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An Investigation of the Determination of Germanium by Flame Photometry and Atomic-fluorescence Spectroscopy by Using a Separated Nitrous Oxide - Acetylene Flame

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The flame photometry and atomic-fluorescence spectroscopy of germanium in a nitrogen and argon separated nitrous oxide - acetylene flame have been investigated. With the optimised operating conditions the detection limits at 265·1 nm were 1·1 and 0·1 p.p.m., respectively.

A germanium microwave-excited electrodeless discharge tube was prepared and used for excitation of the atomic fluorescence. The optimum conditions for the determination of germanium have been investigated, and the effects of elements commonly associated with germanium ores and the common inorganic acids were studied for interference.

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The atomic fluorescence of germanium has been observed in the nitrogen - oxygen - acetylene flame,[1] while the determination of this element by atomic-absorption spectroscopy has been reported by several workers who used both oxy-acetylene[2,3] and nitrous oxide - acetylene[4,5] flames. The application of a nitrogen or argon separated nitrous oxide - acetylene flame to improve the detection limit for the determination of germanium by atomic absorption has also recently been reported.[6,7] This paper describes an investigation of the optimum operating conditions for the determination of traces of germanium by both flame photometry and atomic-fluorescence spectroscopy with a nitrogen or argon separated nitrous oxide - acetylene flame. A commercially available flame spectrophotometer is used, and an electronically modulated germanium electrodeless discharge tube source[8] is used to excite atomic fluorescence.

Germanium forms a refractory oxide species in hydrocarbon or hydrogen flames supported by air, and the sensitivities available for the determination of germanium by flame spectroscopy in these flame are, therefore, low. The pre-mixed fuel-rich nitrous oxide - acetylene flame has a sufficiently reducing atmosphere to ensure partial dissociation of the metal oxide species at the high effective flame temperature. In consequence, the germanium free-atom population in the flame under these conditions is sufficient to permit the determination of the element by flame photometry, atomic-absorption or atomic-fluorescence spectroscopy. This paper outlines the relative sensitivity and selectivity available with these techniques for the determination of germanium.

Experimental

Apparatus—

The apparatus used to excite the electrodeless discharge tube (EDT) and record the fluorescence and flame emission has been previously described.[9,10] For the fluorescence study a $\frac{3}{4}$-wave resonant cavity (Electro-Medical Supplies Ltd., London, Model 210L) was used to maintain the source discharge. The burners used throughout these studies have been described elsewhere.[9,11]

Preparation of germanium electrodeless discharge tubes—

Germanium discharge tubes were produced from elemental germanium metal and iodine by the same general procedure described for other elements.[12] The most satisfactory tubes for use in the $\frac{3}{4}$-wave cavity were found to be about 4 cm long, and contained about 2 mg of germanium and 2 mg of iodine. The argon filler gas pressure was 4 torr. The tubes produced greatest intensity and stability when operated at 55 W (20-W reflected power). The tube was slightly cooled by compressed air via the central slot of the cavity. Under these conditions

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the tubes exhibited a bright steel-blue emission and output intensity was stable to within a noise level of ±1 per cent. The warm-up period was about 10 minutes, and the long period fluctuation over 1 hour was within ±2 per cent.

Optical arrangement—

The optical arrangement of the apparatus used here for the atomic-fluorescence studies has been described elsewhere.[9]

Reagents—

Stock germanium solution, 1000 p.p.m.—Dissolve 1·44 g of high purity germanium dioxide in about 20 ml of 1 F potassium hydroxide solution, and dilute to 1 litre with distilled water and sufficient hydrochloric acid to make the solution slightly acidic.

Diverse ions—Stock 10 per cent. solutions were prepared from analytical-reagent grade salts of the elements.

Spectral characteristics of discharge tube—

The emission spectrum from the germanium discharge tube was obtained between 255 and 305 nm. The atomic germanium lines obtained were those shown in Table I, which also records the line intensities obtained. The most intense line was found to be the 265·12 to 265·16 nm doublet, which was not resolved with the instrumentation used. The intensities obtained for a germanium hollow-cathode lamp (Varian Techtron Pty. Ltd., Victoria, Australia) are also shown.

The line-to-background ratio obtained at 265·1 nm for the electrodeless discharge tube was 98:1; for the hollow-cathode lamp it was 80:1. The stabilities over 1 hour were found to be comparable from both sources, *i.e.*, ±3 per cent. for the germanium hollow-cathode lamp and ±2 per cent. for the discharge tube. Both sources exhibited short-term noise levels of less than ±1 per cent.

Table I

Principal source emission characteristics

Line, nm	Transition	Relative emission intensity*	
		Hollow-cathode lamp	Electrodeless discharge tube
259·3	$^3P_2^0 \longrightarrow {}^3P_1$	0·3	23
[265·12†	$^3P_2^0 \longrightarrow {}^3P_2$	0·8	100
265·16]	$^3P_1^0 \longrightarrow$		
269·1	$^3P_1^0 \longrightarrow {}^3P_2$	0·2	16·7
270·9	$^3P_0^0 \longrightarrow {}^3P_1$	0·3	25·4
275·5	$^3P_1^0 \longrightarrow {}^3P_2$	0·4	32·8
303·9	$^1P_1^0 \longrightarrow {}^1D_2$	0·4	73·5

* Emission intensities expressed relative to intensity of 265·1 nm doublet from the electrodeless discharge tube.
† Most sensitive for atomic absorption.

Results

Flame-emission measurements—

The flame background and germanium flame atomic-emission spectra between 263 and 268 nm are shown in Fig. 1 (*a*) and (*b*) for the nitrogen separated nitrous oxide - acetylene flame. The flame background exhibits a broad peak (266·3 to 266·8 nm), possibly due to OH and CO band emission. On the introduction of germanium into the flame significant germanium atomic emission is observed. The magnitude of this is considerably greater than the background emission at 265·1 nm, see Fig. 1 (*b*). Flame photometry thus provides good sensitivity for germanium in the separated and conventional flames at 265·1 nm. Lower detection limits are observed in the separated flame as a direct consequence of the lower background and noise levels in the interconal zone, and because of the increased volume[6] of the latter. The use of argon instead of nitrogen as the shielding gas results in further improvement of the germanium detection limit.

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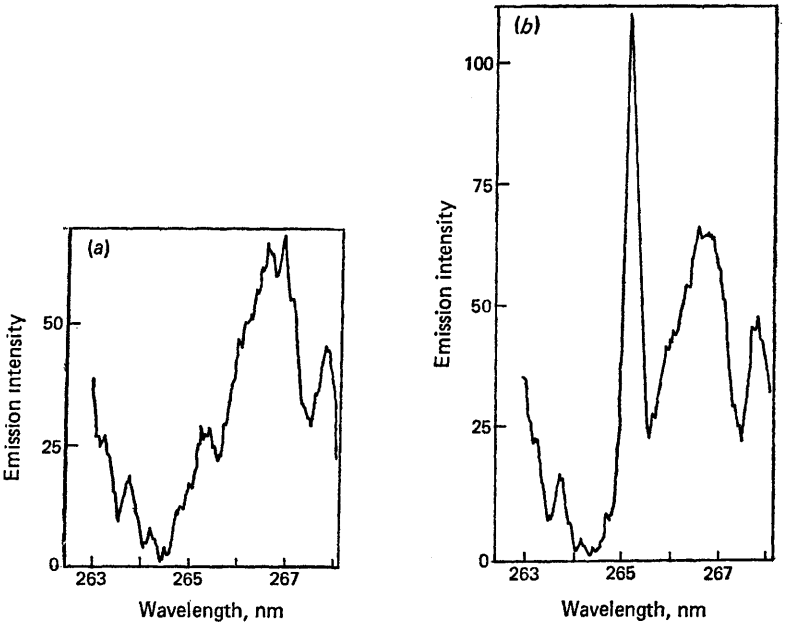

Fig. 1 (*a*) Emission spectrum for flame background between 263 and 268 nm. Spectral slit width 0·33 nm; (*b*) emission spectrum for 100 p.p.m. germanium solution between 263 and 268 nm. Spectral slit width 0·33 nm

ATOMIC-FLUORESCENCE MEASUREMENTS—

The ability of the Techtron AA4 amplifier to differentiate between flame atomic emission and atomic fluorescence of germanium has been described elsewhere.[9] The fluorescence emission was scanned from 255 to 275 nm, by using the optimum acetylene flow-rate and height of observation. The relative fluorescence intensities shown in Fig. 2 were obtained. It was found that negligible interference from the source was received at the monochromator by reflection from the burner assembly or apparatus structure. The atomic emission obtained at 265·1 nm when germanium solutions were introduced into the flame with the EDT in

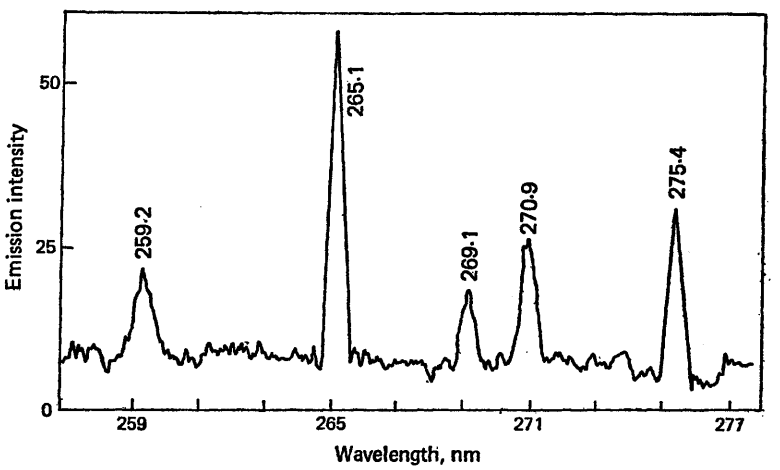

Fig. 2. Atomic-fluorescence spectrum for 10 p.p.m. germanium solution between 258 and 277 nm. Spectral slit width 0·99 nm

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operation was assigned as germanium fluorescence rather than scatter from particulate material in the flame, for the following reasons.

(*i*) Appreciable absorption is observed in the atomic-absorption spectroscopy of germanium with similar flame conditions.

(*ii*) Nebulisation of a 20,000 p.p.m. solution of sodium tungstate into the flame causes negligible scatter of incident radiation from the germanium source.

(*iii*) No scattered radiation from the mercury 253·6 nm line is observed when the germanium EDT is replaced by an intense mercury EDT and a 1000 p.p.m. germanium solution is introduced into the flame.

(*iv*) The absence of interference by diverse ions in the germanium atomic-fluorescence study also indicates that scattered radiation is minimal.

Fig. 2 shows that germanium fluorescence arises from the principal germanium lines scanned, but that greatest emission occurs at 265·1 nm. This fluorescence signal originates from the unresolved 265·12 and 265·16 nm lines. However, the spectral slit width used for the greatest sensitivity (0·99 nm) is such that the fluorescence emission from both lines is transmitted by the monochromator, so that the integrated fluorescence intensity of both is measured.

Optimum flame operating conditions—

The flame operating conditions were chosen to produce the most intense fluorescence and thermal-emission signals with the minimum background and noise; spectral slit widths of 0·99 and 0·33 nm, respectively, were used. The nitrous oxide flow-rate was maintained at a constant (5·8 l minute^{-1}) and the nitrogen or argon gas flow-rate initially set at about 10 l minute^{-1} to separate the flame effectively. Under these conditions the effect of variation of the acetylene flow-rate on the atomic fluorescence and thermal-emission sensitivity from germanium was observed. Fig. 2 shows that the maximum fluorescence and thermal-emission intensities are observed with about 3·2 l minute^{-1} and about 3·0 l minute^{-1} of acetylene, respectively, and these flow-rates were used for all further work. With the optimum acetylene flow-rate the most intense fluorescence and thermal emission for germanium was observed in the red interconal zone of the flame immediately above the primary reaction zone. The slit viewed the interconal zone between 3 to 13 mm above the primary reaction zone.

Detection limits for germanium by thermal emission and atomic fluorescence—

The limits of detection for germanium at 265·1 nm by atomic fluorescence, with the germanium EDT, and flame photometry were established for both separated and conventional flames under their optimised conditions of fuel flow-rate, height of observation and spectral slit width. The detection limit was defined as the concentration of germanium in aqueous solution required to produce a signal-to-noise ratio of unity for each technique.

The observed detection limits are summarised in Table II, and are compared with the atomic-absorption detection limit obtained with the same equipment.

TABLE II

DETECTION LIMITS FOR GERMANIUM WITH APPARATUS USED

Technique	Detection limit, 265·1 nm: Un-separated	Nitrogen separated	Argon separated	Slit width, nm
Flame photometry	4	1·3	1·1	0·33
Atomic fluorescence.. ..	0·2	0·10	0·066	0·99
Atomic absorption*.. ..	2	—	—	0·33

* With germanium hollow-cathode lamp and 5-cm nitrous oxide - acetylene slot burner. A similar detection limit was obtained with the germanium electrodeless discharge tube as source.

Linear calibration graphs were obtained for germanium flame photometry at 265·1 nm in the nitrogen and argon separated flames over the range 20 to 1000 p.p.m. For germanium atomic fluorescence with the optimum conditions established for the nitrogen or argon separated flame, linear calibration graphs were obtained over the range 1 to 1000 p.p.m.

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Repetitive introduction (10 times) of a 200 p.p.m. germanium solution into the separated flames under the optimum conditions used above indicated a coefficient of variation in the germanium atomic-line emission intensity of 1 per cent. at 265·1 nm. Similar experiments for germanium atomic fluorescence with a 10 p.p.m. germanium solution resulted in a coefficient of variation in fluorescence intensity of 1·25 per cent. at 265·1 nm.

INTERFERENCE STUDIES—

The effects of 100-fold excesses by weight of a range of cations and anions commonly associated with germanium in ores on the intensity of the atomic emission and atomic fluorescence produced by 100 p.p.m. and 10 p.p.m. of germanium at 265·1 nm, respectively, were investigated. Foreign ions were considered not to interfere when they produced a variation in signal intensity of not greater than twice the standard deviation. The effect of each ion is summarised in Table III.

TABLE III

EFFECT OF FOREIGN IONS ON THE DETERMINATION OF GERMANIUM

Element or ion	Atomic-fluorescence spectroscopy	Flame photometry
As(III)	No interference	No interference
Cd	No interference	No interference
Cu	No interference	No interference
Fe(II)	No interference	No interference
Mg	No interference	No interference
Na	No interference	No interference
Ni	No interference	No interference
Pb	No interference	No interference
Si	No interference	No interference
Ta	No interference	No interference
Zn	No interference	No interference
Cl^-	No interference	No interference
F^-	No interference	No interference
NO_3^-	No interference	No interference
PO_4^{3-}	No interference	No interference
Al(III)	No interference	+570%
Co	No interference	+ 40%
Cr	No interference	+ 40%
K	No interference	+ 30%
Mo(VI)	No interference	+130%
V(V)	No interference	+240%
W(VI)	No interference	+ 50%

CONCLUSION

The separated slightly fuel-rich nitrous oxide - acetylene flame is sufficiently hot and exhibits sufficient reducing properties to ensure efficient reduction or dissociation of the germanium oxides liable to be formed within the flame, resulting in the maintenance of a substantial population of free ground-state atoms of germanium. The principal germanium resonance lines are excited by the high temperature of the flame, thus producing good sensitivity in flame photometry. The selectivity of germanium flame photometry is moderately good, with only a few elements producing significant spectral interference effects. The observed sensitivity for the determination of germanium by atomic-fluorescence spectroscopy is higher, and the method is relatively free from physical or chemical interference. The atomic-fluorescence arrangement ensures that spectral interference is scarcely possible. As the atomic-fluorescence signal is not critically dependent on burner height it indicates that the flame provides a population of ground-state atoms of germanium extending well above the primary reaction zone. The sensitivity of the atomic-fluorescence determination is, of course, critically dependent on the intensity of the irradiating discharge-tube source. Even with the simple tubes used in this study the sensitivity of the atomic-fluorescence determination is one order of magnitude better than for the determination by flame photometry or atomic absorption. Both emission techniques give linear calibrations over a wide range of germanium concentrations, with a high precision in replicate analyses of germanium sample solutions.

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