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Inter-elemental selectivity, spectra and computer-generated specificity of some main-group elements in the flame photometric detector☆

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ABSTRACT

Inter-elemental selectivities (ratios of emission intensities) of some important main-group elements —B, Ge, Sn, Pb, N, P, As, Sb, S and Se— have been measured in a filter-less flame photometric detector (FPD) under one common set of conditions. In cases of unknown, unassigned or doubtful spectral distributions —*e.g.* from B, Pb, N and Sb— luminescences were recorded directly from the detector under analytical operating conditions. Despite the detector's dependence on broad, low-resolution spectra that frequently overlap, a computer algorithm using dual-channel data allowed specific (= infinitely selective) chromatograms to be recorded for any FPD-active element. The spectral requirements of this method, which is based on the conditional access (CONDAC) of slope ratios, were minimal: one optical filter permitted a single computer-stored run to produce several CONDAC chromatograms. Each of these was specific in the sense that it showed only the peaks of one particular element.

INTRODUCTION

A variety of factors have contributed to the ever-increasing presence of complex, multi-element chromatograms in the analytical laboratory. Some factors are task-related, such as the prevailing trend toward environmental and biochemical samples. Others are technique-related, such as the ready availability of high-resolution chromatographics for both volatile and non-volatile organics, and the improvements in sensitivity and scope of various gas chromatography (GC) detectors.

The flame photometric detector (FPD) provides a case in point. The only elements to which it was once considered sensitive were phosphorus and sulphur; and its function was restricted to *gas* chromatographic effluents [1]. In the years since its commercial introduction [2], some twenty elements have been shown to respond in the FPD, and the detector has been used with separation methods for *non*-volatile analytes such as micro-high-performance liquid chromatography and supercritical fluid chromatography. The FPD is often used for surveys —particularly for the presence of compounds containing P, S and Sn— in chromatograms that contain hundreds of peaks.

In such cases it is important to recognize those compounds that contain FPD-active elements, since these are more likely to exhibit biological activity and, consequently, represent the analytes of interest. Beyond the mere recognition that *some* hetero-atom is present in a particular peak, its identity has to be established. This means that inter-elemental selectivity and, if attainable, element-specific response become crucial quality parameters.

We have recently studied comparative FPD spectra as well as FPD selectivity ratios of various *transition* elements from conventional (interference-fil-

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ter equipped) and open (filterless) detector channels [3,4]. We have also suggested dual-channel methods to improve that selectivity for compounds of Mn, Ni, Fe, Ru, Os, etc. [4–6]. In the present study we intend to explore selectivity among *main-group* elements, and to devise approaches of increasing their selectivity to apparent specificity. Note that the terms "selectivity" and "specificity" retain here their original analytical meaning, *i.e.* "specificity" indicates infinite selectivity and, derived from that, "apparent specificity" refers to a situation where compounds of only one particular element appear on the chromatogram.

While specificity, thus defined, is a simple and unambiguous term, the term "selectivity" can have several meanings. Traditionally, selectivity ratios in flame photometric detection of GC effluents have been used to compare the response of a particular analyte element within a narrow wavelength range (typically a 10-nm interference filter bandpass) to that of a hydrocarbon. Comparison with another FPD-active element was rare. Not surprisingly, then, the detector conditions of these literature measurements were most often those at which the element of primary interest exhibited the highest signal/noise ratio (rather than, say, the conditions at which it displayed the largest discrimination against some other species).

Current interest in *multi*-element mixtures suggests the determination of inter-elemental selectivity ratios at conditions that are deliberately not optimized for one particular element, but that suit as many elements as possible. Among the earlier investigated transition metals, individually optimized flame conditions did not differ excessively from one element to the other [3]. Also, the luminescence of many elements did spread out over most of the photomultiplier's spectral range, thereby severely curtailing attempts to improve selectivity by spectral means alone. In fact, the selectivity among transition metals proved to be much more a function of their comparative overall emission intensities ("innate" sensitivities) than a function of the —however carefully chosen— wavelengths of the various interference filters deployed to monitor each metal individually. The increase in various selectivity ratios from a channel that is open to the full spectrum, to one that is restricted to a narrow bandpass, was usually less than ten. In contrast, the comparative luminescence yields of the transition elements varied by several *powers* of ten [5].

Main-group elements could be expected to behave likewise. Spectra from different elements do differ by several orders of magnitude in intensity. And, more often than not, their wavelength ranges overlap severely. As a historical example, the interference of S_2 bands —which stretch over and beyond the HPO emission range— caused the earliest interference problem in the FPD. Even at that time, its solution involved a *dual*-channel approach [7] (*cf.* ref. 8). For any method that relies on two or more simultaneous chromatograms being obtained under different optical circumstances, spectra valid *at the analytical operating conditions* of the detector are needed for a rational choice of wavelengths to monitor. Only a few of the more prominent emissions —S_2, Se_2, HPO, SnH, SnOH and the like— have been obtained from a conventionally operating FPD.

A complete account of interelemental selectivity, even at one and the same set of conditions, can only be provided by the full ranges of all calibration curves. If single-number selectivity ratios are to serve instead —as they are often asked to do, for instance in this report— the data must at least be taken from within the linear range of *both* elements. To illustrate: deceptively high metal/carbon selectivity ratios have resulted when hydrocarbon standards were used in amounts beyond their linear range.

Selectivity ratios (of linearly responding elements) are traditionally defined as ratios of response produced by injecting *equal amounts* of elements (or compounds). Alternatively, selectivity ratios are defined as those ratios of injected amounts that produce *equal response*. These definitions correspond, of course, directly to the vertical and horizontal distances between calibration curves plotted in log–log format. Since luminescence intensities cover several orders of magnitude (*i.e.* more orders than the typical linear range), the latter mode of measurement is called for. Also, "mol of element per second" data are used here for analytical convenience.

Beyond the necessary mapping of "innate" selectivities, we were interested in upgrading these selectivities to apparent specificities. This proved possible by letting a computer decide which dual-chan-

nel signals did and which did not originate from a particular element — and directing it to report only the latter. This "conditional acceptance" or "conditional access" (CONDAC) chromatography has been used before [6], although then focused on transition elements and hampered by a still awkward computational procedure. The present study retains the basic principle but uses a direct, simple and more convenient CONDAC-type algorithm on main-group elements.

Now, the conditional acceptance of a particular chromatographic peak is based on the agreement of its ratio of response from the two channels with the "true" value determined previously from an appropriate standard. Thus, if R_A and R_B be the responses (signals, peaks) and S_A and S_B their slopes (first differentials, changes in signal with respect to time) in channels A and B, data pairs are accepted on condition that

$$(S_A - f \cdot S_A) < S_B \cdot SR < (S_A + f \cdot S_A)$$

wherein f is a (user-selectable) factor defining the allowable deviation from the "true" slope ratio SR (ratio of emission intensity changes in the two channels during elution of the hetero-element standard). To be accepted into the CONDAC chromatogram, each peak has to contain a certain percentage (typically 50 to 90%) of data pairs already accepted by the above algorithm. These pairs must stretch over a reasonable time interval (typically 1 to 4 standard deviations of the average Gaussian peak), besides conforming to certain obvious criteria like starting with an increase in positive slope. The data pairs of an accepted peak can be averaged

$$R = (R_A + R_B \cdot SR)/2$$

but the choice of either one or the other single channel is also available to the analyst. All three response modes can be plotted directly or after multiplication by a user-selected scaling factor for convenient recorder display. A "zero" (= "no information") line obtains for data pair sequences failing to gain access.

This approach requires prior knowledge of the slope ratio SR. So far, its value has been determined, very roughly, from peak heights —or, much more precisely but also much more slowly, from an operator-adjudicated iterative matching of peak shapes [4,6]. In this study, the slope ratio average is determined from a "standard peak" on the screen, whose beginning and end (its calculation limits) are defined by the operator through the use of vertical cursors.

The "standard peak", from which the slope ratio is to be determined, can be introduced internally or externally. As an internal standard, the peak is a constituent of the chromatogram under investigation; as an external standard, it has been measured earlier. As is generally the case for chromatographic standards —*e.g.* those of retention or calibration— *spectral* standards, too, provide better analytical performance when used internally than externally. The more demanding and variable the chromatographic circumstances, the more important and decisive the role of the internal standard. It may be mentioned that slope ratios, their "true" value notwithstanding, can be adjusted in their error-band to provide maximum protection against interference from other hetero-elements.

The obvious questions to be answered in regard to the new algorithms are how reliable and convenient they work, how well they suit main-group elements, and how sophisticated the optical discrimination of the dual-channel FPD system has to become in order to result in specific chromatograms.

The objective here is to show that even the simplest of spectral differences between the channels (one channel being used with, the other without, a filter) is enough to allow CONDAC chromatograms for several main-group elements to be obtained from a single chromatographic run. In other words: the objective is to demonstrate that apparent specificity can indeed be extracted from an experimental situation of very limited selectivity. Necessary for achieving and assessing success in this venture is, of course, a thorough knowledge of the analytically relevant spectra and their comparative intensities. Even beyond CONDAC chromatograms, these should be of basic interest to both spectroscopists and analytical chemists.

EXPERIMENTAL

The program used to process the inputs from the dual-channel FPD, and to produce element-specific chromatograms, was assembled for this study by building on the relevant sections of three existing programs. The first, named CHROM, is a laborato-

ry-developed, general-purpose, high-resolution program for the acquisition and manipulation of dual-channel data [4]. From it were taken the input/output functions and the zoom and digital-filtering modes, plus statistical diagnostics that define noise in Gaussian terms for determination of detection limits (*cf.* ref. 3). The second program, BC, had originally been adopted from the common domain and provides a cubic-spline manual baseline correction useable on CHROM data. The third program, CORR, is a laboratory-developed, special-purpose correlation algorithm designed to compare amplitude-matched two-channel peaks for conformity of the first and second differentials [6]; it was further adjusted and augmented by the new routines described in the Introduction.

The dual-channel data, as received from the (modified) Shimadzu electrometers, were converted to digital pulse trains by a laboratory-made interface [4] and, after counting at 0.1-s intervals, were processed by a 12 mHz AT-compatible computer equipped with 1 megabyte of memory, 40 megabyte hard disk, 80287 math coprocessor, VGA display adapter and Multi-Sync monitor.

The gas chromatograph, a Shimadzu Model GC-4BMPF, was used with a short packed column (100 · 0.3 cm I.D. glass, 5% OV-101 on Chromosorb W, 100–120 mesh) under a nitrogen flow of 20 ml/min and temperature-programmed conditions. The Shimadzu dual-channel FPD (with its quartz chimney normally left in place, in contrast to earlier work with transition metals [3,4]; and with its flame shield down for viewing the unshielded flame) was run at the "*common*" conditions of *200 ml/min hydrogen and 45 ml/min air* (unless otherwise indicated) under an efficient exhaust duct. The two photomultipliers were both Hamamatsu R-374 tubes. These have a nominal 180–850 nm range with maximum yield at 420 nm; and were run with a roughly signal/noise ratio-optimized supply voltage (for instance, *ca.* 550 V for the comparatively large light input of an open, *i.e.* full-spectrum channel). For the acquisition of spectra, two types of instruments were used depending on the light level available from the typical FPD operating conditions. Both the quarter-meter grating monochromator (Jarrell-Ash Model 82-415) and the variable interference filter (Oriel Model 7155 "filter monochromator") employed a Hamamatsu R-1104 (180–850 nm, 420 nm maximum) photomultiplier tube. Interference filters were mostly Ditric stock items; where their optical specifications are relevant they are indicated in the legends.

The compounds used for the determination of innate sensitivities/selectivities are listed in Table I; they were used without further purification and in amounts commensurate with their linear range in the FPD.

RESULTS AND DISCUSSION

Our choice of particular main-group elements for this study is, to a certain extent, arbitrary. Some main-group elements have never been seriously tested for response in the FPD. Others are known to respond —*e.g.* In, Bi, Te— but are excluded here for lack of general importance or analytical interest, or for the commercial scarcity or premature decomposition of the compounds supposed to carry them through the GC system. Still others —*e.g.* Cl, Br, I— are disregarded here because they respond adequately only in the presence of another metal (Cu, In, etc.). Of the remaining elements, the ones slated for present scrutiny are primarily those that do hold (or could hold) wider interest, that do occur (or could occur) in environmental samples, and that —most important for us— are inexpensive to acquire, easy to handle, and convenient to test.

Our choice of conditions, too, is somewhat arbitrary. Different elements do respond best at *differ-*

TABLE I

COMPOUNDS USED FOR DETERMINATION OF SELECTIVITY RATIOS

Note: The calculation uses moles of *element*, not moles of *compound* (*cf.* S, Se, B, C).

Sn	*n*-Tetrabutyltin	$(n\text{-}C_4H_9)_4Sn$
Ge	Tetraethylgermanium	$(C_2H_5)_4Ge$
P	Triethylphosphate	$(C_2H_5O)_3PO$
S	*tert.*-Butyldisulphide	$(tert.\text{-}C_4H_9)_2S_2$
As	Triphenylarsine	$(C_6H_5)_3As$
Se	Dimethyldiselenide	$(CH_3)_2Se_2$
Sb	Triphenylantimony	$(C_6H_5)_3Sb$
Pb	Tetraethyllead	$(C_2H_5)_4Pb$
B	*o*-Carborane	$1,2\text{-}H_2C_2B_{10}H_{10}$
N	*n*-Tributylamine	$(n\text{-}C_4H_9)_3N$
C	*n*-Hexadecane	$n\text{-}C_{16}H_{34}$

ent flow settings. (In addition, absolute and relative elemental responses depend on the construction of the detector.) However, since response variations with flow are rarely exorbitant, and since inter-element selectivity properly comes into play only if two or more FPD-active elements are to be considered, we felt that using a *common* set of conditions was both more realistic and of greater value to the analyst than comparing data that were separately optimized for each particular element. Still, in an experimental detour we did indeed optimize performance for individual elements, but only to ascertain that their optimized settings did not differ drastically from the "common" conditions (see Experimental) selected to accommodate all of them.

In this context two special groups of elements need to be mentioned. Tin (also germanium) can produce a blue luminescence on the surface of quartz [9]. This luminescence is far more intense than the SnOH and SnH (or GeOH and GeH) emissions, and it is easy to obtain from an HCl- or HBr-doped chromatographic system [10]. In a recent study involving butyltins in a mussel sample, for instance, the surface emission proved about a hundred times more sensitive than the commonly used hydride band [11]. However, the surface emission requires for maximum presence the careful adjustment of conditions, and the absence of (larger amounts of) elements such as phosphorus that "poison" the quartz surface. These circumstances were not compatible with our testing protocol. The more sensitive blue emissions of tin and germanium were therefore deliberately minimized in this study, primarily so by removing the quartz chimney.

Certain elements (*e.g.* boron and arsenic) noticeably increase in signal and, more importantly, also in signal/noise ratio as the air flow increases toward stoichiometric. If such conditions were chosen for a multi-element analysis, the selectivity ratios would change significantly (for instance, B and As response would become stronger while P, S, and Sn response would become weaker). It should be mentioned in this context that arsenic can produce a vastly superior response in a special detector configuration [12].

Solely for this study it would not have been necessary to check and, in some cases, to chart the actual spectra. Yet, knowing these made the task of wavelength selection so much easier —and, beyond this study, such knowledge can be extremely helpful for designing solutions to various FPD selectivity problems. Also, certain spectral features, by virtue of not having been reported before, may attract the interest of the spectroscopist. As discussed earlier [3], analytically reliable spectra should originate from the same detector as used in the actual analysis, running at the same operating conditions. Some such spectra —HPO, S_2, etc.— have been amply documented in the literature and will not be reproduced here. However, for purpose of discussion we need to record the luminescences generated in the FPD by compounds of boron, lead, nitrogen and antimony. Note that the following spectra were obtained by repeatedly injecting the analyte while manually advancing the monochromator's wavelength drive; they are hence free of flame background emissions.

Spectra

Boron. The green flame bands of boron have been studied for over one-and-a-half centuries, and much analytical work has been done with them [13]. Boron spectra are included here only because of the analytically as well as spectroscopically relevant presence in the FPD of *two* emitters; and because the relative contributions of the latter, not surprisingly so, do change with the air flow. The two analytical studies [14,15] closest related to the present context both mention the *ca.* 546 nm emission (and interference filters with central wavelengths of 550 and 546 nm, respectively); they attribute the band to BO. It is interesting to note that Braman and Gordon's "borane monitor" ran with a flame that was air-rich and much larger than that of a typical FPD. For sensitivity reasons, the monitor seems to have actually used a green glass filter [14] (the text is ambiguous on that point). Sowinski and Suffet's work on the Melpar FPD preferred an interference filter; their smaller flame (as judged by the conditions given for the calibration curve) was hydrogen-rich but just barely so [15]. Neither study shows a spectrum. Pearse and Gaydon [16], with some historically justified hesitation (*cf.* ref. 17), list the 546-nm band under "boric acid fluctuation bands, BO_2". They note that "BO bands are usually present as well" (the closest bands of the BO α system occur at 551 and 555 nm [16]).

Indeed, the spectrum taken at our "common"

FPD conditions (Fig. 1, upper part) represents a mixture of systems. If the flame is changed to consume more air, almost up to stoichiometry, the spectrum (Fig. 1, lower part) takes on the appearance of a single system whose bands coincide with those listed for BO_2 [16], $A^2\Pi_u$–$X^2\Pi_g$. The additional spectrum present in the upper part of Fig. 1 is the α system of BO, $A^2\Pi$–$X^2\Sigma^+$. A comparison of the two scans shown in Fig. 1 provides an instructive example of the strong influence FPD flame conditions exert on the spectral distribution, hence the choice of wavelength (or *vice versa*, depending on the optimization mode). This is important not only for spectroscopic assignments but also for the objectives of *this* study: spectra representing more than one emitter alert the analyst to a likely change in the dual-channel slope ratio with a change in detector gas flows.

Lead. Fig. 2 shows the luminescence obtained from injections of tetraethyllead, at the "common" conditions of this study. Some bands are superimposed on a continuum (whose relative contribution grows as the air flow is lowered —*i.e.* under those filterless conditions that produce the maximum signal/noise ratio). The presence or absence of the quartz chimney seems to be of no importance. There is little if any evidence of the 405.8 nm line (*cf.* ref. 3 for energy considerations) that has been used in the photometric detection of lead in gasolines samples fed to an oxyhydrogen flame [18]. The response of lead in a typical FPD has been mentioned before in the literature [19]; however, no spectral data were given there.

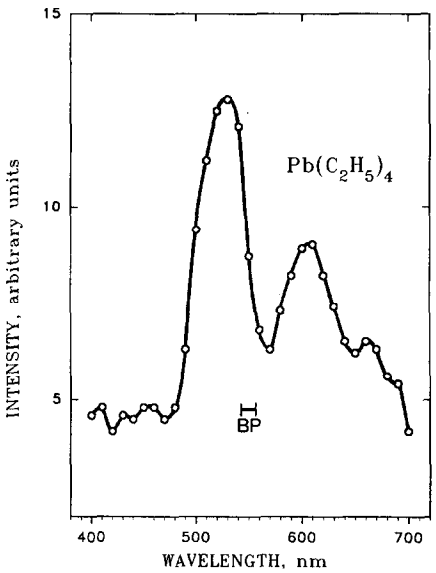

Fig. 2. Spectrum from tetraethyllead at "common" conditions. Filter monochromator with R-1104 PMT. BP = Bandpass (as per Oriel specification).

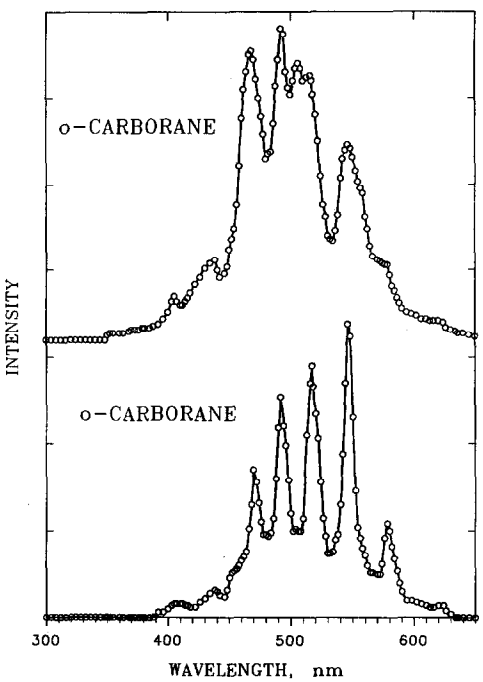

Fig. 1. Spectra from *o*-carborane at "common" conditions (upper part; bandpass 6–7 nm); and close to stoichiometric conditions (lower part; hydrogen 47, air 100, nitrogen 20 ml/min; bandpass 1.6 mm). Grating monochromator, Hamamatsu R-1104 photomultiplier tube.

The low light level (consequently the poor resolution) prevents a possible spectroscopic assignment. The PbH bands could be involved, but the B system of PbO also occurs in that region [16]. Analytically (not spectroscopically) interesting may be the fact that the maximum luminescence of lead is located very close to that of phosphorus, which is conventionally monitored as HPO at 526 nm.

Nitrogen. Fig. 3 shows the flame luminescence due to the introduction of indole. There is no significant difference in the spectra taken with and without the quartz chimney. That this weak luminescence does not originate from the carbon part of the molecule is obvious from the fact that it can also be

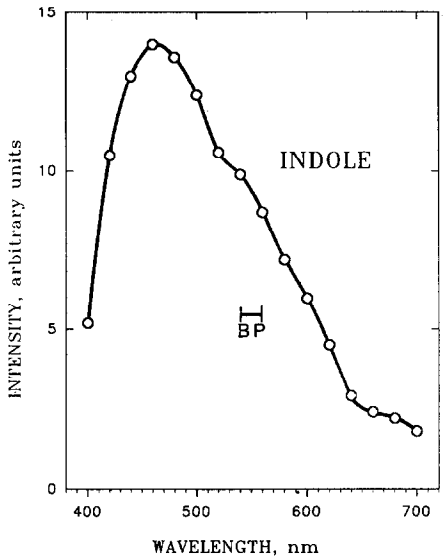

Fig. 3. Spectrum from indole at "common" conditions. Filter monochromator.

obtained from N_2O. The low intensity of organonitrogen response is probably the reason that, to our knowledge, it is not described by any detailed report in the FPD literature, despite the fact that nitrogen compounds are ubiquitous constituents of environmental and biological samples.

For the history of direct and indirect nitrogen emissions in flames, Gilbert's detailed account [13] should be consulted; we shall cite here only information that is of particular relevance to the FPD. The interference of nitrogen compounds in the "borane monitor" (a device related to the FPD) was attributed to the NH_2 α bands [14], and a later paper by the same author contains a spectrum and a comparison of the response of nitrogenous *vs.* carbonaceous compounds. The spectrum presented there for triethylamine [20] shows a certain similarity with the luminescence envelope of Fig. 3; however, it is clearly located farther toward the red. The same is true of the spectrum shown for ammonia in a hydrogen-nitrogen diffusion flame [21]; and of the "bright, white" emission in the molecular emission cavity analysis (MECA) oxy-cavity tentatively attributed to the NO–O continuum and monitored for analytical purposes at 500 nm [22]. Interestingly enough, the same study also contains the spectrum of a "faint blue" emission [22, Fig. 1A], which was obtained in the absence of additional oxygen and closely resembles the one obtained by us in the FPD (see Fig. 3). In a hydrogen–nitrogen diffusion flame —where the 336-nm NH band was most prominent and was therefore used for the detection of ammonia— "the wavelength of maximum emission for the NH_2 band varied between 425 and 575 nm". Viewed on a long-slot burner, "a persistent blue emission" was observed at the base of the flame and (with larger amounts of ammonia) a "yellow emission" appeared above it [23].

Note that all these literature flames were oxygen (air) rich; and that, with the possible exception of the regular MECA cavity, they were much hotter than the puny, strongly hydrogen-rich flame of the FPD. Under the "common" conditions of this study, the highest temperature of the FPD flame, as suggested by the response of a thin-wire thermocouple, remained below 550°C. Different emission behaviour is thus to be expected, although both hydrogen-rich and air-rich types of diffusion flames do, of course, contain all three of hydrogen-rich, stoichiometric and air-rich zones. Furthermore, the spectral distribution (wavelength of maximum emission) is likely to vary if two or more chemiluminescent emitters of roughly comparable strength are present.

It may be reasonably assumed that the weaker *blue* emissions referred to in refs. 22 and 23 came from cooler and more hydrogen-rich flame zones and hence were more likely to correspond to the emission shown in Fig. 3. Equally reasonable is the assumption that more than one excited species contributed to the luminescence in the 400–600 nm region, particularly so in the hotter flames of the literature. In several of our own experiments, in which constant doping levels of N_2O entered a variety of FPD flames monitored by a grating monochromator, we, too, found slightly shifting spectral envelopes. The relative and absolute hydrogen and air flows of these FPD flames varied from very hydrogen rich up to almost stoichiometric; and their temperatures from very low to moderately high. At larger air flows and hence hotter conditions, the slight shoulder around 550 nm (see Fig. 3) became more pronounced and, as a consequence, the emission maximum appeared to shift slightly toward the red. This is consistent with the literature behaviour of various types of much hotter flames [14, 21-24], for which visible nitrogen emission occurs at clearly

longer wavelengths than in the conventional FPD.

Neither the NH_2 bands [16] nor any of the other nitrogen emissions commonly found in high-energy sources [13, 16] could be clearly attributed to the FPD luminescence shown in Fig. 3. The 300–400 nm region (which, in typical spectroscopic flames, contains CN and NH bands) was scanned in separate experiments but contained little radiation short of some flame background (OH). Although the presence of NH_2 and/or NO_2 [16] emissions cannot be excluded, we prefer to characterize nitrogen response in the FPD as still being of *unknown* (and possibly mixed) origin. Since the spectral range happens to overlap the emission regions of several important elements —though with low intensity— nitrogenous analytes should be considered capable of causing false positives in various types of FPD-based analyses.

Antimony. Fig. 4 shows the spectrum derived from the luminescent response of triphenylstibine. From a low-temperature hydrogen diffusion flame, a similar spectrum was obtained [25] and attributed to the A system of SbO, particularly $A^2\Pi_{3/2}$–$X^2\Pi_{3/2}$ [16].

For comparison only, we are including in Fig. 4 the spectrum derived from triphenylarsine. It appears to be the long-known "arsenic continuum" [13], similar to the emissions recorded from a laboratory-made FPD [12] and a low-temperature hydrogen diffusion flame [25]. The emitter is generally considered to be unknown (although in some places it is referred to as AsO). We also attempted to check triphenylbismuthine (*cf.* ref. 19) but, encountering problems of reproducibility and contamination, soon gave up.

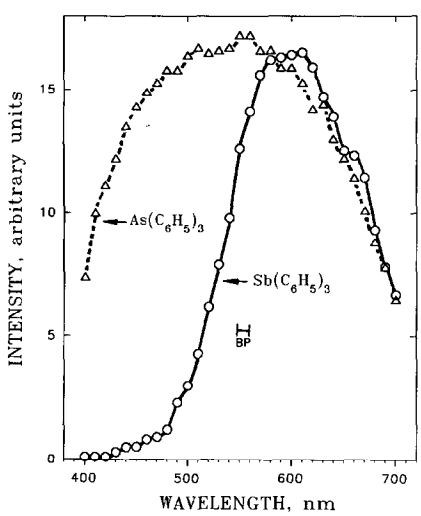

Fig. 4. Spectrum from triphenylantimony and triphenylarsenic at "common" conditions. Filter monochromator.

Selectivity ratios

Table II presents a listing of "innate" selectivity ratios, *i.e.* the ratios of luminescence intensity from an "open" (filter-less) channel. The data describe how much more light the (red-extended) phototube picks up per atom of a particular element (listed vertically) than per atom of another element (listed horizontally). (Sulphur and selenium are included here even though their calibration curves are non-linear, hence inadequately characterized by a single-number selectivity ratio. To compensate in a minor way, their injected amounts are listed in a Table II footnote.)

No untoward surprises lurk in Table II. Clearly, different flow conditions would have lead to a somewhat different set of numbers. Such numbers are valuable for predicting relative elemental responses from a multi-element sample monitored by a *filterless* FPD channel. Given, in a particular case, knowledge of the prevailing spectra on one hand and specifications of interference filters and photomultiplier tubes on the other, the numbers of Table II could be further extended to estimate detector performance from a *spectrally selective* channel. (As will become apparent later, the difference between a channel that is equipped with an interference filter and one that is not, is often quite small.)

Although our measurements and calculations used a minimum of two significant digits, only one digit is shown in the final result. This is meant to remind the reader of further aspects that influence such numbers. Some are obvious, such as the construction or contamination of the detector, and the response profile of the chosen photomultiplier tube. Others are less obvious, such as the question whether some of the chosen test compounds perhaps suffered from premature decomposition; or whether different compounds of the same element would have given different results. For instance, it is well known that aliphatic carbon responds less strongly than aromatic carbon; and the debate whether the

TABLE II

INTER-ELEMENT FULL-SPECTRUM FPD SELECTIVITIES OF MAIN-GROUP ELEMENTS UNDER COMMON CONDITIONS

Molar response of element A (column) over molar response element B (row); both within linear range. "Common" conditions as cited in Experimental section.

Element A	Element B										
	Sn[a]	Ge[a]	P	S[b]	As	Se[b]	Sb	Pb	B	N	C[c]
Sn[a]	"1"	6	$4 \cdot 10^1$	$(9 \cdot 10^1)$	$6 \cdot 10^2$	$(6 \cdot 10^2)$	$2 \cdot 10^3$	$6 \cdot 10^3$	$2 \cdot 10^4$	$3 \cdot 10^4$	$9 \cdot 10^6$
Ge[a]		"1"	8	$(2 \cdot 10^1)$	$1 \cdot 10^2$	$(1 \cdot 10^2)$	$4 \cdot 10^2$	$1 \cdot 10^3$	$4 \cdot 10^3$	$6 \cdot 10^3$	$2 \cdot 10^6$
P			"1"	(2)	$1 \cdot 10^1$	$(1 \cdot 10^1)$	$6 \cdot 10^1$	$1 \cdot 10^2$	$6 \cdot 10^2$	$7 \cdot 10^2$	$2 \cdot 10^5$
S[b]				"1"	(7)	7	$(3 \cdot 10^1)$	$(6 \cdot 10^1)$	$(2 \cdot 10^2)$	$(3 \cdot 10^2)$	$(1 \cdot 10^5)$
As					"1"	(1)	4	$1 \cdot 10^1$	$4 \cdot 10^1$	$5 \cdot 10^1$	$2 \cdot 10^4$
Se[b]						"1"	(4)	$(1 \cdot 10^1)$	$(4 \cdot 10^1)$	$(5 \cdot 10^1)$	$(2 \cdot 10^4)$
Sb							"1"	2	$1 \cdot 10^1$	$1 \cdot 10^1$	$4 \cdot 10^3$
Pb								"1"	4	5	$2 \cdot 10^3$
B									"1"	1	$4 \cdot 10^2$
N										"1"	$3 \cdot 10^2$
C[c]											"1"

[a] Mainly Sn. H and SnH; or GeOH and GeH emissions; the more sensitive blue surface luminescence on quartz is deliberately held to a minimum.

[b] Sulphur and selenium have mostly quadratic calibration curves. For this reason, their values are given in parentheses; they refer to $9 \cdot 10^{-12}$ or $1 \cdot 10^{-10}$ mol/s of S or Se, respectively.

[c] Hydrocarbons produce negative response (inverted peaks) at the chosen conditions with a red-extended phototube.

response of sulphur does indeed vary with the nature of its functional group, has not yet subsided. Beyond these elements, though, we are not aware of any other glaring case where an element's FPD response would strongly depend on its original valence state and/or molecular surroundings. (A reviewer of this manuscript pointed out a report to the contrary, which describes the behaviour of nitrogen in ammonia as opposed to amines [26]).

Apparent elemental specificity

CONDAC chromatograms can perform a variety of tasks. One of the easiest is to distinguish between two congener elements whose spectra overlap (*e.g.* S and Se, As and Sb, etc.), or between two emitters whose low-resolution spectral envelopes closely resemble each other (*e.g.*, surprisingly, Se_2 and GeOH). Once the relevant FPD spectra are known, the choice of wavelength becomes trivial. Incidentally, this type of analytical situation can also be handled —though to different ends— by *non*-conditional dual-channel FPD algorithms [4]. Being fairly obvious, it needs no further belaboring.

Somewhat more interesting for us (and, we hope, more revealing for the reader) are situations in which several hetero-atoms appear at different positions in the chromatogram; and in which only one gas chromatographic injection, *i.e.* only one spectral setting, is used. (Should multiple injections be permitted, optical changes be possible, and spectral distributions be known, the task of distinguishing among the elements simply reduces to repeats of the process suggested in the preceding paragraph.)

Particularly in the case of samples that are not only in short supply (so that every injection counts) but that are also undefined in regard to the elemental composition of their components (so that a survey-type analysis is called for), the smallest reasonable extent of optical discrimination can ensure that none of the possibly present FPD-active elements is overlooked. Typical for such a low-resolution mode is the combination of one channel without filter (an "open" channel) with another one using only a wide-band or a long- (or short-)pass filter. Another reasonable mode (checked out but not reduced to a figure here) is the combination of a long-pass with a short-pass filter, whose transmission ranges may overlap to a major or minor degree. Even the use of

stable colour glass filters would seem quite suited to the purpose (as long as sharp cut-offs are not required for a particular analytical task). Because such configurations are spectrally much less discriminating than, say, two channels equipped with two narrow-band interference filters, they should help to demonstrate how far the optical conditions can be relaxed in the CONDAC approach. Modes that make use of longer sections of the available wavelength range can also produce higher sensitivity for a larger number of elements. Both of these considerations are reflected in the protocol for the CONDAC demonstration experiments of this study. A further consideration was to use not just one but several peaks containing the *same* hetero-element. This tests the reliability of the CONDAC algorithm: all of the peaks that contain the target element (but none of the peaks that do not) must be present in a *bona fide* "element-specific" chromatogram.

Analyte mixtures and spectral conditions designed along these lines are involved in the following three figures. In each case will the pictorial sequence first show the open (filterless) channel; then the wavelength-selective channel; then the sequence of (vertically off-set) CONDAC chromatograms derived by the computer from the two original inputs displayed on top.

Fig. 5 shows a temperature-programmed separation of standard compounds identified by the FPD-active hetero-atom they contain, *i.e.* nitrogen or phosphorus or selenium. Note that the differences in relative peak size between the open and the 40 nm wide-band channel are small (a *narrow*-band filter centered on the main HPO emission, while increasing selectivity and decreasing sensitivity, would not have changed these correlations by much). That the presence of an interference filter —as compared to its absence in an open channel— brings about only small improvements in selectivity, does not represent the exception but, rather, the rule among FPD-active elements (compare the following figures as well as refs. 4 and 6).

For the CONDAC algorithm to work best, the slope ratios for all peaks of a particular hetero-element should be precisely the same. This, unfortunately, may not always be the case. A variety of reasons could be responsible for a deviation in slope ratio, the most obvious being random error. In an

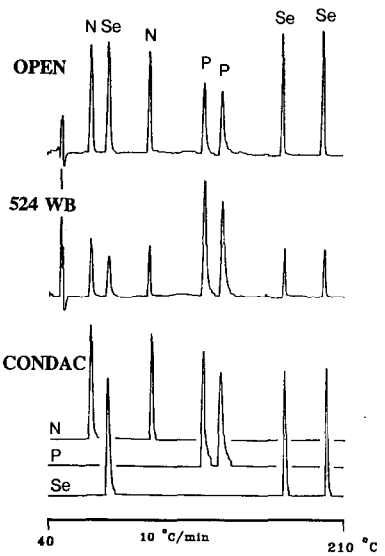

Fig. 5. Two-channel and CONDAC chromatograms from a temperature-programmed separation of (in order of elution) 300 ng triallylamine, 22 ng dimethyldiselenide, 500 ng *n*-butylamine, 1.0 ng trimethylphosphate, 0.6 ng triethylphosphate, 18 ng methylbenzselenazole, and 20 ng diphenylselenide. One channel open, the other fitted with a 524 nm wide-band (WB) interference filter (Ditric, 40 nm bandpass).

effort to demonstrate applicability to trace analysis, the amounts of the substances used here had been kept deliberately low so that the two baselines, even after some digital filtering, still carried noise. Obviously, a similar band of noise distorts the necessary slope measurements on the peaks (this is not visually apparent in the figures due to a sluggish recorder pen climbing up and down steep slopes, but it can be easily ascertained from time-extended analog or digital computer representations). Of course, there are also basic chemical rather than random statistical processes that could cause the slope ratio to vary among compounds of the same element (see below).

Despite the relatively small amounts of analyte in our experimental mixtures, the noise-induced variation of slope ratios was not large enough to prevent the CONDAC algorithm from identifying all three FPD-active hetero-elements. To demonstrate this, the individual CONDAC chromatograms for nitrogen, phosphorus and selenium are stacked up in the lower part of Fig. 5. Apparent specificity has been successfully achieved.

Chromatographers may find the principle of a CONDAC chromatogram logically convincing but its appearance strangely surprising. It is for graphical expediency that the recorder (really: the computer) draws a "zero" line during the absence of acceptable peaks. This zero line may usurp the role of a conventional baseline —yet it is only an impostor devoid of true chromatographic credentials.

Another aspect that may make Figs. 5–7 confusing to the perceptive reader, concerns the heights of CONDAC peaks when compared to those of their parent peaks. The explanation of certain size discrepancies is simple: the CONDAC algorithm accepts or rejects peaks but, having two channels at its disposal, allows the operator to choose which version of the accepted peak to send to the recorder (*i.e.* the peak from channel 1, or from channel 2, or from their average —either in original intensity or after multiplication by a convenient scaling factor). In many cases it made sense for us to select the "better" channel, *i.e.* the one in which the particular element displayed the larger signal/noise ratio.

Providing yet another cause for possible confusion, close inspection of any CONDAC chromatogram reveals that the very start and end of most peaks is characterized by a vertical jump of the recorder pen —a jump that forms the visual connection of the "zero" (= no information) line with the first and then the last datum of an algorithmically accepted stretch of signals. (Actually, the operator *does* have the option of extending that stretch beyond computer acceptance limits in a subroutine called "skirting", but this expedient had been designed for other purposes and was deliberately not invoked in this study). A *short* vertical trace normally reflects the position of the signal in relation to the "true" chromatographic baseline. A *long* vertical trace, on the other hand, indicates that the algorithm has rejected a significant part of the peak itself, usually because that part happens to overlap the peak of another FPD-active hetero-element. (To deal analytically with such a problem, a subtraction chromatogram [4] can be obtained from the computer.) The short vertical artifacts do not prevent proper quantitation; however, a full discussion of analytical performance as related to the CONDAC algorithm is beyond the scope of this qualitatively-minded manuscript.

Fig. 6 presents a situation similar to that of Fig. 5, except that the FPD-active hetero-elements are now sulphur, arsenic, boron and selenium. (It must be admitted that we experienced some difficulties in coming up with convincing test mixtures: of certain elements there are few suitable representatives commercially available and, occasionally, chromatographic overlap or chemical reactions rendered them unfit for the task.)

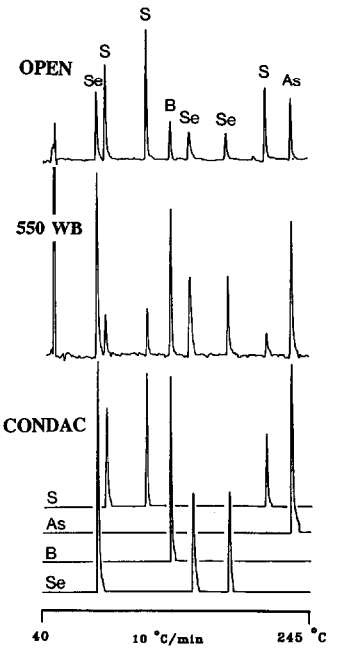

Fig. 6. Two-channel and CONDAC chromatograms of (in order of elution) 14 ng dimethyldiselenide, 1.0 ng diethyldisulphide, 1.6 ng di-*tert.*-butyldisulphide, 100 ng *o*-carborane, 20 ng methylbenzselenazole, 15 ng diphenylselenide, 1.0 ng thianthrene, and 10 ng triphenylarsine.

As demonstrated in the bottom half of Fig. 6, the CONDAC algorithm is able to distinguish among all four hetero-atoms and provide chromatograms of apparent elemental specificity for each. It should be noted that this is achieved with one wide-band filter as the lone wavelength-selective device present in the system. The choice of the filter's optical characteristics is reasonable but not crucial: several other wavelengths or filter types could have been used as well.

While the slope ratios of all peaks carrying the same hetero-atom were close enough to allow the CONDAC algorithm to succeed, it is interesting to speculate why the *SR* value of just one particular

peak happened to be significantly different from those of its congeners. That peak was the second in elution order, *i.e.* the peak of diethyldisulphide. It followed close on the heels of the first-eluting peak, dimethyldiselenide. Some selenium likely remained in the gas phase due to the proximity of the two peaks (note also that selenium —even more so than sulphur— is prone to form residues adhering to, and eluting only very slowly from, the GC system). Thus, the luminescence forming the diethyldisulfide peak probably included the interchalcogen emitter SeS (*cf.* ref. 27) in addition to the predominant S_2. This would have effectively changed the spectral envelope and hence the slope ratio.

It may be argued that such effects could make the use of the CONDAC algorithm a risky business. We prefer to look at it the other way around: it is the CONDAC algorithm that warns the analyst of a potentially risky situation. After all, the same effects must occur in conventional use of the FPD. While the FPD, in our opinion, is one of the most reliable of all the selective GC detectors, the presence of such an interference, and its effect on quantitation, could go unrecognized in everyday analysis. Perhaps the routine use of comparative slope ratios would lead to more reliable analyses; as well as to a better understanding of the processes in, and limitations of, the FPD and other dual-channel detection devices? The concurrence of the slope ratio (in addition to the concurrence of the retention time) between a sample analyte and its calibration standard can certainly reassure the analyst that the two are indeed identical. Caution is, of course, always called for: the FPD (and certain other detectors) are not just simple optical or electrical transducers. Rather, their signals portray dynamically complex, transient chemical systems with individual memories and inhibitions.

Fig. 7 uses CONDAC algorithms on some more main-group elements; namely lead, antimony, germanium and tin. The only spectrally selective device in this configuration is a 540 nm long-pass (LP) filter. Again, the CONDAC algorithm successfully separates/identifies the hetero-elements present.

While the numerical slope ratios of the two germanium peaks were practically identical, those of the two tin peaks were slightly different. This may simply be due to experimental noise, but more basic spectrochemical interferences cannot be ruled out.

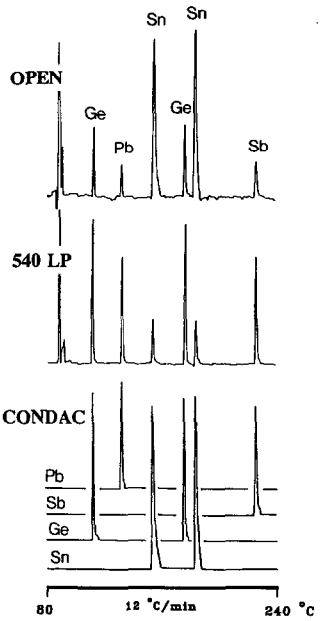

Fig. 7. Two-channel and CONDAC chromatograms of (in order of elution) 1.8 ng tetraethylgermanium, 12 ng tetraethyllead, 0.20 ng tetra-*n*-propyltin, 4.8 ng tetra-*n*-butylgermanium, 0.20 ng tetra-*n*-butyltin and 24 ng triphenylantimony.

For instance, despite our best efforts at suppressing it, some residual surface luminescence of Sn (or Ge) may have been present on, say, the quartz windows shielding the filters/photomultipliers. That type of luminescence is known to be subject to protracted quenching by a variety of elements. If the blue luminescence happened to be present (together with the usual green SnOH and red SnH gas-phase emissions [9]) the potential for changes in slope ratio among tin compounds —eluting at different positions in a temperature-programmed chromatogram and/or following compounds that contain different hetero-elements— cannot be ruled out. Fortunately, the repetitive nature of samples as well as the controlled conditions in a typical analytical laboratory will usually be able to prevent or circumvent such potential errors.

In the past few paragraphs we have drawn considerable, perhaps even undue, attention to certain hypothetical problems that could beset the dealings of CONDAC algorithms with S/Se and Sn/Ge containing samples. This was done for a purpose: by these speculations we wanted to illustrate two *general* types of processes, which can cause variations

in slope ratio among peaks containing the same hetero-atom: *contamination* and *multiple spectra*. It should be noted that the extent of both effects may depend, *inter alia*, on the concentration of the analyte, or on the temperature, or on the concentration of other species in the gas phase (the temperature program alone causes significant changes in carrier flow and column bleed). A variety of other interferences could be surmised even from what little we know about the basic chemistry and chemiluminescent spectroscopy of various FPD-active elements in hydrogen-rich, low-energy flames. Fortunately, the demonstration mixtures of this study were literally more colourful, and the resulting chromatograms hence visually more alarming, than the proverbial "real-life" sample.

It is now obvious that by judicious selection of wavelength in the two channels, the compounds of *any* selected element can be granted exclusive access to, hence sole presence on, the computer-drawn CONDAC chromatograms. Still, it remains the perceptionally most surprising aspect of this rather primitive algorithm that its output is element-*specific*. Somehow it just does not seem right that a device like the FPD —which monitors broad, usually overlapping molecular bands at low resolution— should be capable of infinitely selective response.

While the chromatograms do indeed appear specific for any selected element, they are also subject to obvious limitations. The CONDAC version of specificity is neither intrinsic nor inclusive; rather, it is created by computer and confined by circumstances. For instance, the CONDAC chromatogram may exclude part or all of a peak (despite the fact that the latter does contain the targeted element) if the peak of a different element overlaps it. This implies that the algorithm can successfully operate only on (at least partially) separated peaks. And compounds that, in addition to the targeted element, contain one of similar or higher radiative power, may not show up on the chromatogram at all: only the predominant emitter gains access. As an extreme example, a CONDAC scan set for carbon compounds will not recognize the carbon matrix of an organophosphate.

Such extreme situations aside, it is astonishing how well the CONDAC approach works in practice — particularly in light of the fact that *several* chromatograms of apparent elemental specificity can be derived from the *same* injection (*i.e.* from the same set of weak optical discriminants and the same set of stored data). CONDAC could be dismissed as a gimmick from the computer, or be misused as an oracle from the black box. We hope that it will neither, but that it will simply permit faster and firmer analyses.

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