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PHOTOMETRIC DETECTION OF SELENIUM COMPOUNDS FOR GAS CHROMATOGRAPHY

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SUMMARY

Various selenium compounds were detected in gas chromatographic effluents by a modified flame photometric detector (FPD). It responds to a broad system of bands likely due to Se_2, with dominant emissions between 450 and 500 nm. Similar to S_2 response in the FPD, Se response is essentially quadratic, and quenched by carbon compounds. However, quenching is less severe for selenium and can, in fact, be used to provide additional selectivity against sulfur or other carbon compounds.

In the absence of deliberate quenching, the selectivity of selenium *vs.* carbon typically amounts to two to three orders of magnitude at lower, more than three orders at higher Se levels. The FPD response for selenium is somewhat weaker than that for sulfur, but the detection of subnanogram amounts of organoselenium compounds can be readily achieved. The minimum detectable amount is *ca.* 2×10^{-12} g Se per sec.

INTRODUCTION

It is difficult not to notice the presence of selenium compounds. Beyond their sensory impact on the research laboratory, however, their effects can be traced throughout the biosphere. The introduction of selenium into the environment is due to both man and nature, and but few quantitative data are available on its cycles or sinks[1].

There has been a flurry of research activity on selenium in past years. Some of it relates to a not uncommon ambivalence, perhaps best exemplified by selenium: it is both toxic and essential; it both causes and protects against certain diseases.

The literature on selenium and its various effects is extensive (for some reviews, see refs. 1–4, also 5–8). Not surprising for an element whose nutritional and toxic levels are low and not too far apart (0.1–0.3 and 2–10 mg/kg, respectively), analysis is difficult. Almost exclusively the determination is restricted to that of total selenium (see refs. 9 and 10 for reviews and refs. 11–30 for some newer papers, many involving hydride formation) as opposed to an analysis for various selenium species[17].

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As recent history has demonstrated with the case of mercury, it is often useful to know the particular chemical form in which an element interacts with life systems. Selenium occurs in many forms, some of which are volatile. For these, gas chromatography (GC) is an obvious analytical approach. If it is to be successful at trace levels, a sensitive and, preferably, selective detector is required.

Several of the common GC detectors should, by analogy with sulfur, show selective responses for selenium compounds, *e.g.* electron capture, electrolytic conductivity and, of course, alkali flame detectors. The latter has shown some minor selectivity[31].

Some years ago we removed the interference filter from a commercial flame photometric detector (FPD) of the Brody-Chaney design[32] and tested with it a variety of hetero-organics. Among these was piazselenole, which showed a minimum detectable amount of 10 ng and, like sulfur, quadratic response[33]. When we recently gained access to a different photometric detector noted for its sulfur response, the particulars of selenium detection were further pursued.

We decided to optimize the detector, chart the spectra emitted, check for various interferences, and establish its sensitivity and selectivity.

EXPERIMENTAL

A Shimadzu 4B gas chromatograph with a dual-channel photometric detector was used in a manner similar to a study of tin response[34]. This relates to the optical channels, to response optimization, and to doping with methane. Both the 3 mm I.D. quartz enclosure (constricted tube) used for tin and the regular quartz tube were used. The 484-nm interference filter (8.6 nm bandpass at half height), which was occasionally inserted into the optical path, happened to be one available to us —it does not necessarily represent the optimum arrangement.

The GC columns used were 1.5 m × 3 mm I.D. 5% PEGA on 100–120 mesh Chromosorb W AW; and 1.0 m × 3 mm I.D. 5% OV-101 on 45–60 mesh Chromosorb W AW.

To take a spectrum, a Jarrell-Ash ¼ m monochromator with a Hamamatsu R268 photomultiplier (PM) tube was connected to the FPD on one side, while the other side was operated without wavelength discriminator for comparison. Piazselenole was repeatedly injected and the response monitored at different wavelengths.

RESULTS AND DISCUSSION

The flow conditions for maximum response, established with piazselenole, did not vary much from those best suited for sulfur compounds. They were 35 ml/min hydrogen, 40 ml/min nitrogen, and either 20 or 25 ml/min (for constricted or regular quartz tubes) of air.

The spectrum seen under these circumstances is shown in Fig. 1. (It should be noted that this is not a spectrum in the usual sense, since it consists of chromatographic peak height measurements, uncorrected for the PM tube response profile.) It corresponds to some of the bands noted by Salet[35] for selenium burning in air, by Emeléus and Riley[36] for a flame of alcohol burning in selenium dioxide vapor, and, presumably, by Mitscherlich[37] for selenium in a hydrogen diffusion flame. Emeléus

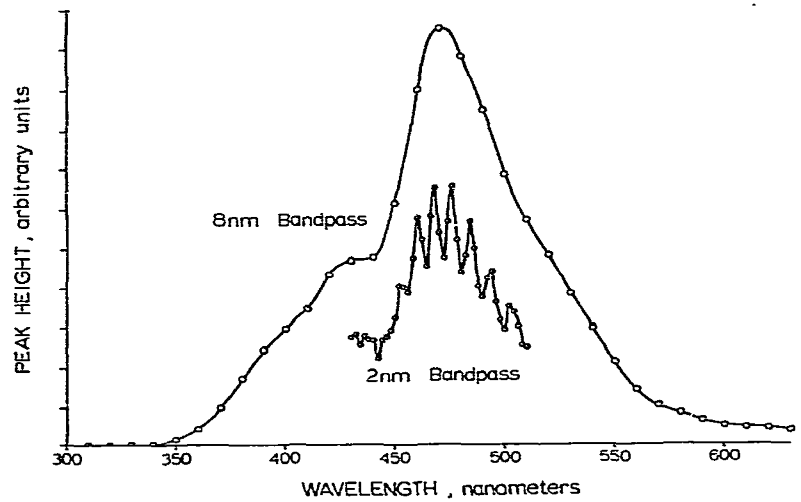

Fig. 1. Peak heights for piazselenole at different wavelengths, using two sets of slits. The ordinate values are different for the 8-nm and 2-nm tracings.

and Riley thought, with some hesitation, that these bands were due to Se_2. Gilbert, to whom we are highly indebted for his excellent labor-of-love review on the subject[35], draws attention to Mitscherlich's 1864 hydrogen diffusion flame and, in analogy to the response of sulfur in the FPD, the likely analytical utility of selenium band emissions.

The area monitored in our case was above the (shielded) flame. Visual observation of the emission in a normal quartz tube shows it filling a significant fraction of the available space above the flame shield in the viewing area of the photomultiplier. In the limited context of this study, the matter of the spectrum was not further pursued. It should be mentioned as an aside, however, that an FPD-like device could prove of some value in generating various band spectra with good sensitivity and in relatively uncluttered form for basic studies of spectrum origin.

In the case of selenium, the approximately quadratic response due to these bands supports the contention of Emeléus and Riley that the emitting species of the broad bands from 4600 to 5620 Å is Se_2.

Fig. 2 shows calibration curves for di(*tert.*-butyl)disulfide, piazselenole, phenanthrene and pentadecane, taken with the constricted quartz tube and the 484-nm filter (see Experimental). The selenium response is less than that of sulfur, although the choice of test compounds in this case tends to overemphasize the point.

Since sulfur response is well known to decrease when carbon compounds are present, potential interference by carbon was evaluated by re-running the calibration curves of Fig. 2 with 1 ml/min of methane being added to the carrier gas. The results were dramatic and are shown in Fig. 3.

Selenium response dropped to a minor, sulfur response to a major degree, such that the selenium compound was now the far stronger responding one of the two. Thus, doping with methane (which also, at certain conditions, decreases the background) can be used to increase drastically the selectivity of selenium *vs.* sulfur.

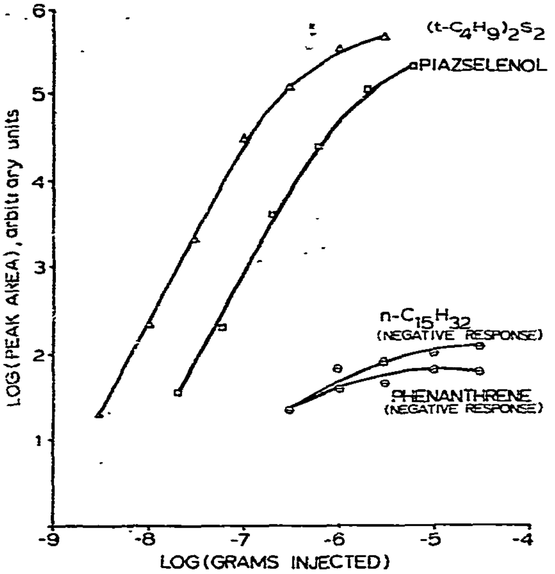

Fig. 2. Calibration curves for various compounds as indicated using constricted quartz tube and 484-nm filter.

A very small, positive response for pentadecane was noted. Thus, carbon doping can also influence the selectivity of selenium *vs.* carbon compounds.

The matter of carbon doping seemed interesting enough to reproduce on the commercial FPD (*i.e.*, using a normal quartz tube rather than the constricted one peculiar to our experiments). The FPD was otherwise operated at the same conditions, *i.e.* those found best for selenium. Fig. 4 shows the correlation of response with added methane flow for a selection of compounds.

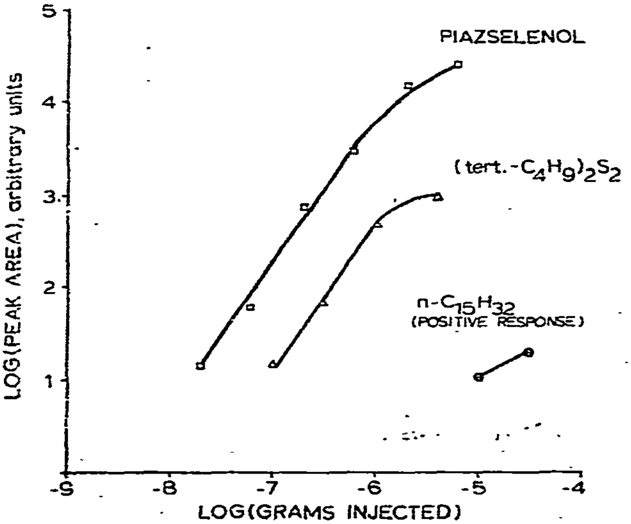

Fig. 3. Calibration curves as in Fig. 2, but 1 ml/min methane added to carrier gas.

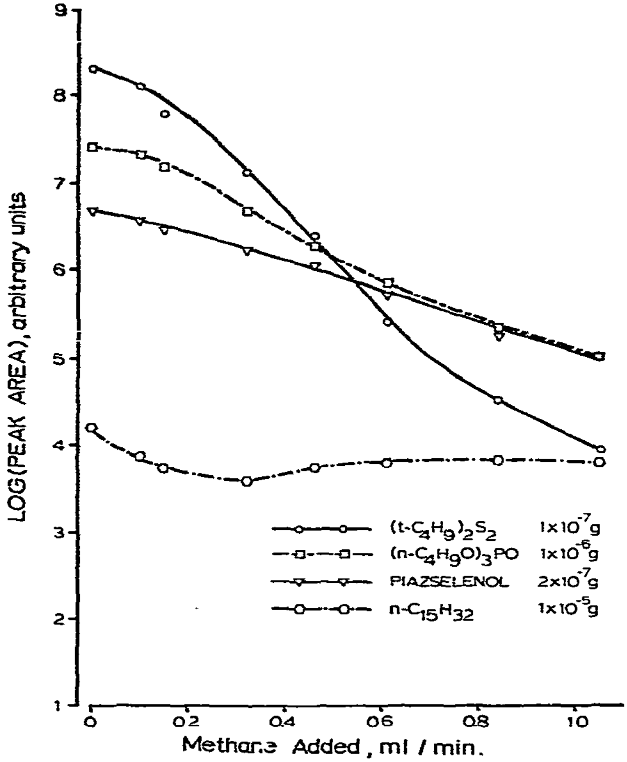

Fig. 4. Effects of methane doping. Normal quartz tube, no optical filter. Methane was added to nitrogen carrier. Compounds and injected amounts are as indicated. Note logarithmic ordinate.

All hetero-organics decrease in response, but to very different degrees. Di(*tert.*-butyl)disulfide shows the strongest drop over some four orders of magnitude. The phosphorus and selenium compounds drop much less, leading to increased selectivity (and decreased sensitivity) for them as the methane flow is increased. Equal amounts of methane produce stronger effects in the normal tube than in the constricted one, but the overall trends are the same. It should also be noted that the response of pentadecane and similar compounds is very small and subject to great variation with the history and operating conditions of the FPD.

Returning to non-doped conditions, typical low-level chromatographies were run, using temperature programming. The results are shown in Fig. 5. From these it appears that typical selenium compounds can be determined at subnanogram levels; the minimum detectable amounts of the three, late-eluting selenium compounds was approximately 2×10^{-10} g or *ca.* 2×10^{-12} g Se per sec.

As can be seen by a comparison of Figs. 2, 3 and 4, the selectivity of selenium *vs.* sulfur or *vs.* carbon is difficult to define, since it depends on the conditions of carrier and detector, the choice of a carbon standard, the amounts injected, etc. For Se *vs.* C, values 10^1–10^3 and higher can be easily found; the most reasonable ones to expect are between two and three orders of magnitude at trace levels, and beyond 10^3 at higher levels.

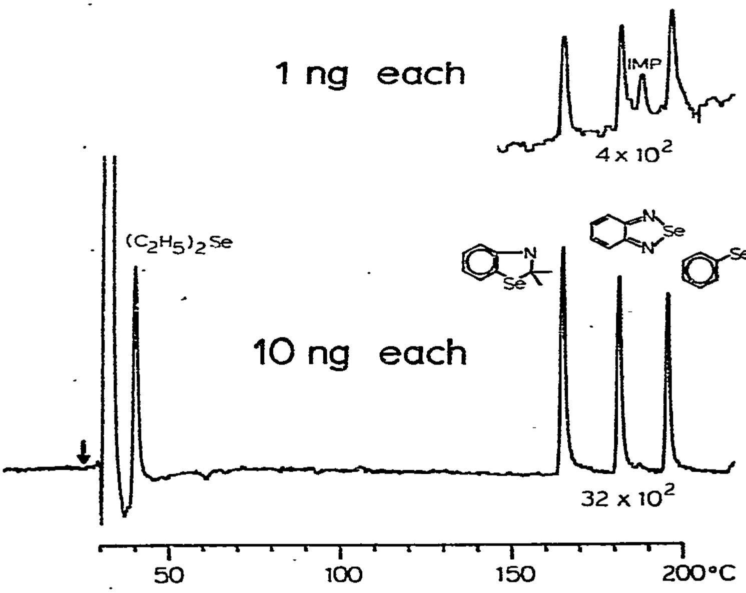

Fig. 5. Temperature-programmed GC of four selenium compounds at 1- and 10-ng levels. IMP = impurity. The peak for diethylselenide is partially quenched by solvent tailing and appears only as a trace at the 1-ng level.

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REFERENCES

1 Committee on Medical and Biological Effects of Environmental Pollutants, NRC, *Selenium*, National Academy of Sciences, Washington, D.C., 1976.
2 I. Rosenfeld and A. O. Beath, *Selenium, Geobotany, Biochemistry, Toxicity and Nutrition*, Academic Press, New York, London, 1964.
3 O. H. Muth (Editor), *Selenium in Biomedicine*, Avi Publ. Co., Westport, Conn., 1967.
4 R. A. Zingaro and W. C. Cooper (Editors), *Selenium*, Van Nostrand-Reinhold, New York, 1974.
5 E. Browning, *Toxicity of Industrial Metals*, Butterworth, London, 2nd ed., 1969.
6 Anonymous, *Chem. Eng. News*, 55, No. 3 (1977) 35.
7 D. V. Frost, *World Rev. Pest Contr.*, 9 (1970) 6.
8 H. W. Lakin, *162nd Nat. ACS Meet., Washington, D.C., Sept. 1971*, Abstract Water 77, American Chemical Society, Washington, D.C., 1971.
9 N. T. Crosby, *Analyst (London)*, 102 (1977) 225 and references cited therein.
10 A. D. Shendrikar, *Sci. Total Environ.*, 3 (1974) 155.
11 F. J. Schmidt and J. L. Royer, *Anal. Lett.*, 6 (1973) 17.
12 B. L. Dennis, J. L. Moyers and G. S. Wilson, *Anal. Chem.*, 48 (1976) 1611.
13 H. H. Walker, J. H. Runnels and R. Merryfield, *Anal. Chem.*, 48 (1976) 2056.
14 M. McDaniel, A. D. Shendrikar, K. D. Reiszner and P. W. West, *Anal. Chem.*, 48 (1976) 2240.
15 J. A. Fiorino, J. W. Jones and S. G. Capar, *Anal. Chem.*, 48 (1976) 120.
16 J. C. Chambers and B. E. McClellan, *Anal. Chem.*, 48 (1976) 2061.

17 Y. K. Chan, P. T. S. Wong and P. D. Goulden, *Anal. Chem.*, 47 (1975) 2279.
18 F. D. Pierce and H. R. Brown, *Anal. Chem.*, 48 (1976) 693.
19 P. D. Goulden and P. Brooksbank, *Anal. Chem.*, 46 (1974) 1431.
20 Y. Talmi and A. A. Andren, *Anal. Chem.*, 46 (1974) 2122.
21 D. D. Siemer and P. Koteel, *Anal. Chem.*, 49 (1977) 1096.
22 F. D. Pierce and H. R. Brown, *Anal. Chem.*, 49 (1977) 1417.
23 H. D. Fleming and R. G. Ide, *Anal. Chim. Acta*, 83 (1976) 67.
24 R. Belcher, T. Kovimtzis and A. Townshend, *Anal. Chim. Acta*, 68 (1974) 297.
25 C. F. Poole, N. J. Evans and D. G. Wibberley, *J. Chromatogr.*, 136 (1977) 73.
26 Y. Shimoishi, *J. Chromatogr.*, 136 (1977) 85.
27 T. Stijve and E. Cardinale, *J. Chromatogr.*, 109 (1975) 239.
28 K. G. Brodie, *Amer. Lab.*, 9, No. 3 (1977) 73.
29 E. E. Peck, *3rd FACSS Conf., Nov. 1976, Philadelphia, Pa.*, Abstract No. 165.
30 M. Ihnat and H. J. Miller, *J. Ass. Offic. Anal. Chem.*, 60 (1977) 813.
31 W. A. Aue and K. O. Gerhardt, 1972, unpublished results.
32 S. S. Brody and J. E. Chaney, *J. Gas Chromatogr.*, 4 (1966) 42.
33 W. A. Aue and C. R. Hastings, *J. Chromatogr.*, 87 (1973) 232.
34 W. A. Aue and C. G. Flinn, *J. Chromatogr.*, 142 (1977) 145.
35 G. Salet, *C.R. Acad. Sci.*, 73 (1871) 742; *C.Z.*, 42 (1871) 641 (as cited in ref. 38).
36 H. J. Emeléus and H. L. Riley, *Proc. Roy. Soc. Ser. A*, 140 (1933) 378; *C.A.*, 27 (1933) 3400 (as cited in ref. 38).
37 A. Mitscherlich, *Ann. Phys. (Leipzig)*, 121 (1864) 459 (as cited in ref. 38).
38 P. T. Gilbert, in R. Mavrodineanu (Editor), *Analytical Flame Spectroscopy*, Macmillan, London, 1970.