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SELECTIVE DETECTION OF ORGANOMETALLICS IN GAS CHROMATOGRAPHIC EFFLUENTS BY FLAME PHOTOMETRY*

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SUMMARY

A spectrophotometric channel was added to a regular flame ionization detector and used to determine several volatile organometallics. The minute flame proved capable of exciting a number of atomic species well enough for analytical ends. Both air-rich and hydrogen-rich flames were tested to establish relevant analytical parameters including vertical emission profiles. The hydrogen-rich flame was the preferable one, with sensitivities in the lower nanogram ranges for iron, tin and lead compounds, and strong discrimination against hydrocarbons.

INTRODUCTION

Metals and organometallics are ubiquitous on earth. Their distribution throughout the environment is largely natural, although man has lately been involved in some redistribution, *e.g.* introducing lead into the atmosphere, increasing the level of methylmercury in fish, etc.

Trace analysis of metals or metal compounds has been of interest only to a specialized few from several scientific disciplines—at least till the middle of this century. The realization of its importance to solid-state physics or to biochemical investigations—to name just two areas—has spurred considerably the development of analytical methods. The strongest impetus in this direction, however, coincides with the advent of the environmental panic.

The role of trace elements and their compounds in the human environment became a popular concern. Most of the analytical development it prompted occurred on the "inorganic" side of the fence: atomic absorption and emission with and without flames, nuclear activation, electroanalytical methods. Surprisingly, however, some of the concern also surfaced in gas chromatography (GC).

The analysis of organometallics by GC can be useful to a variety of ends: Determination of metals as chelates, determination of toxic materials from biological

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systems, determination of various additives to technical products, and so forth. In almost every case, a detector selective for the particular metal is highly desirable yet rarely available.

The ideal detector, of course, would be highly sensitive, rugged, fast, linear, and insensitive to temperature programming—besides being selective to any metal chosen at will. This last piece of wishful thinking implies a detector based on mass or light spectrometry.

Among the various detectors used in the GC of metals, the photometric types have probably the greatest—however unfulfilled—potential for inexpensive versatility: The exchange of an interference filter or the small angular displacement of a grating would allow the operator, at least in theory, to "dial-in" the particular metal of interest.

The first photometric detector of GC effluents was introduced by GRANT in 1957[1,2]. It monitored the total emission of a bunsen burner-type flame with a photocell. To obtain selectivity, and better sensitivity, JUVET AND DURBIN[3] adoptèd the large oxygen/hydrogen flame—an excitation source of higher energy and lower background—in conjunction with a spectrometer to the GC analysis of metal chelates. They were able to demonstrate good selectivity by choice of wavelength between hexafluoroacetylacetonates of iron and chromium.

Since that time, the development of photometric GC detectors has progressed considerably—although it was rarely directed anymore toward the determination of metals. ZADO AND JUVET[4] had already used two (photometric) channel operation and other dual- or triple-channel detectors soon became known.

BRAMAN[5] added to the photometric detector a collector electrode for simultaneous detection of the ionization current. Generally, dual-channel operation is of obvious value for analytical purposes, but it also allows some speculation on the nature and interaction of ionized and light-emitting species.

The best-known and most-used of the photometric detectors is no doubt the hydrogen-rich, shielded flame developed by BRODY AND CHANEY[6] for GC. In current models it can give simultaneous triple-channel output: Two interference filter/photomultiplier arrangements detect phosphorus and sulfur via the POH and S_2 bands, and a collector electrode senses changes in electric conductivity. Its selectivity for phosphorus against carbon compounds is surprisingly high (about 20,000), establishing its important role in the area of pesticide residue analysis. It is also sensitive to boron[7] and, one may surmise, may detect other elements as well.

Other types of photometric detectors utilize flames in contact with alkali[8,9], copper[10,11], indium[12,13], or calcium[14], mainly for the selective detection of halides. (All references in this paragraph *inter alia*.)

The flames used in GC detectors can vary considerably in size and energy, all the way from the minute hydrogen/air diffusion flame of the regular FID to the high-energy flames adopted from atomic emission (or absorption) spectroscopy.

There, the steady trend has been toward flames of higher temperature. The importance of strong flames, or other sources of energy, lies in the fact that a sizeable portion of the metal has to be converted from aqueous droplets of its salt solution to free atoms. It was pointed out early that the alternative introduction of metals as volatile organometallics into flames could increase the sensitivity of the method considerably[15].

Given the introduction of metals as gases, for instance as chelates emerging from a gas chromatograph, the energy of the flame could still be expected to play a major role in determining the sensitivity of emission measurements. JUVET AND DURBIN[3,15] consequently used a sizeable oxygen/hydrogen flame as excitation source while MORROW et al.[16] switched between nitrous oxide/acetylene for absorption and oxygen/acetylene for emission measurements.

The only "small" flame used in photometric detection of gas chromatographic effluents is that of BRODY AND CHANEY. It monitors, however, the chemiluminescent POH and S_2 bands above a hydrogen-rich flame, and any deduction therefrom on how well the atomic emission of metals would do, appears to hold little substance. The strong and tall flame would therefore appear the one of choice.

Yet, one can plead in a roundabout way for the puny flame, specifically the flame known from the hydrogen flame ionization detector: It is cheap, relatively stable, and easily managed in mechanical terms. Most important of all, the flame ionization mode can be used simultaneously with the flame photometric mode to obtain a chromatogram of carbon compound distribution. High sensitivity dual-channel operation would be especially helpful when extracts from complex biological or environmental systems are to be scanned for hetero-organic components. The only question is: How well do metals respond in the diminutive FID flame?

In recent studies utilizing indium and tin atomic emissions, we used a regular flame ionization detector modified by the addition of a photometric channel. This FID-cum-FPD arrangement performed remarkably well[17] even though its puny flame could not in the least be compared with the high-energy flames commonly employed in flame emission methods.

The same physical arrangement served in the present study to investigate the photometric detectability of several metals, i.e. organometallics which were available and could be easily chromatographed.

Both air-rich and hydrogen-rich diffusion flames were to be investigated. Their electric conductivity was monitored simultaneously but will not be detailed in this manuscript. The air-rich flame is well covered in the literature and behaved as expected, and the hydrogen-rich flame gave rise to some unexpected results which need to be reported in a separate context.

EXPERIMENTAL

Detector arrangement

The detector is virtually identical to one used in our previous study on the dual-channel detection of tin compounds[17]. A 1/8-in. stainless-steel tube is connected to the GC column exit and serves as the jet tip. It is housed in a cast aluminum cylinder fitted with a quartz window through which the flame can be observed. The slits of a half-meter Jarrell-Ash grating monochromator were removed—giving the spectrometer an effective slit width of approximately 3 mm—and the instrument was focused on the flame. The exit slit assembly carried an RCA IP-28 photomultiplier tube connected to a Keithley 240A power supply at 800 V and a Keithly high-speed picoammeter which, in turn, fed the signal to a 10-mV Leeds and Northrup strip chart recorder.

Emission profiles in the air-rich flame

In order to monitor emission intensities of different flame zones, the detector had to be slightly modified. The quartz window was removed and replaced by an aluminum foil through which a 150 × 3 mm coherent light guide (image conduit purchased from Edmund Scientific) was directed toward the flame. The light guide was twisted 90° in a bunsen burner and painted black on one end, leaving only a 1-mm-wide slit untouched. This end was inserted into the spectrometer's slit assembly such that the 1-mm slit appeared vertical to the spectrometer but horizontal to the flame. The light guide ended a distance of approximately 4 mm from the flame—the closest permissible before the flame assumed a tale-telling yellow. The height of the light guide in regard to the jet tip was regulated by resting it on one jaw of a vernier caliper affixed vertically to the detector housing.

Emission profiles in the hydrogen-rich flame

Since the hydrogen-rich flame detector had to remain gas-tight for obvious reasons, the profile of the flame was measured through the quartz window with the spectrometer inlet slit assembly a distance of 15 mm away from the flame. Black tape was used to form a horizontal slit of 3 mm width at the spectrometer inlet. The spectrometer itself rested on two large labjacks and could be raised or lowered in a level position.

"Shielded" hydrogen-rich flame

In an effort to eliminate possible effects of light reflection from the aluminum housing, the detector inside was blackened with soot from a burning candle, and the flame was shielded in a way reminiscent of the BRODY AND CHANEY construction. A 1/4-in. stainless-steel Swagelock nut was perforated at the bottom to allow free passage of hydrogen, was slid onto the detector jet tip and held at the desired height by a piece of Teflon tubing heat-shrunk onto the jet. Its height was set such that the spectrometer saw the space just above the flame or, alternatively, this space plus the top one-third of the flame.

Detector conditions

The same conditions as reported previously in our study of tin compounds were used for the air-rich flame, namely 335 ml/min of air and 90 ml/min of hydrogen, with a nitrogen flow from the column of 50 ml/min.

Obtaining an efficient, hydrogen-rich flame proved somewhat more difficult. The gas connections to the detector were reversed, such that a controlled mixture of air and oxygen was premixed with the column effluent, and hydrogen was brought in from the detector base. A toggle valve and a fine metering valve were incorporated into the hydrogen line in order to switch the hydrogen on and off without disturbing the preset flow. The flame was ignited by a model airplane glow plug mounted inside the detector housing. One of the disadvantages of this detector arrangement—as compared with the detector described by BRODY AND CHANEY—was its large internal volume (113 cm³). While this seemed acceptable for exploratory purposes, we strongly recommend that any version of this detector intended for routine analysis have a smaller internal volume.

Using a trial-and-error procedure punctuated by a few minor explosions, the

easiest ignition was determined to occur at the following flow-rates in ml/min: hydrogen, 830; oxygen, 120; air, 100; and nitrogen, 50. These flows could be varied somewhat once the flame was lit; however, an oxygen flow of at least 90 ml/min had to be maintained to keep the flame lit during the passage of the 1-μl solvent peak.

Gas chromatography

Gas chromatographic separations were carried out on 3% OV-101 on Chromosorb-W, HP, 80–100 mesh, in a 2-m × 3-mm-I.D. Pyrex column. A carrier gas flow of 50 ml/min of nitrogen was maintained throughout this study.

Initial experiments

A number of commercially available organometallics plus compounds containing phosphorus, sulfur, nitrogen, and a few other non-metals, were used to test responses of the photometric detector mode. The wavelengths of choice were either predetermined by spectral scans of the substance (continuously introduced to the detector in a nitrogen stream) or by checking emission lines or bands reported in the literature[18]. These initial survey experiments served merely to point out a few elements with good response in the photometric mode which could serve to characterize the detector's potential. Organometallics devoid of noteworthy responses were therefore dropped from the list of candidates without regard to the reason of their failure. Experimental conditions for some of the tested compounds can be found in Table I. From these data, four compounds were selected for further study.

Further studies

The compounds selected for further study were ferrocene and tetraethyllead to demonstrate good sensitivity, trimethylphosphate to permit comparisons with the BRODY AND CHANEY detector, and tetraethyltin to relate to our earlier experience. Their emission profiles along the vertical axis of the flame and their minimum detectable amounts were established.

RESULTS AND DISCUSSION

The experiments above were devised with the question in mind whether or not the typical miniscule flame used in ionization detectors held any potential for the photometric detection of various metals. Since "potential" was the key word, we devoted no attention to optimizing instrumental parameters for a particular element.

For instance, the same, inexpensive IP28 photomultiplier tube was used throughout the study; the detector was left essentially unchanged when switching from air-rich to hydrogen-rich operation; and a variety of test compounds were dropped from the list of prospective candidates because of minor difficulties, even though these difficulties may have been chromatographic in nature. It is probable, in fact, that the volatile derivatives of a number of metals would have given analytically useful results if properly treated.

As a completely arbitrary definition, we considered minimum detectable amounts between 1 and 1,000 ng combined with a selectivity against carbon compounds greater than 1,000, as "analytically useful".

Under these criteria, the small hydrogen/air flame showed an unignorable

TABLE I

MINIMUM DETECTABLE AMOUNTS OF VARIOUS HETERO-ORGANICS IN THE AIR-RICH FLAME

Compound	Nominal wavelength (Å)	Solvent	Column temp. (°C)	MDA (ng)
Methylborate	5200	diethyl ether	28	1,200
Trimethylphosphate	5260	acetone	107	80
Dicyclopentadienylnickel	3415	toluene	144	120
Phenylmercuric acetate[a]	4358	methanol	188	5,400
Tetraethyllead	4058	acetone	122	40
Ferrocene	3735	acetone	130	2
Di-n-butyldisulfide	3940	acetone	130	310
Hexafluoroacetylacetonate of Cu(II)	3274	toluene	130	670
Piaselenol	3350	toluene	144	600

[a] This, as well as possibly other organometallics listed, may not be the compound which actually reaches the detector.

potential for the analysis of metals or organometallics. Tables I and II list minimum detectable amounts together with some pertinent instrumental data. Fig. 1 shows the vertical emission profiles for the four selected compounds, acetone, and the background, in a hydrogen-rich flame.

It is apparent even from these very rough curves that the system offers the analyst a great deal of flexibility to adjust selectivities according to the requirements of the sample. Although the data are fairly imprecise due to instrumental difficulties and the averaging effect of the broad slit, they do give a good indication of working ranges. The air-rich flames showed small differences only—phosphorus, iron and tin responded relatively strongly at the bottom and middle of the flame, lead at its tip.

In this system, "sensitivity" as characterized by minimum detectable amounts (MDA) has little to do with absolute response as seen in the emission profiles. For instance, the absolute response is always much greater in the flame than in the area above it. Yet, background current and noise decrease sharply above the flame, too— and the signal/noise ratio may often be better above the flame, especially in its hydrogen-rich form.

While sensitivity does not vary in too wide a range—even when both air-rich and hydrogen-rich flames are compared—selectivity (response of the organometallic

TABLE II

MINIMUM DETECTABLE AMOUNTS OF TEST COMPOUNDS AT VARIOUS FLAME CONDITIONS

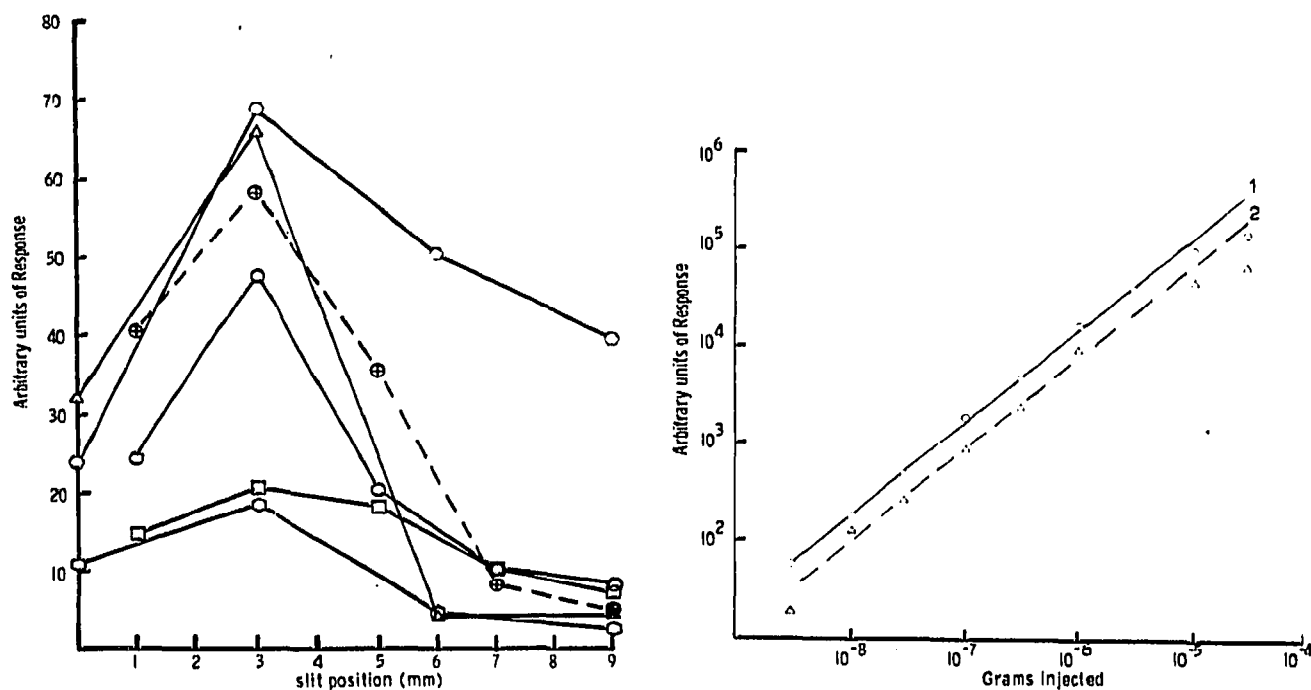| Compound	Nominal wavelength (Å)	MDA (ng)			
		Air-rich total flame	Above H_2-rich flame	Shielded H_2-rich flame	2/3 Shielded H_2-rich flame
Tetraethyllead	4058	40	12	100	
Tetraethyltin	4850	5	5	25	
Ferrocene	3735	2	0.8	5	0.5
Trimethylphosphate	5260	80	24	28	12
Dodecane	4058	4,000	>10,000		
Acetone, 1 µl	5260, 4058			not detectable	

Fig. 1. Hydrogen-rich flame profiles of 1 μg trimethyl phosphate at 5260 Å (O), 1 μg ferrocene/10 at 3735 Å (△), 1 μg tetraethyllead at 4058 Å (□), 1 μg tetraethyltin at 4850 Å (◯), 1 μl acetone at 4058 Å (O), and one half the background response at 4058 Å (⊕).

Fig. 2. Calibration curve of ferrocene in an air-rich flame, monitored at (1) 3650 and (2) 5500 Å.

vs. a typical carbon compound) can vary excessively. Take, for instance, tetramethyllead. Its response in the air-rich flame at 406 nm was not all that could be hoped for, with the MDA 40 ng and the selectivity over dodecane a meager 100. Monitoring the area above the non-shielded, hydrogen-rich FPD improved the MDA to 12 ng and the selectivity to 1,500 (calculated from the solvent peak). The shielded, hydrogen-rich flame, on the other hand, sacrificed sensitivity to an MDA of 100 ng, but the selectivity of lead against carbon now verged on specificity: 1 μl solvent gave no measurable response.

Ferrocene provided a similar case. Its minimum detectable amount in the air-rich flame was 2 ng with a selectivity against acetone of 3,000. Fig. 2 shows a calibration curve under these conditions, taken at two different wavelengths chosen from a spectral scan. The ferrocene response in the non-shielded, hydrogen-rich flame was even better with a minimum detectable amount of 0.8 ng and a selectivity vs. the acetone solvent peak of 8,300. The best choice for an analysis requiring very high selectivity may have been the shielded, hydrogen-rich configuration, where 1 μl of solvent gave no response while 5 ng of ferrocene could still be detected.

It is interesting, furthermore, to compare response ratios between the HPO band of trimethylphosphate and the Fe line of ferrocene in the hydrogen-rich flame. Both species emit predominantly in the flame; above it, however, the iron response drops off much more sharply than the phosphorus response. Thus, the MDA's for trimethylphosphate and ferrocene above the flame were 28 and 5 ng (a 6:1 ratio) compared to 12 and 0.5 ng (a 24:1 ratio) at the flame tip.

It appears obvious that for practical determinations phosphorus should be monitored above the flame. This conclusion was known long ago, of course, as evidenced by the shielded-flame construction of BRODY AND CHANEY[6]. If iron is the element to determine, however, the sensitivity and selectivity required by the sample will decide whether the flame tip or the space above the flame should be monitored.

Speculation though it may be, a comparison of the BRODY AND CHANEY detector with the hydrogen-rich flame used in this study appears to be of some interest. We had included trimethyl phosphate in the list of test compounds expressly because of the commercial availability of that detector and its excellent performance with phosphorus compounds. The BRODY AND CHANEY detector is, indeed, more sensitive to phosphorus by about two orders of magnitude—an effect it owes to a highly sensitive photomultiplier/interference filter combination and to the fact that it was engineered specifically for the detection of chemiluminescence with a hydrogen-rich flame. It is true, of course, that the nature and dissimilar width of molecular bands like the HPO emission *versus* atomic lines like the Fe radiation render any comparison between different means of wavelength discrimination such as the grating spectrometer *vs.* the atomic interference filter a rather difficult task. It appears probable, however—and this is the crux of the matter—that most of the MDA's listed in Tables I and II are relatively high and that they could be lowered significantly by the choice of a system optimized for a particular element. Thus the detector may attract interest for the determination of volatile Fe, Sn, or Pb compounds[19,20].

In summary, the minute hydrogen/air flame typical of the FID, with either air-rich or hydrogen-rich chemistry, shows a definite potential for the determination of volatile metal compounds—a potential which, as yet, appears largely untapped.

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