced by mercury vapour on selenium sulphide test-papers. Confirmation was sought that the ignition stage of the procedure afforded complete recovery of the mercurials trapped either on active carbon or on a cadmium sulphide pad.

Aliquots of mercurials containing 5, 10 and 20 μg of mercury in water or aqueous ethanol were added to 0·75 g of active carbon, heated to redness in a silica tube (Institute of Petroleum Standards for Petroleum and its Products 63/55, Tube Type 1) in a stream of air, and the mercury vapour produced was collected in acid permanganate solution (Fig. 1). The mercury was then determined by a dithizone procedure as previously described.

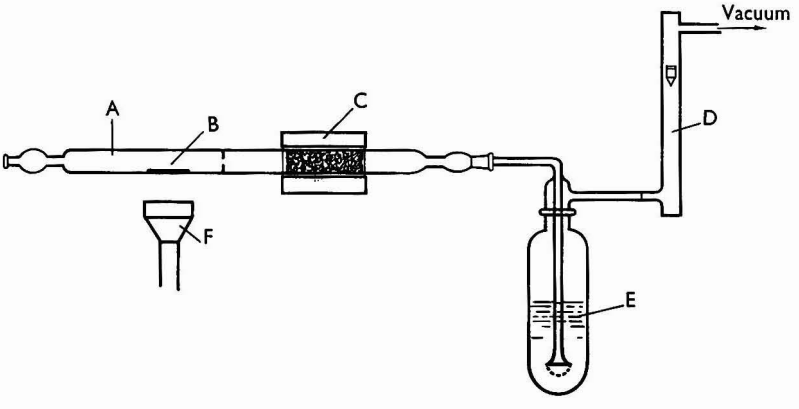
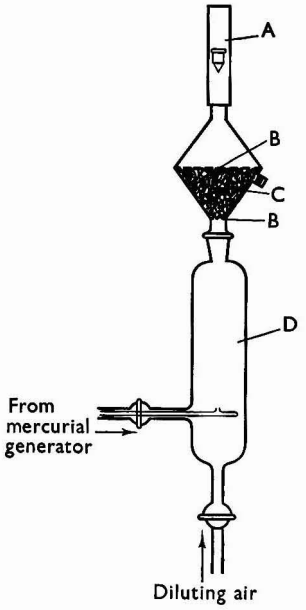


Fig. 1. Recovery of mercury from active carbon or cadmium sulphide pad



A = Flow-meter
B = Stainless-steel gauze
C = Fluidised carbon
D = Mixing chamber

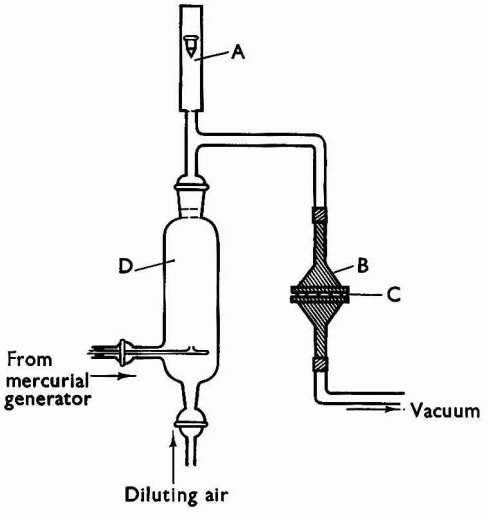
Fig. 2. Collection of mercurial vapours on active carbon

Percentage recoveries of mercurials from active carbon are as shown—

Mercurial	DPM	EMC	EMP	MMDD
Recovery, per cent. ..	80	90 to 95	95 to 100	95

For the purposes of a rapid field test these recoveries were considered to be acceptable.

In a similar way the recovery of mercurials added to active carbon or a cadmium sulphide pad was determined by using the ignition conditions recommended by Sergeant, Dixon and Lidzey,[2] and comparing the colours produced on selenium sulphide test-papers with a range



A = Flow-meter
B = Stainless-steel holder
C = Cadmium sulphide pad
D = Mixing chamber

Fig. 3. Collection of mercurial vapours on a cadmium sulphide pad

of standard colours equivalent to 25, 50, 100 and 200 μg of mercury per cu. m of air.[10] Results obtained by this method agreed with those obtained by the dithizone procedure within the limits imposed by the increments of the range of standard colours.

RECOVERY OF MERCURIALS FROM ATMOSPHERES OF KNOWN COMPOSITION—

Mercurials were collected on active carbon and cadmium sulphide pads from atmospheres prepared and calibrated as previously described, with the apparatus shown in Figs. 2 and 3. Sampling rates of 50 litres per minute for 10 minutes, and 33·3 litres per minute for 15 minutes, respectively, were used for the two procedures. For the latter the flow-rate through the apparatus was 50 litres per minute, of which 33·3 litres per minute passed through the cadmium sulphide pad. The amount of mercurial collected was determined by transferring the carbon or cadmium sulphide pad to the ignition tube and comparing the colour produced on selenium sulphide test-paper with the range of standard colours. This value was then related to the amount of mercurial present in the air sample, which had been calculated from the air flow-rate and the known concentration of the mercurial in the calibrated atmosphere.

The results obtained for EMC, DEM, DPM and MMDD at 5, 10 and 20 μg of mercury per cu. m of air by the fluid-bed technique, with active carbon as absorbent, were in good agreement with the calculated values. This also applied to EMP up to 15 μg per cu. m, above which it was difficult to generate atmospheres. Similar results were obtained for these mercurials by the cadmium sulphide method, with the exception of diethylmercury which had a collection efficiency no greater than 20 per cent. of that attained by using the fluid-bed method. A typical set of results is shown in Table II.

TABLE II

RECOVERY OF ETHYLMERCURY CHLORIDE FROM ATMOSPHERES OF KNOWN COMPOSITION, CONCENTRATION AS μg OF MERCURY PER CU. M OF AIR

Standard atmosphere	Fluid-bed method	Standard atmosphere	Cadmium sulphide method
6	6	5	5
	5		
	5·5		
10	10	9	10
	10		10
			10
13	14	13	13
	13		
20	18	20	19
	18		

PROPOSED FIELD METHODS FOR ORGANOMERCURY COMPOUNDS

COLLECTION OF SAMPLE BY THE FLUID-BED TECHNIQUE

APPARATUS—

Fluid-bed apparatus—This was designed to operate between 20 and 50 litres per minute, as described by Lidzey and Longmaid.[3] A silica-gel filter was used for moisture removal.

REAGENT—

Active carbon—Heat active carbon, Ultrasorb S.C. II, 50 to 100 mesh (British Carbo Norit Union Ltd.), at 600° C for 2 hours and cool in a desiccator. Store in a closed container.

PROCEDURE—

Place 0·75 g of active carbon in the absorber unit of the apparatus and pass 500 litres of air through the carbon at a rate of 50 litres per minute, *i.e.*, for 10 minutes. To remove any excess of moisture that may have been absorbed by the active carbon, place the silica-gel filter in the filter holder and pass air through the carbon at a rate of 20 litres per minute for 1 minute. Remove the carbon from the absorber unit in readiness for the determination of mercury.

Collection of sample with a cadmium sulphide pad

Apparatus—

Filter holder—This is for use with 7-cm diameter cadmium sulphide pads. A suitable holder is obtainable from M.P.C. Ltd., Montgomery Street, Birmingham.

Pump and flow-meter assembly—An assembly suitable for aspirating at a rate of 33·3 litres of air per minute through the prepared pad is required.

Cadmium sulphide pads—Slide a glass-fibre filter, Whatman GP/A, 7 cm in diameter, into a 2 per cent. aqueous solution of cadmium acetate. After immersion for 2 minutes withdraw the filter and remove the excess of solution between two pieces of filter-paper. Invert the filter and slide it into a 2 per cent. aqueous solution of sodium sulphide. After immersion for 2 minutes withdraw the filter, remove the excess of solution between filter-papers, invert the paper and repeat the treatment with cadmium acetate solution. Wash the filter on a Buchner funnel with water and dry it in an oven at 100° C for 1 hour, away from chemical fumes. Store the prepared pads in a closed container.

Procedure—

Place a cadmium sulphide pad in the filter holder and connect it to the flow-meter and pump. Draw 500 litres of air through the pad at a rate of 33·3 litres per minute, *i.e.*, for 15 minutes. Remove the pad from the holder and fold it in readiness for the determination of mercury.

Determination of mercury

Charge the ignition tube as described by Sergeant, Dixon and Lidzey[2], substituting either the active carbon or the folded cadmium sulphide pad for the iodised carbon and omitting the mineral-wool. Heat the ignition tube in the prescribed manner and complete the determination of mercury by comparing the colour produced on selenium sulphide test-paper with the standard colour chart that is available.[10] The result, when divided by 10, will give μg of organomercurial, as mercury, per cu. m of air.

Effect of humidity—

Neither method is affected by atmospheres within the normal range of humidity found in this country. At higher humidities, water vapour absorbed by active carbon results in the formation of blurred stains on the selenium sulphide test-papers and so causes serious interference. This can be readily overcome, without significant loss of mercurial, by passing 20 litres of dry air in 1 minute through the carbon, before transferring it to the ignition tube. The cadmium sulphide method is affected in the same way only at exceptionally high humidities which are unlikely to be encountered in practice.

Scope and applications—

The fluid-bed method with active carbon as absorbent is applicable to the determination in air of the vapours of the following organomercury compounds at concentrations in the region of 10 μg of mercury per cu. m: ethylmercury chloride, ethylmercury phosphate, diethylmercury, diphenylmercury and methylmercury dicyandiamide. Other mercurials would probably also be included.

The cadmium sulphide method is applicable to the same range of organomercurial vapours with the exception of diethylmercury. Neither method is capable of determining mercury vapour in air because of the low collection efficiencies of about 4 per cent. or less. However, if iodised carbon[2] is used as absorbent in place of active carbon in the fluid-bed method, mercury vapour can be determined satisfactorily.

Although fluid-bed techniques are unlikely to be of value in collecting mercury-bearing dusts, tests performed by the Ministry of Defence, Chemical Defence Experimental Establishment, Salisbury, have shown that penetration by methylene blue and sodium chloride aerosols (of mass median diameter 0·6 μ) of glass-fibre pads, before and after treatment with cadmium sulphide, is between 0·05 and 0·1 per cent. It was concluded from this observation that cadmium sulphide pads would be satisfactory for trapping mercury-bearing dusts.

As the methods described above are capable of distinguishing between various forms of mercury, an assessment of the relative concentrations of organomercurial vapour, mercury vapour and mercury-bearing dust in a mixed atmosphere should be possible. For example,

if such a mixed atmosphere were examined in turn by (*a*) the fluid-bed method with active carbon as absorbent, (*b*) the same technique with iodised carbon as absorbent and (*c*) the cadmium sulphide method, it would be expected that the organomercurial vapours would be represented by (*a*), mercury vapour by (*b*)–(*a*) and mercury-bearing dusts by (*c*)–(*a*). This, however, has not yet been demonstrated experimentally.

This work was carried out on behalf of the Ministry of Labour Committee on Tests for Toxic Substances in Air. We are grateful to the Government Chemist for permission to publish this paper.

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The Determination of Warfarin in Animal Relicta

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A method is described for the quantitative analysis of warfarin in animal relicta. Basically the method consists in the extraction of relicta, column clean-up of the extract, separation of the warfarin by thin-layer chromatography, elution from the layer and spectrophotometric assay at 305 mμ.

Warfarin, the recommended British Standard name for 3-(acetonylbenzyl)-4-hydroxycoumarin, has been in use both as a rodenticide and for human therapy for many years. The need for a sensitive and specific method for detecting warfarin in biological material has long been apparent.

The assay of warfarin present in rodenticidal baits was first reported by La Clair,[1] but in this and subsequent papers[2,3,4] no general method was completely satisfactory. Garner[5,6] has described a method for detecting the presence of warfarin in post-mortem material, but like Pyöralä[7] we have been unable to apply this quantitatively. Similarly, the method suggested by Wanntorp[8] has been found reliable only with fresh relicta, otherwise high blank values are encountered, and these cannot be allowed for by the method described. O'Reilly, Aggeler, Hoag and Leong[9] have described a method for determining warfarin in human plasma but this has not been found suitable for low levels of warfarin owing to difficulties with emulsions. No sensitive colour reactions specific for warfarin appear to be known. The 2,4-dinitrophenylhydrazone can be prepared from warfarin, but once a fairly pure tissue extract has been prepared there is no advantage over a direct spectrophotometric determination. Investigation of the reaction between the carbonyl group and *m*-dinitrobenzene were not pursued as the colour produced was not significantly different from the reagent blanks. The oxidation of warfarin with alkaline potassium permanganate gives a carboxylic acid, 3-(α-carboxybenzyl)-4-hydroxycoumarin, but in such poor yield as to be of low value analytically. The gas - liquid chromatography of warfarin has been described[10] but the method is rather insensitive.

Experimental

It was considered that the best results would be obtained from a method dependent on the isolation of warfarin followed by spectrophotometric measurement, rather than on a more chemical approach. Various ways of isolating warfarin from biological tissues by using ion-exchange resins, paper electrophoresis and column and thin-layer chromatography have been investigated.

Ion-exchange resins—

Warfarin is taken up by De Acidite FF in the OH^-, Cl^-, HCO_3^- and HSO_3^- forms; De Acidite G in the OH^- and Cl^- forms; and De Acidite E in the OH^- form.

It was found to be extremely difficult to elute warfarin from any of these, except De Acidite FF, in which case it was found that boiling with a 1 per cent. solution of sodium hydroxide was effective. Elution with methanolic ammonium chloride, as described in British Patent specification 881,855, gave variable recoveries and introduced the additional problem of isolating the warfarin from a large volume of eluate.

Paper electrophoresis—

Warfarin will move 5 cm in 4 hours in a borate buffer of pH 9 with a potential gradient of 10 volts per cm with Whatman 3MM paper. It is then possible, by viewing the paper under ultraviolet light of 254 mμ, to cut out the band containing the warfarin. This paper strip is then pulped and the warfarin eluted with a 1 per cent. sodium pyrophosphate solution. After acidification with 5 N hydrochloric acid and extraction with chloroform, the compound is recovered by removing the solvent on a steam-bath, and after dissolution in isopropyl alcohol containing 1 per cent. of acetic acid the extinction is determined at 305 mμ. This solvent,

first suggested by Armstrong,[11] has been found to be more specific and subject to less interference than either sodium hydroxide or sodium pyrophosphate solutions. One of the difficulties of this method is in deciding on the width of the band to be removed from the electrophoretogram; the wider the band the more interfering substances are removed; the narrower the band the lower the recovery of warfarin. Recoveries from pig's liver have been in the range of 65 to 85 per cent., and subject to wide variation.

COLUMN CHROMATOGRAPHY—

Several absorbents for column clean-up of extracted material have been tried. Florisil showed a batch-to-batch variation even when the pre-treatment was standardised, and alumina gave consistently low recoveries. Untreated silica gel gave little clean-up, but it was found that by activating the gel at 120° C for 16 hours and subsequently adding 15 per cent. w/w of water, a product was obtained that gave sufficient clean-up to avoid emulsion formation at the later stages of the analysis without reducing the recovery.

A further reduction in the proportion of total solids in the extract is brought about by extraction of the eluate from the column with a 1 per cent. sodium pyrophosphate solution, which is then acidified and the warfarin transferred into chloroform. This solution is suitable for the separation of warfarin by thin-layer chromatography on kieselgel plates. Recovery experiments of pure warfarin from thin-layer plates are given in Table I.

TABLE I

RECOVERY OF WARFARIN FROM THIN-LAYER PLATES

Warfarin added, μg	Warfarin recovered, μg	Mean recovery, per cent.
126	117	92·6
86·6	82·3 81·4	94·5
56·3	49·1 48·5	86·9
30·6	26·2 27·2	87·4
18·1	14·9 17·8	90·1

METHOD

The method consists in the extraction of relicta by ether, column clean-up of the extract, purification of the eluate by chloroform partition, separation of the warfarin by thin-layer chromatography, elution from the layer and spectrophotometric assay at 305 mμ.

APPARATUS—

M.S.E. Homogeniser—Catalogue No. 7700. This is fitted with a 100-ml beaker.

Quickfit and Quartz liquid - liquid extraction unit—Catalogue No. EX9/33. This is fitted with sintered-glass distributor EX9/30S.

Glass tubes for chromatography—Aimer. Catalogue No. AGG/type F of 1-cm diameter and 30 cm long.

Spectrophotometer—Hilger Uvispek, type 700H.

Ultraviolet light source—Hanovia Chromatolite, 254 mμ.

Thin-layer spreading apparatus—Suitable for the preparation of thin-layer plates (10 × 20 cm) with a layer thickness about 250 μ.

Pasteur long-form pipettes.

REAGENTS—

All materials should be of analytical-reagent grade.

Ethyl acetate.

Diethyl ether, peroxide free—Diethyl ether is washed with concentrated iron(II) sulphate solution, followed by 0·5 per cent. potassium permanganate solution and 2 N sodium hydroxide solution. It is then dried over calcium chloride and redistilled.

Isopropyl alcohol containing 1 per cent. of acetic acid.

Hydrochloric acid, 5 N.

Sodium pyrophosphate solution, 1 per cent. in water.

Celite 545—Obtainable from Johns-Manville Co. Ltd.

Silica gel—Hopkins and Williams, M.F.C. grade. Prepared by heating at 120° C for 16 hours, then adding 15 per cent. w/w of water and shaking the mixture for 3 hours.

Sodium sulphate, anhydrous.

Chloroform.

Kieselgel *~~Kieselguhr~~ GF254*—Available from E. Merck, Darmstadt.

Mobile solvent for thin-layer chromatography—Diethylether - hexane - acetic acid, 75 + 25 + 1 (v/v).

PROCEDURE—

Macerate 6 g of tissue with 30 ml of water and transfer the suspension with washing to the liquid - liquid extraction unit. Add 5 ml of 5 N hydrochloric acid and extract the mixture with ether for 45 hours. Fill a chromatographic column with ether and add 1 g of Celite 545. Allow the mixture to settle on the sinter and pour a suspension of 9 g of the prepared silica gel in the minimum volume of ether on to the top of the column and assist the gel to settle down by tapping the column. Cover the silica gel layer with a 3-cm layer of anhydrous sodium sulphate and allow the ether to drain to the upper surface of the column packing. Transfer the ether extract, reduced by distillation to not more than 5 ml, to the top of the prepared column and allow it to percolate into the column packing. Wash the distillation flask thoroughly with successive 10-ml volumes of ether, combine the washings and add them to the column; wash the column with sufficient ether to bring the total volume to 150 ml. Transfer the effluent to a separating funnel and extract with 15-ml and 10-ml volumes of sodium pyrophosphate solution. Combine the alkaline extracts acidified with 3 ml of 5 N hydrochloric acid and extract with two 10-ml aliquots of chloroform. Combine these extracts and evaporate them on a water-bath to less than 1 ml.

Prepare thin-layer chromatographic plates by suspending 30 g of ~~Kieselguhr~~ Kieselgel GF254 in 63 ml of water, shake the mixture vigorously for 30 seconds and apply to 10 × 20-cm plates in a conventional way to give a layer about 250-μ thick. Allow the layer to set and dry in an oven at 110° C for 30 minutes. Apply the concentrated chloroform extract to the layer as a streak (great care is needed at this stage to avoid losses). Develop the plate in the mobile solvent to 12 cm from the origin in a lined and sealed tank at ambient temperature. Allow it to dry, and locate the warfarin under ultraviolet light of wavelength 254 mμ; the R_F value is about 0·46. Firmly plug a Pasteur pipette with a small piece of cotton-wool and rinse it with ethyl acetate. Transfer the warfarin band to the pipette and elute the warfarin with not less than 8 ml or more than 10 ml of ethyl acetate. Collect the eluate in a test-tube and evaporate to dryness over a water-bath. Dissolve the residue in 5 ml of isopropyl alcohol - acetic acid mixture and read this solution on the spectrophotometer at 305 mμ in a 1-cm cell against a solvent blank. The $E^{1\%}_{1cm}$ value for warfarin in this solvent at a wavelength of 305 mμ is 361.

RESULTS

In preliminary investigations with the liver from several animal species the interfering substances from pig's liver have caused more trouble than any other. As most of our field samples have involved this animal, it was selected for determining recovery values. Blank

TABLE II

RECOVERY OF WARFARIN FROM LIVER

Warfarin added, μg	Warfarin recovered, μg	Mean recovery, per cent.
128	125	96·9
	123	
	124	
56·3	44·6	78·2
	41·7	
	45·7	
	44·3	
30·6	22·7	79·8
	24·1	
	24·5	
	26·3	
18·1	15·6	84·0
	14·7	
	16·1	
	14·8	

values on reagents are equivalent to 0·48 p.p.m., expressed as warfarin. Blank values have been determined on three different samples of liver, and 12 determinations gave a mean optical density of 0·040 and standard deviation of ±0·014, equivalent to 0·92 p.p.m. of warfarin. Recovery experiments at four levels are given in Table II. These values are corrected for a liver blank of 0·44 and a reagent blank of 0·48 p.p.m. of warfarin.

We thank Dr. H. G. Dickinson, of Ward, Blenkinsop & Co. Ltd., for several interesting discussions, and Miss M. R. Boulton for invaluable technical assistance.

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The Use of Iron (II) Sulphate for the Reduction of Nitrate to Ammonia in the Microdiffusion Method for Determining Nitrate in Soil Extracts

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Because of the variable nature of technical titanium(III) sulphate normally used for the determination of nitrate in soil extracts by the Bremner - Shaw microdiffusion method, the possibility of replacing this reagent with iron(II) sulphate was studied. It was found that 1 ml of M iron(II) sulphate (in 0·5 M sulphuric acid) *plus* 0·1 ml of saturated silver sulphate could be used to successfully determine up to 200 μg of nitrate nitrogen in 5-ml aliquots of soil extracts.

The use of titanium(III) sulphate with magnesium hydroxide suspension for the simultaneous reduction of nitrate, and its determination as ammonia in soil extracts when using a microdiffusion method, has been described by Bremner and Shaw.[1] Bremner[2] developed the method by using steam-distillation instead of microdiffusion to drive off the ammonia.

The technical titanium(III) sulphate solutions available often give high blank values for ammonia and tend to lose their nitrate-reducing ability, even when stored in a refrigerator. Bremner and Shaw[3] found that nitrate was quantitatively reduced to ammonia during steam-distillation with iron(II) hydroxide (iron(II) sulphate with excess of magnesium hydroxide), providing the iron(II) concentration in the distillation flask exceeded 7 g per litre.

Steam-distillation with alkali may cause hydrolysis of organic nitrogenous compounds usually present in soil extracts, thus giving high values for ammonia and also for nitrate, when this is being determined simultaneously by reduction. Because of this, the ability of iron(II) hydroxide to reduce nitrate to ammonia at room temperature in the Bremner - Shaw microdiffusion cells was studied.

Experimental

Preliminary tests were made with pure nitrate solutions by using various concentrations of added iron(II) sulphate (analytical-reagent grade) and excess of light magnesium oxide suspensions. When 5 ml of nitrate solution, 1 ml of M iron(II) sulphate (in 0·5 M sulphuric acid) and 3 ml of 12 per cent. w/v light magnesium oxide suspension were used in the outer chamber, there was always complete recovery of up to 100 μg, but not of 200 μg, of nitrate nitrogen as ammonia in the central chamber when using the normal 48-hour diffusion period. The use of 2 ml, instead of 1 ml, of M iron(II) sulphate sometimes gave incomplete recovery of even 100 μg of nitrate nitrogen, presumably owing to the restriction of diffusion of ammonia through the immobile gel of iron and magnesium hydroxides. However, it was found that the use of a silver catalyst[4] increased the amount of nitrate that could be recovered as ammonia, even when using 1 ml of M iron(II) sulphate. The use of 1 ml of M iron(II) sulphate, 0·1 ml of saturated silver sulphate solution and 3 ml of 12 per cent. w/v light magnesium oxide suspension always gave complete recovery of up to 200 μg of nitrate nitrogen from 5-ml aliquots of test solution. It is worth noting that the minimum concentration of iron(II) sulphate required in the outer chamber for complete recovery of nitrate as ammonia is similar to that required in the distillation flask when using steam-distillation.[3]

The method was then tested on extracts of several soils. The extracting reagents used were (*i*) N sodium chloride and (*ii*) the "Morgan reagent" (0·5 N acetic acid - 0·75 N sodium acetate, pH 4·8). Ten grams of air-dried, 2-mm sieved soil were shaken with 20 ml of extracting reagent for various times and filtered. When using 5 ml of the extracts, the results obtained with iron(II) sulphate *plus* silver sulphate were almost identical with those obtained with titanium(III) sulphate (ammonia present was allowed for after determination on a separate aliquot by reaction with light magnesium oxide suspension). Both methods also gave 100 per cent. recovery of known amounts of nitrate nitrogen added to the extracts. When an unusually high amount of nitrate or ammonia, or both, is present in an extract, necessitating

the use of an aliquot of less than 5 ml, water should be added to the outer chamber to dilute the aliquot to 5 ml before adding the other reagents.

Conclusions

One millilitre of M iron(II) sulphate (in 0·5 M sulphuric acid) *plus* 0·1 ml of saturated silver sulphate can be used instead of titanium(III) sulphate for the determination of up to 200 μg of nitrate nitrogen in 5-ml aliquots of soil extracts by using the Bremner - Shaw micro-diffusion cells. Iron(II) sulphate has the following advantages over technical titanium(III) sulphate: it is of constant quality; it is stable for at least 2 months when kept in a well stoppered bottle at 2° to 4° C; and it gives a low blank value for ammonia.

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A Simple, Rapid Method for Determining Glucose in Blood or Plasma

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HULTMAN[1] studied the reaction between sugars and aromatic amines, which yields coloured azomethines. Hyverinän and Nikkilä[2] devised a method for determining glucose in blood by using orthotoluidine and stabilising the reagent by adding thiourea; the present note describes a modification of their method, with a further simplification when applied to plasma. Dubowski[3] has reported on the specificity of the method; the reaction involves the aldehyde group, and other reducing substances do not interfere. Although other sugars react, they either do so to a lesser extent, or absorb at a different wavelength; in the absence of galactose the method can be regarded as virtually specific for glucose when applied to blood or plasma, and it gives about the same range of normal values as the enzyme methods, or the more specific of the copper methods.

EXPERIMENTAL

REAGENTS—

Methanol - thiourea—Saturate 100 ml of methanol by adding 10 g of thiourea; shake the solution well, and allow to settle.

Orthotoluidine.

Glacial acetic acid, AnalaR.

Colour reagent—Dilute 30 ml of saturated thiourea solution and 60 ml of orthotoluidine to 1 litre with glacial acetic acid. Prepare the solution 24 hours before use; the reagent can be dispensed from a "Zipette" (Jencons). It is stable for at least 2 weeks at room temperature.

Glucose solution—Dissolve 50, 100 and 250 mg of dried glucose in saturated benzoic acid solution and make each solution up to 100 ml with the benzoic acid solution.

Trichloroacetic acid—Dissolve 3 g of trichloroacetic acid in 100 ml of water.

PROCEDURE—

Plasma—Separate plasma from blood preserved with fluoride by lightly spinning the mixture in a centrifuge for 2 to 3 minutes. If the specimen is grossly haemolysed, treat it as for whole blood. Place 4 ml of the colour reagent in a series of tubes (6 × $\frac{5}{8}$ inches). Add 0·05 ml of plasma or standard (with no addition for the blank), mix, place in a boiling water bath for 5 minutes, then cool the solution. Measure the optical density at 640 mμ within 30 minutes; calculate the glucose content by proportion.

Whole blood—Place 1·5 ml of 3 per cent. trichloroacetic acid in a centrifuge tube; add 0·1 ml of whole blood, or 0·1 ml of standard. Mix the solutions and spin them in a centrifuge for 5 minutes at about 1500 r.c.f. Place 4 ml of colour reagent in a tube (6 × $\frac{5}{8}$ inches), add 1 ml of supernatant liquid and mix; heat in a boiling water bath for 5 minutes, and measure the optical density at 640 mμ within 30 minutes; calculate the glucose content by proportion.

The extra water in the second procedure diminishes the colour yield, so the standards read lower. The methods have been in trouble-free use for over 1 year. The reaction does not appear to measure some hexose - phosphates, therefore stored fluoride blood may give low values on the red cell fraction. High colours can be measured by diluting with a further 4 ml of reagent, with no extra heating; the readings were linear up to 1000 mg per 100 ml.

NORMAL VALUES—

The mean and standard deviation for this method are as follows—

Plasma—Males, fasting: 101 ± 12 mg; males, random: 129 ± 13 mg; females, fasting: 102 ± 13·5 mg; and females, random: 119 ± 19 mg.

Whole blood—Males, fasting: 91 ± 12 mg; males, random: 118 ± 13 mg; females, fasting: 92 ± 13·5 mg; and females, random: 108 ± 19 mg.

I thank the Research Committee of the East Anglian Regional Hospital Board for the use of a printing calculator in connection with the statistical work involved.

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A Simple Device for Transferring Gases Evolved at Low Pressure to a Gas Chromatograph

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When using in this laboratory some 4 years ago a technique similar to that described by Lilburne[1] for the gas-chromatographic analysis of gases extracted from metals by vacuum fusion, the same problem was faced of quantitatively transferring gases evolved from a low pressure system to one involving a flowing carrier gas at atmospheric pressure. This problem was overcome in a simple way by using the specially made glass stopcock* shown in Fig. 1, which, it is thought, may be of interest to other workers.

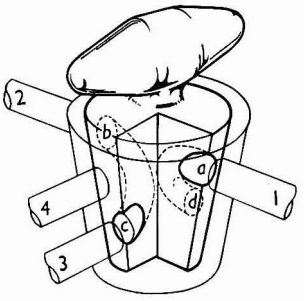

Fig. 1 Cut-away view of stopper

The hollow-blown key has two curved bores (about 3 mm i.d.) labelled *a*, *d*, *c* and *b*. Side-arm 1 consists of an 8-inch length of 3-mm standard bore tubing and constitutes the upper limb of a normal Toepler pump. The remaining side-arms are constructed from normal 3-mm bore tubing. Helium carrier flows in the direction 3, *c*, *b*, 2. Side-arm 4 is permanently connected to the vacuum backing-line. Both curved bores are calibrated so that the amount of gas collected in the volume between *a* and *d* is immediately known from the Toepler pump readings. Rotation through 180° in an anti-clockwise direction transfers the gas sample to the helium carrier. The second bore has meanwhile been emptied of helium by passing side-arm 4 on its way round to side-arm 1.

Operation of the Toepler pump in the normal way permits the selection of different proportions of the total gas mixture evolved and the transfer of various amounts as samples for the chromatographic analysis, without the need for intermediate storage bulbs. The volume of the gas sample for analysis can thus be adjusted to the requirements of the ionisation detector on the one hand, and those of the original metal specimen on the other. Rapid repetitive sampling is possible, and as the gas-chromatographic analysis is virtually automatic, full attention can be given to the vacuum fusion operations.

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* Constructed for the British Welding Research Association by A. D. Wood Limited, London.

An All-plastic Suction Funnel

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For the gravimetric determination of silica as potassium silicofluoride it was necessary to collect the precipitate in apparatus unaffected by hydrofluoric acid. A suitable funnel, in which some of the disadvantages of normal filtration apparatus are avoided, was cheaply and easily constructed by using the upper half and the cap of a polypropylene bottle.

Holes (1 to 2 mm in diameter) were bored in the top of the cap, and a disc of porvic* (0·75-mm

* Porvic is a permeable material of fine and uniform porosity made from poly(vinyl chloride); Grade M has a pore size of 5μ and Grade S of 12μ. Available from Porous Plastics Ltd., Dagenham Dock, Dagenham, Essex.

thick) was cut to fit closely the inside of the holed surface. The cap was screwed into position on the upper half of the bottle locking the porvic disc between the cap and the top of the neck. The funnel was used with a Buchner flask and a conventional adaptor. To eliminate the problem of static electricity associated with the weighing of plastic materials a hygrostat was used instead of a desiccator.

Precipitates do not seep under the porvic disc, and when the disc is wetted before filtration no supernatant liquid is held against washing in the periphery of the disc. Chemicals that attack glass can be used, and cleaning is simplified by replacing the porvic disc.

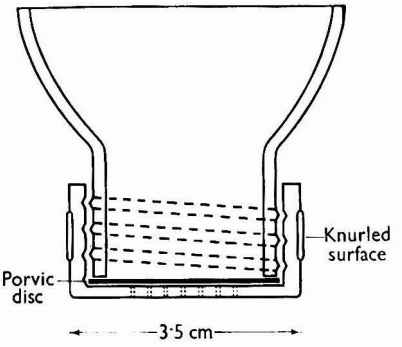

Fig. 1. Details of the funnel

The funnel, illustrated in Fig. 1, weighs 8 g and has an effective filter area of 5·7 cm².

To check thermal stability a funnel fitted with a porvic disc was heated at 60° C for varying lengths of time up to 16 hours, and then weighed after standing in a hygrostat at 75 per cent. relative humidity for 1 hour. The maximum change in weight was 40 μg.

For gravimetry the drying temperature is restricted to 60° C, but many gravimetric precipitates can be dried to constant weight at, or below, this temperature[1]; porous Teflon with a funnel of Teflon or fluorinated ethylene - propylene would allow higher temperatures to be used.

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Effect of Impurity in Dichloroethane Solvent on the Determination of Boron with Methylene Blue

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(*Research Department, Murex Ltd., Rainham, Essex*)

DURING an investigation into the spectrophotometric determination of boron in niobium oxide, an attempt was made to extract the fluoroborate - methylene blue complex by using a technique based on published work[1] devised for the determination of boron in steel.

After certain preliminary difficulties had been overcome an accurate and precise method was developed, but this subsequently appeared to give incomplete recovery of boron when applied by another analyst.

The errors were traced to a batch of dichloroethane, which presumably contained an impurity that decreased the solubility of the boron complex at the solvent-extraction stage.

If viewed through a sufficient depth of solvent (about 2 inches) a slightly yellowish tint could be detected in the impure solvent. The effectiveness of the solvent was restored by washing it with small portions of sodium hydroxide, until the latter was colourless. Excess of alkali was removed by washing with dilute sulphuric acid and then water.

REFERENCE

1. Pasztor, L., Bove, J. D., and Fernando, Q., *Analyt. Chem.*, 1960, **32**, 277.

Received *January 13th*, 1967

Book Reviews

STANDARD METHODS OF CHEMICAL ANALYSIS. Sixth Edition. Volume III—Instrumental Methods, Parts A and B. Edited by FRANK J. WELCHER, Ph.D. Pp. xviii + 973 (Part A); Pp. xii + 2018 (Part B). Princeton, New Jersey, Toronto, London and New York: D. Van Nostrand Co. Inc. 1966. Price single volume £18 18s. If part of complete set £16 16s.

The extent to which analytical chemistry has expanded since "Scott" made its first appearance in 1917 is shown by the size of this present edition, which now comprises five books, over 6000 pages, and literally hundreds of diagrams.

Originally, the publication aimed at providing analytical chemists, irrespective of their specialised interests, with a collection of methods that had been well tried and authoritatively approved, hence in previous editions, and also in Volumes I and II of this edition, methods are regarded as standard if they meet this criterion.

Over the intervening half century, analytical chemistry has undergone radical changes, its scope and importance have increased, and the field of chemical analysis has become even more specialised. To keep pace with these changes, and to continue to provide the analyst with a reliable source of collated information, it is understandable that the prime objective of "Standard Methods of Chemical Analysis" has been extended to include instrumental methods, many of which do not meet the earlier requirements of a *standard* method. This clearly recognises the present-day importance and potential usefulness of instrumental techniques, and the ever-growing importance of instrumental analysis, in its current context, in all branches of analysis. It is logical, therefore, and timely with the appearance of these two volumes, that an authenticated appraisal of established instrumental analytical procedures should be made available to the analyst, so that *standard* methods may be supplemented, if not replaced, at his discretion.

Part 1 of Volume IIIA contains forty-three chapters devoted to such subjects as Visible, Ultraviolet, Infrared, Raman, Atomic Absorption, and Emission Spectrometry, Electron Microscopy, Potentiometric, Amperometric and Conductometric Titrations, Coulometric and High-frequency Methods, . . . Particle Size Analysis. Each of the chapters is covered in comprehensive detail, and, like the other chapters in these volumes, all were prepared by experts in their specialised fields.

The remaining five chapters of Volume IIIA (Part II) deal with Instrumental Methods for Industrial Products and Other Special Substances, under the headings, Air Pollutants, Alloys: Iron, Steel, Ferro-Alloys and Related Products, Alloys; Nonferrous, Amino Acid Analysis and Portland Cement.

In Volume IIIB, the application of instrumental methods of analysis to Clinical Medicine, Natural Fats, Fertilizers, Foods, Organic Functional Groups, Glass, Paint, Varnish and Lacquers, Paper, Wood and Pulp, Pesticide Residues, Petroleum, Plastics, Rubber, Semi-Conductors, Detergents, Soils, and Water is described. Naturally, with each chapter written by a different author, the treatment is somewhat varied, but this in no way detracts from their value. Some chapters are fairly comprehensive compilations of official or near-official methods; others are personal selections of non-standard methods that are in day-to-day use, and, in some respects, these have a special value.

In total, these two volumes are an impressive accumulation of information, which the good indexing makes readily available.

With the publication of these two volumes, the sixth edition of this book is complete. It must surely rest within the grasp of every analyst, to be turned to like a good friend, for confirmation of one's own thoughts, for advice—or at times in sheer desperation!

W. T. ELWELL
J. F. HERRINGSHAW

ANALYTICAL CHEMISTRY OF COBALT. By I. V. PYATNITSKII. Pp. xvi + 224. Jerusalem: Israel Program for Scientific Translations. Distributed in Great Britain and the Commonwealth, South Africa, Eire and Europe by the Oldbourne Press, London. 1966. Price 87s. 6d,

Like previous monographs in this series, some of which have been reviewed in *The Analyst*, this is a translation of the original publication by the Institute of Geochemistry and Analytical Chemistry, U.S.S.R., and already about twelve of the series have either been translated, or are in the process of being translated, for publication in English.

These monographs on the analytical chemistry of individual elements will vary in their appeal, depending on the needs of the individual, but more especially on the availability of similar current publications. For this reason only, it is doubtful whether this latest monograph will have the same appeal outside the U.S.S.R. as the earlier members of the series, because of the recent appearance of an English publication under precisely the same title. (Reviewed in *Analyst*, **1966**, **91**, 754.) It would be improper to compare the relative merits of these two books here, but clearly, the contents of each overlap considerably.

This book is devoted almost exclusively to the known chemical reactions of cobalt up to 1963. In addition to nearly 400 Russian references, it contains over 1000 non-Russian references, but of these, a rough assessment indicates that only about half are readily accessible to the average reader.

The book provides a comprehensive coverage of the subject within its declared objectives, *e.g.*, it does not claim to cover spectroscopic or X-ray analytical procedures, although some spectroscopic methods are given; one chapter (4 pages) is allocated to polarographic methods, and radioactivation methods are dealt with in six paragraphs.

This latest release provides a good companion to the earlier publications in the series.

W. T. ELWELL

ALFRED WERNER FOUNDER OF COORDINATION CHEMISTRY. By GEORGE B. KAUFFMAN. Pp. xvi + 127. Berlin, Heidelberg and New York: Springer-Verlag. 1966. Price DM 24.

Not so many years have elapsed since historical chemistry formed an integral and compulsory part of many degree courses. Students were enjoined to read some of the memorial lectures of the Chemical Society dealing with the lives and achievements of such early pioneers as Liebig, Avogadro or Baeyer. If such a stipulation still prevails, the present volume on Alfred Werner deserves to be included among the books for recommended reading. Having said this, despite a contrary statement by the author, it is unlikely to appeal to the general reader who has no particular interest in the stereochemistry of co-ordination compounds.

The author preserves a good balance between the biographical and scientific aspects of Werner's life, and makes no attempt to ignore his human failings. Thus there emerges a portrait of "der grosse Mann," the good-natured victim of buffoonery on social occasions but a stern taskmaster in the laboratory. As he gave of his utmost himself so he expected the same of others, and obviously did not suffer fools gladly.

The various phases in the emergence of the co-ordination theory as developed by Werner are well described, culminating in the optical resolution of a purely inorganic compound and the award of the Nobel Prize in 1913. Professor Kauffmann rightly stresses the importance of Werner's "Lehrbuch der Stereochemie," and his interest in the development of stereochemistry during his lifetime. This provided much of the basis for his conceptions of molecular structure, which were mainly intuitively conceived and, at best, of a semi-quantitative nature. Similarly, in his laboratory work, the simplest of equipment was used to produce the finest crystalline products, recalling the use of tannin by Dr. Schoeller in the analysis of mixtures of tantalum and niobium pentoxides.

To sum up, the book is well produced, and includes an extensive bibliography, a good index, and a particularly fine set of photographs illustrating the work of the master and his pupils. The price is not excessive as judged by present-day standards.

F. G. ANGELL

THE PHASE RULE. By F. D. FERGUSON, B.Sc., A.R.I.C., A.M.I.CHEM.E., and T. K. JONES, M.Sc., A.R.I.C. Pp. viii + 112. London: Butterworth & Co. (Publishers) Ltd. 1966. Price 15s.

This is a very useful little book, especially for students at the Higher National Certificate, Part I G.R.I.C., and Pass Degree levels. It deals with the essentials of the subject in a compact and readable form, and in many places gets away from the rather hackneyed examples that one all too often encounters in treatments of the phase rule.

It covers one-component systems, two-component systems (liquid - liquid, liquid - vapour, solid - liquid, solid - vapour, equilibria) and also gives a short account of three-component systems, including systems of three liquids, ternary eutectic systems and aqueous salt solutions. There is also a useful chapter on experimental methods related to most of the types of system treated in the earlier pages.

This book may also be recommended to those chemists who may be "out of practice" with the phase rule and are looking for a quick revision course.

S. J. GREGG

INTRODUCTION TO ELECTRON SPIN RESONANCE. By H. M. ASSENHEIM. Pp. viii + 200. London: Hilger & Watts Ltd. 1966. Price 42s.

This book is the first in a set of Hilger monographs on electron spin resonance and, as its title implies, it is an introduction to the subject. The second to be issued is reviewed below and forthcoming titles refer to special classes of materials and to instrumentation. These samples and the authorship of the future volumes suggest that the venture will be a useful one.

This particular work covers the entire subject and the balance of the different aspects seems just right. It is written from a fundamentally practical approach, but the theory is not neglected. Those seriously interested in the subject for the first time, including undergraduates, should find this account valuable. The style is generally clear and helpful, and a single rapid reading should leave a bird's eye impression of the field. This book is fairly reliable, although there are a few unfortunate errors. The subject is one that tends to lie between physics and chemistry, and readers trained in either discipline should profit equally. The research specialist will not find much that is novel or of great interest and must wait for the later, more advanced, volumes.

Readers of *The Analyst* will be aware that electron spin resonance is not a major tool in the analyst's locker. It is, however, almost essential on the rare occasion when the problem concerns free radicals in the solid or liquid state. It also has its place if weak concentrations of transition or rare-earth metal ions are significant. There are better ways of detecting such impurities, but in suitable cases electron resonance will identify the metal valency and the geometry of its surrounding co-ordinated ligands. Analysts who wish to learn more about the technique will find this account a good starting point and will certainly expect to find this book in their libraries.

D. H. WHIFFEN

ELECTRON SPIN RESONANCE IN SEMICONDUCTORS. By G. LANCASTER. Pp. viii + 152. London: Hilger & Watts Ltd. 1966. Price 42s.

This is the second published book in the series referred to in the last review. And as might be expected it is at a more advanced level suitable for research workers entering the field. Besides the specific electron resonance topics it forms a useful introduction with more general aspects of semiconductor theory. The main chapters concern both deep and shallow traps in silicon, germanium and III–V compounds and also defects introduced by radiation damage. The reviewer is not very knowledgeable in this detailed field and he found the ideas well presented at the level he would have chosen. There is sufficient mathematics to make a good introduction to research papers and an appendix on the Wannier functions.

A general analyst will seldom be called on to examine semiconductors. Those who do meet this problem will be aware that impurities have a major influence on the electrical properties. They should find food for thought in this book and be aware of the ability of electron resonance not merely to identify any paramagnetic impurity but also to give a detailed account of the electron distribution.

D. H. WHIFFEN

CHEMICAL STUDY OF SOME INDIAN ARCHAEOLOGICAL ANTIQUITIES. By SATYA PRAKASH and N. S. RAWAT. Pp. iv + 100. Bombay, Calcutta, New Delhi, Madras, Lucknow, London and New York: Asia Publishing House. 1965. Price 15s.

This monograph, issued under the auspices of the State Council of Scientific and Industrial Research of the Government of the State of Uttar Pradesh, presents the results of analyses carried out by the authors and other investigators on a wide range of Indian archaeological materials. The first two chapters are devoted to the analysis of ancient Indian mortars and plasters (mostly from Mohenjo-daro, Harappa and Kausambi) and ceramic materials, including glazes and pottery pigments. This is followed by a chapter in which the results of the analysis of glass objects excavated from various sites throughout India are discussed, and the last two chapters are concerned with the analysis of copper and bronze objects and ancient Indian coins.

This monograph is essentially a compilation of analytical results collected from many sources, and, as such, it is a convenient book of reference for the chemist who is interested in archaeology. Its value, however, would have been greatly increased if the authors had given some indication of the actual methods of analysis used, and had offered some critical comments about the methods of analysis and the problem of obtaining representative samples. Information of this kind is necessary if one wants to make valid comparisons of analyses made by different investigators.

The authors have rightly drawn attention to the fact that often there is a great need for further analytical work to be carried out on a systematic basis, before it will be possible to draw definite conclusions of archaeological significance about the composition of ancient Indian objects of different periods and from different localities. Nevertheless, these analytical results have led to some interesting tentative conclusions about the extensive use of lime plaster throughout ancient India, the development of the glazed-tile industry, and the origin of ancient glass at Taxila.

For certain Indian coins, the analytical results have been supplemented by metallographic examination. From these studies it was deduced that silver coins and bronze coins containing a high percentage of tin or lead had a cast structure, whereas copper coins showed evidence of an annealed and worked structure.

The monograph is well produced and reasonably free from misprints; it should, however, be noted that the columns for "grams" and "grains" in Table 6.2 (p. 69) have been reversed.

A. E. A. WERNER

TECHNIQUES IN FLAME PHOTOMETRIC ANALYSIS. By N. S. POLUEKTOV. Translated by C. NIGEL TURTON and TATIANA I. TURTON. Pp. xvi + 219. Princeton, New Jersey, Toronto, New York and London: D. Van Nostrand Company Inc. 1966. Price 40s.

Originally published in Russia in 1959, this work is a paperback reprint edition of the English translation that was first printed in the United States of America in 1961. The text falls into two distinct sections in which the first four chapters describe the fundamental principles of flame photometry, apparatus, factors affecting sensitivity and accuracy, and photometric measurements. The second section emphasises the practical aspects of flame photometry, and gives details for the determination of alkali, alkaline-earth metals, boron, aluminium, iron and manganese, etc., as applied to a wide range of materials. The book concludes with a useful appendix, in which wavelengths of the strongest spectral lines of various elements are given, and here an indication of the relative sensitivities would have been useful.

There have been several important developments in flame photometry since this book was first published, *e.g.*, the use of instruments that incorporate automatic background correction, and many elements are now determined with increased sensitivity after a preliminary extraction of the metal complex into an organic solvent, followed by direct aspiration of the extract into the flame.

The bibliography is extensive, and although most of the references are at least 10 years old, this is inevitable in a double publication such as this. The table of contents is reasonably detailed, but the addition of an index would have been useful.

Over-all, this volume gives a useful account of flame photometry, and should provide a basis for an understanding of the subject, bearing in mind its original date of publication. H. PUGH

THE ANALYSIS OF NICKEL. By C. L. LEWIS, W. L. OTT and N. M. SINE. Pp. x + 214. Oxford, London, Edinburgh, New York, Toronto, Paris and Braunschweig: Pergamon Press. 1966. Price 55s.

Although the literature contains many papers dealing with the determination of individual impurities in nickel, the only previous comprehensive compilations of modern methods are to be found in the American and British standards for the analysis of the grades of nickel used in the electronics industry. This new book is the first monograph that endeavours to provide a complete guide for the analyst concerned with nickel containing less than 1 per cent. of alloying constituents.

The authors have not attempted an encyclopaedic coverage but have mainly limited themselves to those methods which they have tested and adopted for use within their own organisation. Of necessity this has meant some bias towards the requirements of the producers of nickel; the needs of specialist users have not always been covered. Apart from this minor criticism, this book can be highly recommended.

No volumetric or gravimetric procedure is advocated by the authors; in accordance with the best modern practice, preference is given wherever possible for optical and X-ray spectrochemical methods of wide applicability. These are supported by a range of spectrophotometric methods and limited applications of polarography, flame photometry and atomic-absorption spectrophotometry. Separate chapters deal with sampling, the determination of carbon and sulphur, and the determination of gases.

The expert metallurgical analyst will appreciate the authors' mastery of their subject and will find a useful collection of well tried and well presented methods. The young journeyman analyst should obtain rather more from reading this book, for it demonstrates admirably how the competent industrial analyst chooses from the many available techniques to obtain the desired results as cheaply, rapidly and efficiently as possible. C. H. R. GENTRY

BIOCHEMICAL PREPARATIONS. Volume 11. Edited by ANDREAS C. MAEHLY. Pp. xii + 147. New York, London and Sydney: John Wiley & Sons Inc., 1966. Price 60s.

Volume 11 follows the pattern of former volumes in the now indispensable series of Biochemical Preparations, but each year the variety of substances described seems, if that were possible, to grow more varied and intriguing. In this volume the preparations described range from comparatively simple chemicals such as acetyl-β-methyl choline and 2-acetamido-2-deoxy-α-D-glucose (better known as *N*-acetyl-glucosamine), both made by chemical synthesis, to a crystalline protein (ceruloplasmin) prepared from blood plasma and complex molecules such as mesoporphyrin IX, ribonucleic acid and diguanosine tetraphosphate also prepared from natural sources or, as with thymidine polynucleotides, by synthesis. Of particular value to the biochemist are the descriptions of methods for isolating and purifying the enzymes, cytochrome oxidase, enolase, gluconate phosphate dehydrogenase and lactate dehydrogenase. Twenty-five preparations are given in all.

The practice adopted in developing the methods described is the same as with previous volumes, in that a method submitted by the original research worker is checked independently by another worker. In most instances footnotes are appended giving the checker's comments where he wishes to elucidate a point, suggest an improvement or call attention to some difference between his results and those of the original workers. As is customary, instructions are given in such detail that no one should have difficulty in operating the procedures described. The subject index is of particular value as it lists all the preparations described in the preceding ten volumes as well as the current one. Another useful feature is an index of compounds of biochemical interest which have appeared in the forty-five volumes of Organic Syntheses. The book is well bound in strong blue covers that should stand up to the rough handling a laboratory manual may be expected to receive. F. A. ROBINSON

THE RADIOCHEMICAL MANUAL. Edited by B. J. WILSON. Second Edition. Pp. 137. Amersham: The Radiochemical Centre. 1966. Price 50s.

The second edition of The Radiochemical Manual incorporates both parts of the original publication, but has been revised, enlarged and re-arranged so that many of the earlier criticisms no longer apply, although it must still be used in conjunction with the Radiochemical Centre Catalogue. The aim of this manual ". . . is to help the individual user—the scientist, doctor, engineer, or technologist—to choose the right (radioactive) material for his particular purpose and to make effective use of it," and this aim is largely fulfilled by the provision of extensive information on the properties of radioactive materials and detailed discussion of the problems concerned in their use.

The first half of the manual consists of a well written text covering the general nature of radioisotopes, the production process, the synthesis of labelled compounds and the manufacture of radiation sources (chapter 1 to 4); various problems involved in the production, use and measurement of radiochemicals (chapter 5 to 10); details of radiological safety, waste disposal, transport and legislation concerning the use of radioactive substances (chapters 11 to 13); and a comprehensive reading list of journals, abstract journals, books and other publications that cover the subject (chapter 14). Each chapter includes extensive and up-to-date references, but these can be difficult to locate and would have been more convenient if in the form of footnotes or if grouped together in a single bibliography. There has been an obvious attempt to rationalise the style of the different chapters, but with so many contributors there still remains a certain amount of duplication and a lack of uniformity, particularly in the use of commas. Typographical errors are, however, very few for a publication of this size.

The second half of the book comprises some fifty tables which cover physical data for the commoner isotopes (it is difficult to see why certain short-lived isotopes are included when some longer-lived ones are omitted), characteristics of radiation sources, synthesis and decomposition of labelled compounds, measurement techniques and safety. A 17-page index, which is both extensive and accurate, completes an extremely useful manual that is well produced and represents good value for the intending user. D. GIBBONS

SPOT TESTS IN ORGANIC ANALYSIS. By FRITZ FEIGL, ENG., D.SC., and DR. VINZENZ ANGER. Translated by RALPH E. OESPER, PH.D. Seventh English Edition. Pp. xxiv + 772. Amsterdam, London and New York: Elsevier Publishing Company. 1966. Price 170s.

This new edition of Feigl's "Spot Tests in Organic Analysis" makes a welcome appearance six years after the publication of the sixth edition. In the preparation of this new text, Professor Feigl has enlisted the help of Dr. Anger, a colleague and protagonist of spot-test analysis; the result is a completely revised, re-organised and enlarged text. Room for the considerable amount of new material has been found in two ways; by an increase in the number of pages from 675 to 772, and by deletion of the general chapter on spot-test techniques (which is identical with the chapter in the author's "Spot Tests in Inorganic Analysis"). Inessential tables and structural formulae have been severely pruned from the earlier text.

The total number of tests is now over 900—an increase of about 300 on the previous edition. An important feature of the new edition is the inclusion of two entirely new chapters, one dealing with tests for the detection of particular structures and certain types of organic compounds, and the other with the differentiation of isomers and homologous compounds, and the determination of constitution.

Despite the enormous growth of physical methods for the identification of organic compounds, direct chemical methods still have a wide application and, of course, are simpler, easier and very reliable. Surprisingly, these chemical methods can sometimes succeed where the most sophisticated instrumentation fails. This serves to emphasise the premier position of this volume in the literature of qualitative organic analysis. Quite apart from its great utility as a manual of spot tests which can be applied in the most diverse ways, this book is an invaluable source for reaction chemistry, albeit exploited for purely qualitative analytical purposes.

This is, without doubt, the finest edition yet of Feigl's "Spot Tests." The printing and binding are of the usual high standard with which Elsevier are invariably associated, and form an admirable complement to the excellence of the text. The author's personal researches and inspiration to his many colleagues have led, within the space of twenty years, to the development and consolidation of this highly significant branch of analytical chemistry. No laboratory concerned with either pure or applied organic chemistry in any of the diverse fields can afford to be without this new volume.

WILLIAM I. STEPHEN

THE INVESTIGATION OF ORGANIC REACTIONS. By ROSS STEWART. Pp. xvi + 125. London, Sydney, Toronto, Delhi and Tokyo: Prentice-Hall Inc. 1966. Price (cloth) 44s.; (paper) 20s.

In this book the broad outlines of physical organic chemistry are presented in a form suitable for students about to embark on a degree course. If the remaining nine volumes in the Foundations of Modern Organic Chemistry Series are as clearly written, the enterprising teacher and the eager student will have a feast of good things at their disposal. Professor Ross Stewart is a prominent investigator in the field of reaction mechanisms, which doubtless accounts for the clarity of expression and the refreshingly novel outlook that persists throughout the book.

In Chapter 1, starting from elementary thermodynamical concepts the various factors affecting equilibria in organic systems are described. Chapter 2 deals with reaction intermediates and their electronic structures, and is followed by a brief section on the transition states of organic molecules (Chapter 3). In Chapter 4, which discusses reaction paths, the concepts developed in the previous chapters receive more extended treatment. In this section a good balance is struck between the functional and reaction mechanism aspects of organic chemistry. The final chapter deals with catalytic phenomena, illustrated with reference to such diverse phenomena as condensation reactions, Friedel - Craft syntheses, free radical polymerisation, enzyme reactions and so on.

Besides suggestions for further reading, at the end of each chapter several thoughtful problems are given, for whose solution many students will need the guidance of an experienced tutor. A good index is provided and the price of the paper-backed edition is not unduly high for such a valuable monograph.

F. G. ANGELL

Erratum

JANUARY (1967) ISSUE, p. 65, correction to p. 30 of "Official, Standardised and Recommended Methods of Analysis." *For "Dilute standard copper solution," read "Strong standard copper solution."*

Summaries of Papers in this Issue

Analytical Applications of a 0·5-MeV Cockcroft - Walton Set based on the Measurement of Prompt γ-Radiation

γ-Radiation Emitted during Proton Reactions

Nuclear reactions are outlined which yield γ-rays when the elements from lithium to chlorine, with the exception of neon, are irradiated with protons of an energy of 0·5 MeV or less. Energies of the principal γ-rays are listed and analytical applications based on measurements of the γ-rays are discussed.

T. B. PIERCE, P. F. PECK and D. R. A. CUFF

Analytical Chemistry Group, Atomic Energy Research Establishment, Harwell, Didcot, Berkshire.

Analyst, **1967, 92**, 143–150.

The Determination of Fluorine in Fluorite Ores and Concentrates by Isotope-source Fast-neutron Activation Analysis

On irradiation with fast neutrons, fluorine-19 is converted to nitrogen-16 by the (n,α) reaction. The fluorine content of fluorite ores and concentrates can be simply and rapidly determined by measurement of the γ-activity of this nitrogen-16 product. No sample preparation, other than crushing and grinding, is required.

P. G. JEFFERY and J. M. BAKES

Warren Spring Laboratory, Ministry of Technology, Stevenage, Herts.

Analyst, **1967, 92**, 151–155.

The Importance of Fuel Gas Composition in the Atomic-absorption Spectrophotometric Determination of Magnesium

The specifications for commonly used "low temperature" fuel gases permit wide variations in composition. The effect, on the determination of magnesium in nickel, of using two samples of "propane" of differing compositions is considerable, and the use of acetylene is advocated. The results emphasise the need for a complete specification of flame conditions to be given when reporting sensitivities and interference susceptibilities in atomic-absorption procedures when using flame atomisation.

T. R. ANDREW and P. N. R. NICHOLS

Central Materials Laboratory, The Mullard Radio Valve Company, New Road, Mitcham Junction, Surrey.

Analyst, **1967, 92**, 156–161.

The Use of 2-Selenophene Aldoxime for the Gravimetric Determination of Palladium

The use of 2-selenophene aldoxime as a gravimetric reagent for palladium is described. The optimum analytical conditions for precipitation of the palladium complex and the effect of possible interferences have been investigated.

L. S. BARK and D. GRIFFIN

Department of Chemistry and Applied Chemistry, Royal College of Advanced Technology, Salford, Lancashire.

Analyst, **1967, 92**, 162–165.

An Oxidimetric Determination of Molybdenum

The use of silver, mercury, tin(II) and amalgamated zinc as reducing agents in the oxidimetric determination of molybdenum was investigated. Cerium(IV), dichromate and metavanadate solutions were used for the titration of the molybdenum(V) solutions. All of the methods, except when molybdenum(V) prepared by reduction with silver was titrated with dichromate, gave satisfactory results. With the Jones reductor three redox systems were used for determining molybdenum(III) and gave equal, satisfactory results.

J. BECKER and C. J. COETZEE

Chemistry Department, University of the Orange Free State, Bloemfontein, South Africa.

Analyst, 1967, **92**, 166–169.

A Thin-layer Chromatographic Screening Test for Organophosphorus Pesticide Residues

A procedure is proposed for use as a screening test for the presence of traces of organophosphorus pesticides in vegetable tissue. The compounds are extracted with dichloromethane and the extracts are cleaned-up on silica-gel chromatoplates developed with hexane - acetone solution, 5 + 1. Eluted compounds are then oxidised with ammonium persulphate or a nitric acid - perchloric acid mixture for phosphorus determinations by molybdenum-blue procedures. Good recoveries are reported from a range of crop samples. Mobile solvents required for the clean-up of some polar pesticides and metabolites on multi-band chromatoplates are also listed.

D. C. ABBOTT, A. S. BURRIDGE, J. THOMSON and K. S. WEBB

Ministry of Technology, Laboratory of the Government Chemist, Cornwall House, Stamford Street, London, S.E.1.

Analyst, 1967, **92**, 170–175.

The Detection of Adulteration of Fruit Juices by Thin-layer Chromatography

The technique of thin-layer chromatography has been applied to extracts of citrus and non-citrus juices in order to detect adulteration.

Procedures for preparing suitable extracts of the juices are given.

For non-citrus juices, 10 per cent. adulteration with apple juice, or 25 per cent. of another foreign juice can be detected, as can 0·1 μg of glycine in 5 μl of citrus juice extract.

Mrs. B. M. ALVAREZ

Flavour Division, Bush Boake Allen Ltd., Ash Grove, Hackney, London, E.8.

Analyst, 1967, **92**, 176–179.

The Assay of Certain Organic Bases in Aqueous Eye-drops

Methods have been devised for the assay of medicaments in eye-drop solutions containing benzalkonium chloride and chlorhexidine diacetate, in which interference caused by these substances is eliminated.

P. J. COOPER and P. W. HAMMOND

Ministry of Technology, Laboratory of the Government Chemist, Cornwall House, Stamford Street, London, S.E.1.

Analyst, 1967, **92**, 180–184.

Field Methods for Determining Certain Organomercurial Vapours in Air

Two methods are proposed for determining the vapours of certain organomercury compounds in air, at concentrations in the region of 10 μg of mercury per cu. m. The mercurial vapours are collected either on a glass-fibre pad treated with cadmium sulphide or on a fluidised bed of active carbon. Mercury vapour is released by heating, and is determined by comparing the colour produced on selenium sulphide test-papers with a range of standard colours. The cadmium sulphide method is applicable to the determination of ethylmercury chloride, ethylmercury phosphate, diphenylmercury and methylmercury dicyandiamide; the fluidised-bed method is also applicable to this range of compounds and, in addition, to diethyl mercury. Mercurial dusts can be determined by the cadmium sulphide method and mercury vapour by a slight modification of the fluidised-bed technique. In both methods the apparatus used is simple to manipulate and the time needed for a complete determination is less than 30 minutes.

A. A. CHRISTIE, A. J. DUNSDON and B. S. MARSHALL

Ministry of Technology, Laboratory of the Government Chemist, Cornwall House, Stamford Street, London, S.E.1.

Analyst, 1967, **92**, 185–191.

The Determination of Warfarin in Animal Relicta

A method is described for the quantitative analysis of warfarin in animal relicta. Basically the method consists in the extraction of relicta, column clean-up of the extract, separation of the warfarin by thin-layer chromatography, elution from the layer and spectrophotometric assay at 305 mμ.

F. B. FISHWICK and A. TAYLOR

Infestation Control Laboratory, Ministry of Agriculture, Fisheries and Food, Tolworth, Surrey.

Analyst, 1967, **92**, 192–195.

The Use of Iron(II) Sulphate for the Reduction of Nitrate to Ammonia in the Microdiffusion Method for Determining Nitrate in Soil Extracts

Because of the variable nature of technical titanium(III) sulphate normally used for the determination of nitrate in soil extracts by the Bremner - Shaw microdiffusion method, the possibility of replacing this reagent with iron(II) sulphate was studied. It was found that 1 ml of M iron(II) sulphate (in 0·5 M sulphuric acid) *plus* 0·1 ml of saturated silver sulphate could be used to successfully determine up to 200 μg of nitrate nitrogen in 5-ml aliquots of soil extracts.

P. R. PREMI and A. H. CORNFIELD

Chemistry Department, Imperial College of Science and Technology, London, S.W.7.

Analyst, 1967, **92**, 196–197.

A Simple, Rapid Method for Determining Glucose in Blood or Plasma

The glucose in blood or plasma is determined by an orthotoluidine colorimetric method.

J. D. PRYCE

Pathological Laboratory, Ipswich and East Suffolk Hospital, Anglesea Road, Ipswich.

Analyst, 1967, **92**, 198.

A Simple Device for Transferring Gases Evolved at Low Pressure to a Gas Chromatograph

A glass stopcock is described for use in transferring gases evolved from a low pressure system to one involving a flowing carrier gas at atmospheric pressure.

R. COE
British Welding Research Association, Research Station, Abington Hall, Abington, Cambridge.

Analyst, 1967, **92**, 199.

An All-plastic Suction Funnel

D. T. PRITCHARD
Soil Survey of England & Wales, Rothamsted Experimental Station, Harpenden, Herts.

Analyst, 1967, **92**, 199–200.

Effect of Impurity in Dichloroethane Solvent on the Determination of Boron with Methylene Blue

A. STRIZOVIC and J. A. CALDWELL
Research Department, Murex Ltd. Rainham, Essex.

Analyst, 1967, **92**, 200.

Notice to Authors

THE Editor welcomes papers on all aspects of the theory and practice of analytical chemistry, fundamental and applied, inorganic and organic, including chemical, physical and biological methods. Papers are submitted to the Editorial Committee, who decide on their suitability for publication.

Intending authors should consult the current Notice to Authors, last published in full in *The Analyst*, **1966**, **91**, 67, reprints of which can be obtained on application to The Editor, *The Analyst*, 14, Belgrave Square, London, S.W.1. All papers submitted will be expected to conform to the recommendations there laid down, and any that do not may be returned for amendment.

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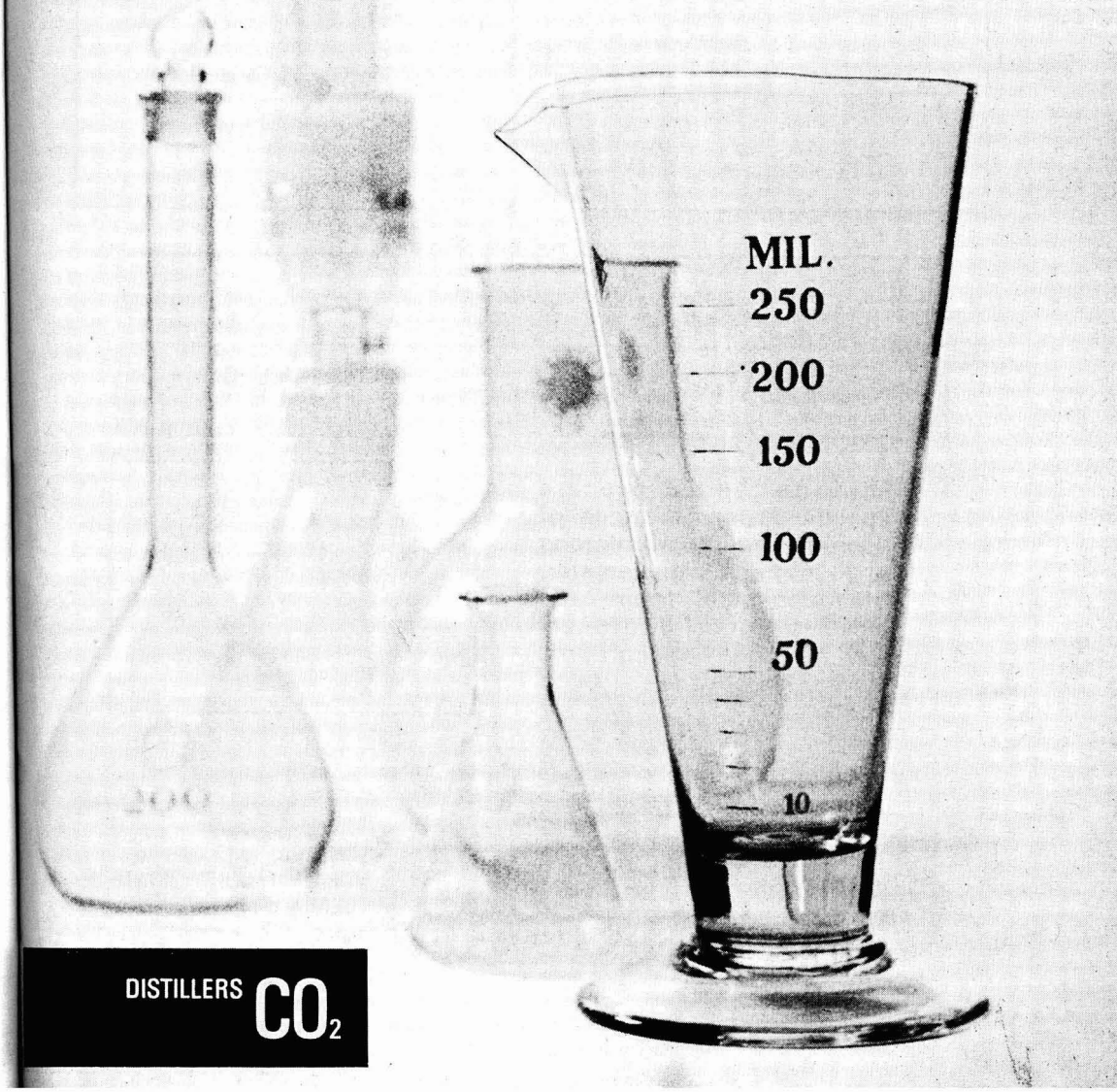

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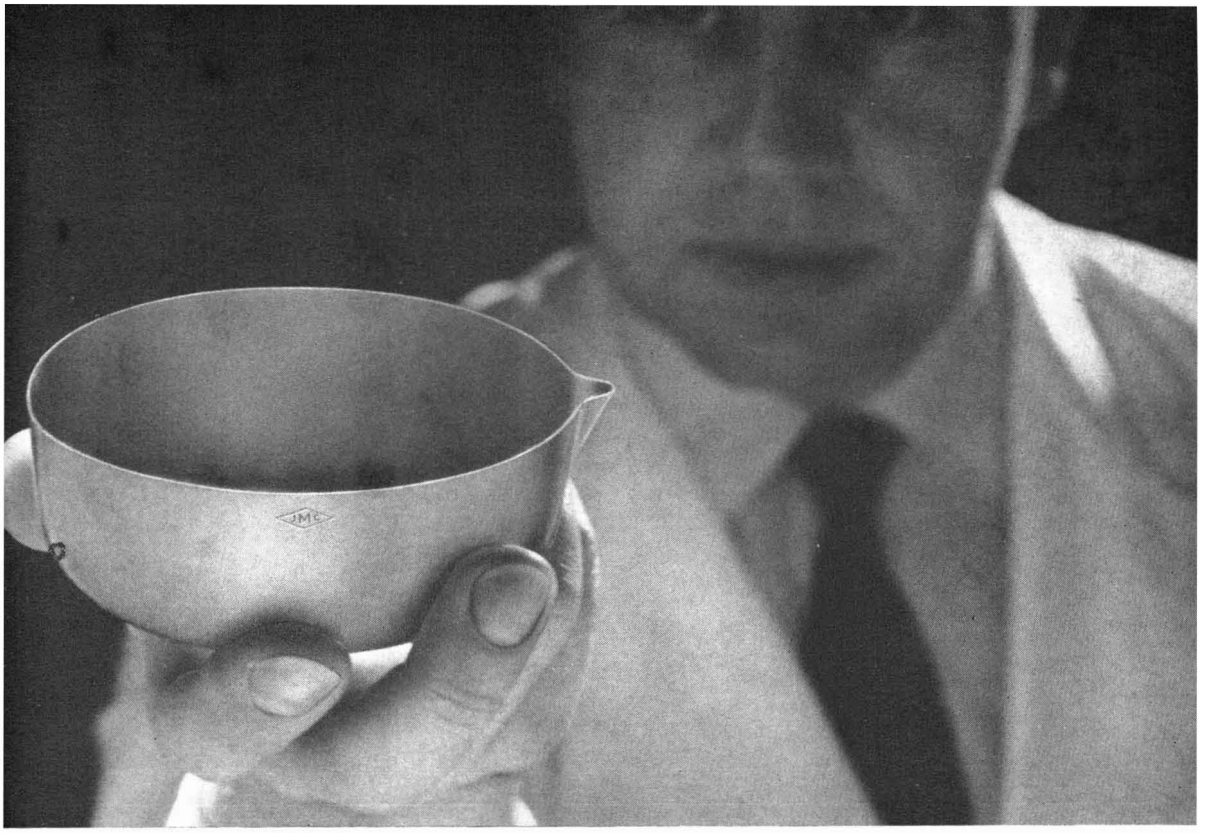

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