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GAS CHROMATOGRAPHIC-INDUCTIVELY COUPLED PLASMA EMISSION SPECTROMETRIC DETERMINATION OF VOLATILE ORGANOMETALLIC SPECIES

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SUMMARY

Gas chromatography (GC) coupled with inductively coupled plasma emission spectrometry (ICPES) offers a powerful analytical tool for screening volatile organometallic compounds in complex mixtures, such as the products of coal conversion processes. Performance of a GC-ICPES system was evaluated for various organometallic compounds. Studies were also undertaken to explore the formation of volatile organoselenium compounds during gasification of coal spiked with inorganic selenium in the form of selenium sulfide. A number of organoselenium compounds were observed in the gasification by-products of the spiked coal.

INTRODUCTION

The specification of organometallic compounds in environmental samples is experiencing rapid growth due to the realization that total elemental concentration-distribution data is insufficient for assessment of environmental and health problems.

Organometallics may enter the environment through biological methylation of inorganic species in the environment and through human activity¹. Increased utilization of coal derived fuels present another, potentially large, source of environmental contamination with organometallics. Koppelaar and Manahan² reported concern for the potential release of organically associated metal and metalloid by-products of coal conversion. Dahl and Weissman³ detected the presence of lipid-soluble iron, chromium, zinc, and aluminum in coal gasification by-products. Fraley⁴ found trace metals associated with heavy tar and volatile organic fractions in simulated coal gasification. Fish *et al.*⁵ reported the speciation and identification of inorganic and organoarsenics in oil shale retort and process waters from *in situ* gasification.

The potential of tandem gas chromatographic (GC)-atomic emission spec-

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trometry in the analysis of organometallic compounds was recognized early. The interest in this combination was enhanced by the capability to analyze several elements simultaneously. The most extensively studied system of this type is perhaps the gas chromatography-microwave emission spectrometry (GC-MES). Extensive research in this area has been conducted by Uden and co-workers⁶⁻⁹. Successful demonstration of the technique for environmental analysis has recently been reported¹⁰. The success of the microwave emission detector has been attributed to its simplicity, performance and compatibility with the gas chromatograph. However, some difficulties in interfacing the microwave emission detector with a GC system have been reported, these primarily lie with the limited sample handling capabilities of microwave emission detection (MED), thus making solvent venting essential. The use of inductively coupled argon plasma emission spectrometry (ICPES) as an element selective detector for GC was demonstrated by Windsor and Denton¹¹. It was shown that, except for halogens, the detector compares favorably with other emission detectors in terms of sensitivity (detection limit), selectivity, and linear dynamic range. However, while the application of ICPES as an element selective detection system for liquid chromatography is gaining in popularity¹²⁻¹⁷, its application with GC has remained limited. In the present study the combination of ICPES with high-resolution capillary GC was explored. The sensitivity and selectivity of the system were examined for a number of organometallics, organometalloids and volatile derivatives of less volatile metallic species. The system was then applied to characterization of volatile organoselenium compounds formed during simulated *in situ* gasification of coal spiked with selenium sulfide.

EXPERIMENTAL

Equipment

The GC-ICPES system consisted of a bench-top gas chromatograph, Tracor Model 560 (Tracor, Austin, TX, U.S.A.). The chromatograph was equipped with packed and capillary split/splitless injection ports. The gas chromatograph was interfaced to an ICPES, Baird Model PS-1 (Baird, Bedford, MA, U.S.A.). The schematic of the interface is shown in Fig. 1. It consisted of a 1/16 inch O.D. (0.4 mm I.D.) glass-lined stainless-steel capillary tube encased in a temperature controlled heating block. The ICPES optics comprised of a Rowland Circle polychromator and associated electronics to monitor twenty elements simultaneously. However, in the present study only three elements were monitored simultaneously through the use of separate electrometers and strip chart recorders. Entrance and exit slits of 50 and 88 μm , respectively were employed. The carbon emission was monitored at 193.1 nm with a 0.5 m monochromator and photomultiplier tube, while the other elements were monitored with photomultiplier tubes positioned and aligned on the Rowland Circle mount of the polychromator. The position of the plasma torch and movable entrance slit were optimized for each element monitored to enhance sensitivity and minimize interference due to the solvent. A forward power of 1.5 kW was supplied to the load coils of the ICP system by an RF generator operating at 27.1 MHz, Plasma Therm type HFP-2500 (Plasma Therm, Kressen, NJ, U.S.A.). A reflected power of less than 10 W was maintained. Coolant, plasma and sample argon flow of 19, 1 and 0.3 l/min, respectively were utilized.

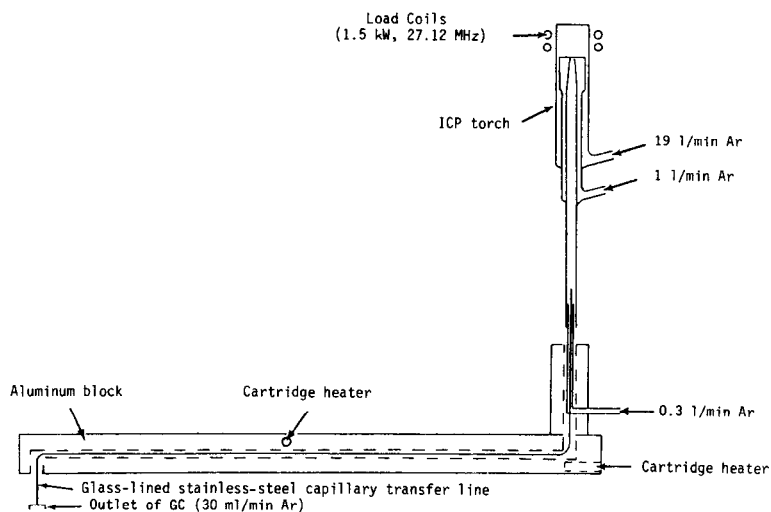


Fig. 1. Schematic of GC-ICP interface.

The chromatographic separations were carried out with a $30 \text{ m} \times 0.25 \text{ mm}$ I.D.) fused-silica capillary column (DB-5; J & W Scientific, Rancho Cordova, CA, U.S.A.). In order to minimize band broadening, the column was pushed through the glass-lined stainless-steel tube such that the column end was approximately 1 cm from the base of the plasma region. Helium was used as the carrier gas, the linear flow velocity was kept at 35 cm/s. In the experiments dealing with characterization of coal gasification products the separations were carried out with a packed column. This column consisted of a $1.8 \text{ m} \times 2 \text{ mm}$ I.D. borosilicate glass tube packed with 5% OV-101 on Chrom W-HP 80-100 mesh. Argon was used as the carrier gas and its flow was kept at 30 ml/min.

Coal gasification

Subbituminous Hanna coal from Wyoming was ground and sieved to 20-60 mesh then spiked with selenium sulfide (Alfa Products, Danvers, MA, U.S.A.) at 1.00 mg Selenium per gram of coal. A schematic of the apparatus used for gasification of coal and collection of samples is shown in Fig. 2. Selenium spiked coal was packed in a quartz tube through which a flow of water saturated oxygen was maintained. The coal in the tube was ignited externally by passing electric current through a nickrome wire, coiled around the quartz tube. Initiation of a forward burn was accomplished by igniting the coal at the end where the oxidant flow enters. In the forward burn the flame front moves with the flow of the oxidant leaving an ash residue. For a reverse burn, the end opposite to the introduction of oxidant was ignited. In this burn mode the flame front moves counter to the oxidant flow and leaves a partially burned char residue. The effluent from the burn tube was passed through a series of traps. The first trap contained quartz wool and was heated in a hot water bath (approximately 90°C). This trap served to remove the heavy tars, etc. which were found to form carbon deposits on the ICP torch. The gases were then bubbled through 10 ml of solvent in a second trap cooled in an ice-methanol bath.

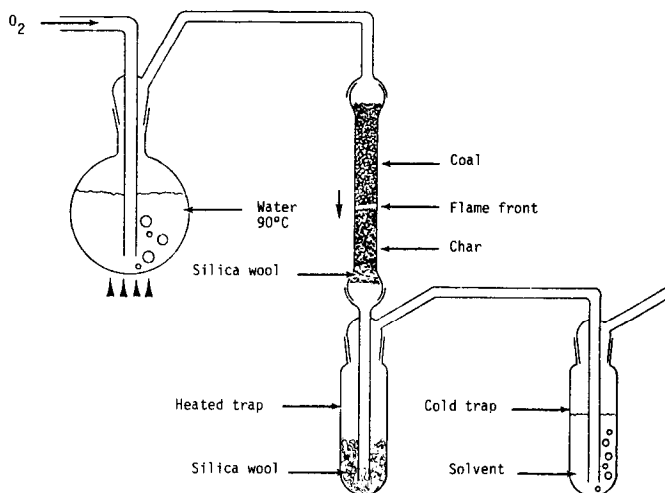


Fig. 2. Schematic of set-up used for gasification of coal and collection of gasification products.

Compounds trapped in the 10 ml of solvent were analyzed by GC-ICP. A third trap identical and downstream from the second trap was used to establish the trapping efficiency for the compounds identified in this study.

Chromatographic grade pentane, heptane and benzene (Fisher Scientific, Fairlawn, NJ, U.S.A.) were used as trapping solvents.

Diethyl selenide, dimethyl diselenide, and diphenyl selenide standards were obtained from Alfa Products (Danvers, MA, U.S.A.).

RESULTS AND DISCUSSION

The chromatographic results obtained with the GC-ICP system are shown in Figs. 3 and 4. Fig. 3 shows the response for 2.5 ng of tetraethyl tin and ferrocene. The response for 250 pg of tetraethyl lead and 15 ng of chromium trifluoroacetate are shown in Fig. 4a and b, respectively. A summary of results obtained for various organometallics is given in Table I.

The utility of GC-ICPES for the separation and detection of organoselenium compounds is shown in Fig. 5. The chromatographic peaks represent 36 ng diethyl selenide, 64 ng dimethyl diselenide and 110 ng diphenyl selenide, as well as a peak for a much larger quantity (approximately 1.5 mg) of hexane (solvent). The selenium emission was monitored at 196.1 nm; the nearest strong carbon emission line is at 193.09 nm. Relative responses for selenium and carbon at 196.1 nm were determined using dimethyl diselenide and heptane at this wavelength. Fig. 6 shows that at 196.1 nm, 11 ng of selenium gives about the same detector response as 1.1 mg of carbon. Selectivity, by weight, for selenium over carbon was found to be $8 \cdot 10^4$. An approximate detection limit for selenium in the GC-ICP system with a packed column was found to be 1 ng, which is an order of magnitude lower than the detection limit found with the capillary column.

Introduction of carbon into the plasma produces molecular emissions attributed to CN and C₂ species, along with the intense 193.09 nm atomic carbon emission.

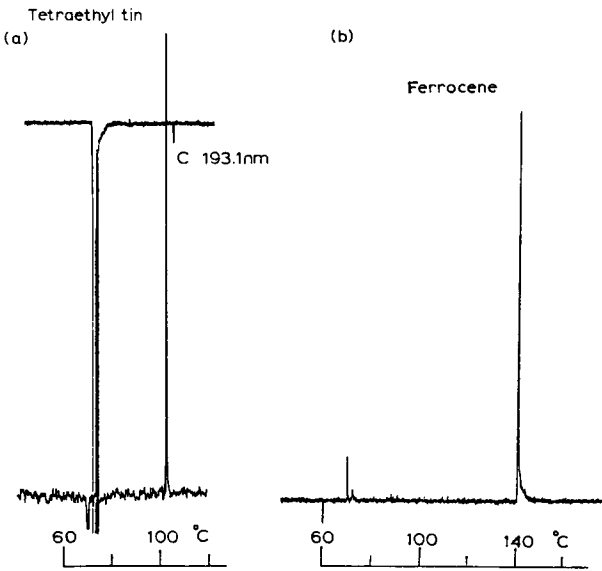


Fig. 3. Chromatograms showing the response with GC-ICP system. (a) Response for 2.5 ng of tetraethyl tin. (b) Response for 2.5 ng of ferrocene. Chromatography was carried out with a 30M SE-54 fused-silica capillary column.

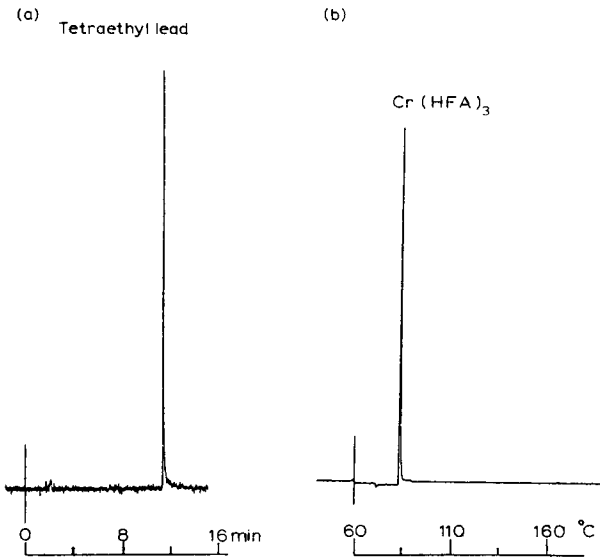


Fig. 4. Chromatograms showing the response with GC-ICP system. (a) Response for 250 pg tetraethyl lead. (b) Response for 15 ng of chromium trihexafluoroacetyl acetate. Chromatographic parameters same as in Fig. 3.

TABLE I
GC-ICPES DETECTION LIMIT AND LINEAR RANGE

Element	Detection limits (pg)	Linear dynamic range	Monitoring wavelength (nm)
Lead	6	$2 \cdot 10^4$	220.3
Tin	25	$1 \cdot 10^4$	189.9
Iron	15	$1 \cdot 10^4$	238.2
Selenium	100	$5 \cdot 10^3$	196.1
Silicon	40	$3 \cdot 10^4$	251.6
Chromium	60	$2 \cdot 10^4$	267.7
Carbon	75	$5 \cdot 10^3$	193.1

These molecular emissions, which do not interfere with the 196.09 nm emission for selenium, are visibly evident in the plasma when a large amount of carbon is introduced.

Fig. 7 shows representative chromatograms with ICP detection of selenium for samples collected during laboratory simulated *in situ* forward burns (A) and reverse burns (B) of coal spiked with selenium sulfide at 1 mg/g of coal. Several selenium-containing compounds can be observed in the products of both burn modes. It should be noted that some selenium compounds elute before the solvent peak, especially in the case of the forward-burn products. These highly volatile selenium compounds were not efficiently collected in the traps. This was borne out by the fact that approximately equal levels of these compounds were found in a second collection trap downstream from the first trap. Loss of these early eluting compounds was also

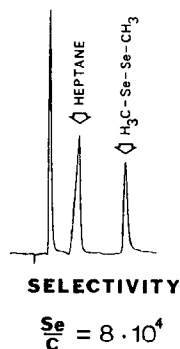
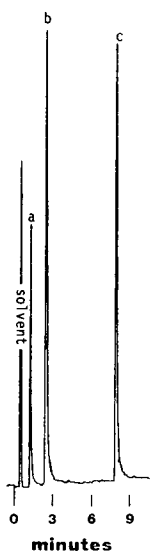


Fig. 5. Chromatography of three organoselenium compounds. (a) 36 ng diethyl selenide. (b) 64 ng dimethyl diselenide. (c) 110 ng diphenyl selenide. Separation was carried out on a 180×0.2 cm I.D. glass column packed with a 5% OV 101 on Chrom W HP 80-100 mesh.

Fig. 6. Chromatogram showing the responses of carbon and selenium at 196.09 nm in the GC-ICP system.

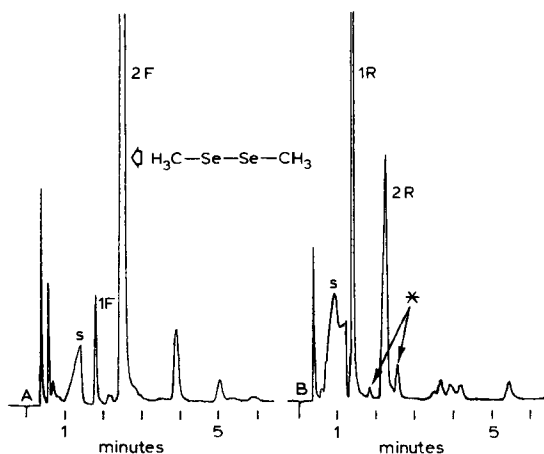


Fig. 7. Chromatography of volatile products of coal gasification. (A) Products obtained during forward burn. (B) Products obtained during reverse burn.

observed from samples stored for several days. Likely candidates for these peaks are H_2Se , dimethyl selenide and other similar low-molecular-weight compounds. However, the identity of these compounds was not confirmed in this study. Selenium compounds eluting after the solvent were efficiently trapped and no losses were observed during a one-week period of refrigerated storage.

A comparison of retention times for peaks in Fig. 7a and b shows that different selenium containing molecules are formed in the forward and reverse burns. Some of the major peaks in the forward burn mode are possibly present as minor peaks in the reverse burn mode. The retention times for two minor peaks denoted by asterices in the chromatogram of the reverse burn effluents correspond to major peaks marked 1F and 2F in the chromatogram of the forward burn products. Furthermore, these chromatograms suggest that larger amounts of organoselenium compounds are produced in the forward burn than in the reverse burn. Quantitation of the peaks obtained from a forward and reverse burn of the spiked coal was carried out using dimethyl diselenide as a selenium standard. Results are expressed as the percent of selenium, originally added to coal as selenium sulfide. These calculations indicate that in the forward burn peaks 1F, 2F and 3F represent 1.6, 3.9 and 0.56% of the selenium spiked as selenium sulfide. Calculations for a reverse burn of selenium sulfide spiked coal gave 1.5 and 0.48% conversion to the compounds represented by peaks 1R and 2R, respectively.

In order to differentiate and identify the type of selenium compounds formed in the two burn modes, the samples from forward and reverse burn were treated with 1 M silver nitrate. The samples were then analyzed by GC-ICP, the results obtained are shown in Fig. 8. The major selenium-containing peaks from the forward burn were lost; however, the peaks of the reverse burn were unaffected, except for those labelled with asterices in Fig. 7, and one other minor peak. These results indicate that the selenium containing products of forward burn are readily removed by silver nitrate, while those from the reverse burn remain unaffected by silver nitrate treatment.

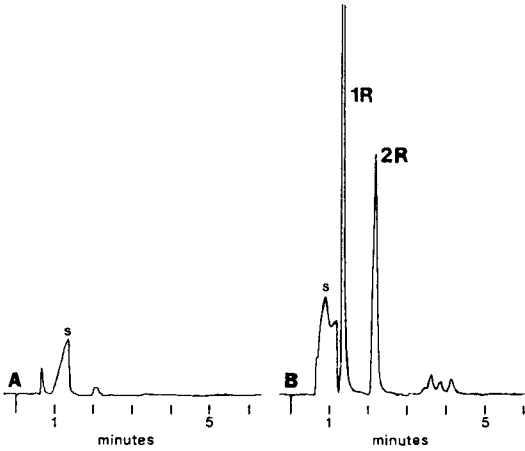
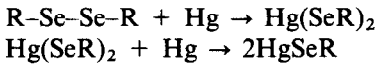


Fig. 8. Chromatography of coal gasification products after treatment with 1 *M* silver nitrate. (A) Products obtained during forward burn. (B) Products obtained during reverse burn.

It has been reported¹⁸ that alkyl diselenides readily form compounds of the type $(R-Se)_2Hg$ on treatment with metallic mercury at room temperature. At temperatures higher than 125°C, these mercury compounds have been reported to decompose back to the diselenide and mercury. A recent study¹⁹ of the polarographic reduction of selenium and sulphur compounds found the following reactions to occur to reduction of organic diselenides and disulfides:



With the above mentioned reactions as a basis, the samples from both the forward and reverse burns were treated with elemental mercury. The results obtained after this treatment are shown in Fig. 9. The results show an increase in Peak 1F and the

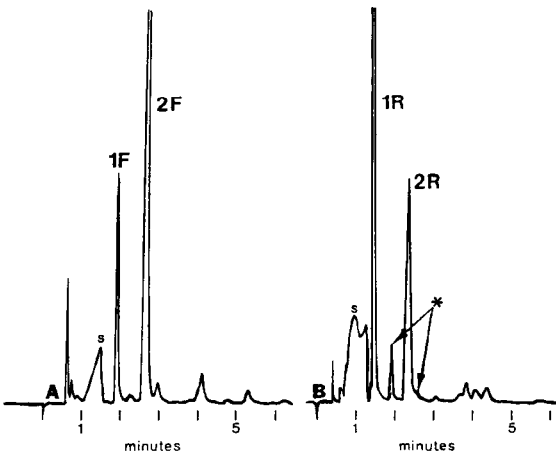
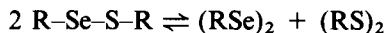


Fig. 9. Chromatography of coal gasification products after treatment with metallic mercury. (A) Products obtained during forward burn. (B) Products obtained during reverse burn.

decrease in peak 2F compared to the corresponding peaks in Fig. 7. The main component peaks from the reverse burn sample were not affected.

Peak 1F was suspected and later identified as dimethyl selenyl sulfide²⁰. Selenyl sulfide species are known to undergo disproportionation²¹, such as



Although the dimethyl disulfide was not positively identified in the study, the presence of this compound is essential to account for the increase in the dimethyl selenyl sulfide upon treatment with mercury.

Since most of the peaks observed in the GC-ICP runs could not be identified by co-chromatography due to the unavailability of standards, the by-products were further analyzed by a GC-mass spectrometry (MS) system. With the aid of GC-MS, peaks 1F, 2F, 1R and 2R were identified as dimethyl selenyl sulfide, dimethyl diselenide, selenophene, and methyl selenophenes, respectively. Similar results were obtained from coal spiked with Na_2SeO_4 . These results are consistent with earlier findings²² that reverse burn by-products are dominated by the presence of aromatics while aliphatic by-products are favored in the forward burn.

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