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Photometric response of a very small, stoichiometric hydrogen–air flame to compounds of the iron group[1]

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Abstract

In contrast to the typical, strongly hydrogen-rich flame of the flame photometric detector (FPD), a very small, stoichiometric flame (using around 16 ml/min H_2 and 40 ml/min air) yields high sensitivity for elements of the iron group. The small, stoichiometric flame's response to gas chromatographic peaks of ferrocene, ruthenocene and osmocene is mostly, if not exclusively, due to spectral continua. The minimum detectable flows [for a signal-to-noise ratio of two, with noise measured peak-to-peak at a 1-s RC (resistance×capacitance) time constant] are $3\cdot10^{-15}$, $4\cdot10^{-16}$ and $1\cdot10^{-15}$ mol of metal per second for Fe, Ru and Os, respectively. For the typical case of osmocene, the linear range measures about five orders of magnitude, and the atomic selectivity of Os/C is about 4.5.   © 1998 Published by Elsevier Science B.V.

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1. Introduction

The metals of the iron group are catalytically active, whether neat or in various inorganic or organometallic forms. The many roles of iron, from engineering to biochemistry, are well known. This explains the analytical interest in this group, and the attention that is given to the detection of iron and its congeners after chromatographic or electrophoretic separation.

Iron, ruthenium and osmium – most conveniently separated by gas chromatography as metallocenes – respond strongly in the flame photometric detector (FPD). The most prominent emission of iron is a line [1], of ruthenium, a band [2], and of osmium, a continuum [3]. Indeed, continua are produced by several metals in the FPD and, as will be seen later, are of particular importance to this study. Their similarity has given rise to speculation about a possibly common origin [4].

Beyond mechanistic provenance, however, continua are of special interest for a device like the FPD. This is because the FPD works under conditions of low (or sometimes [5,6] even no) spectral resolution. The detector differs fundamentally in this respect from the various instruments of atomic spectrophotometry [7,8]. Yet, some detection limits of the FPD, for elements to which it responds strongly, are quite competitive with the best of the latter, at least for gas chromatographic inputs [4]. (More information on the performance of high-resolution spectral tech-

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niques, particularly of the 'hyphenated' variety, can be found in many reviews and monographs, e.g. [9–14].)

Discussions of continua rate low in the spectroscopic literature, e.g. [8,15]. Alkemade and Herrmann [8] summarize: 'Some elements (e.g. As, Al, Mo, V, Cr, Ni, Na, P, S, Cl) in a flame, in addition to a line or band spectrum, often give rise to a (usually weak) continuous spectrum'. Thus, the origin of many continua remains unexplored.

As exploration so exploitation: Continua are rarely monitored for analytical purposes [16,17]. In the FPD, only the blue luminescence of tin has been used to any significant extent [18], and that luminescence is a surface-induced continuum. This situation suggests that it may likely be interesting, and possibly even rewarding, to investigate the analytical use of FPD continua. For this task, the elements of the iron group will be recruited in the form of their stable and easily chromatographed metallocenes.

Analytical utility aside, the continua (and other spectral phenomena) that occur in the FPD may themselves become subjects of interest. The typical FPD flame is very small (a few mm^3) and of low temperature (300 to 800°C). Its emissions arise predominantly, if not solely, from chemiluminescent (as opposed to thermal) excitation, as befits the unique flame conditions. Generally, though, these conditions would be considered detrimental to good spectrophotometric practice (see Ref. [19]). As a consequence, they are infrequently investigated and even less frequently employed in conventional methodologies.

However, while the absolute light level of chemiluminescence is very low, the spectra are usually simple and 'clean', i.e. unencumbered by much of the usual thermally excited clutter. This can, for instance, facilitate vibrational assignments for those band systems that, in high-energy sources, are being seriously eclipsed by competing emissions.

Because of the scanty light level, FPD spectra of intermediate or low intensity are difficult to measure with a conventional (grating) spectrophotometer – yet, they may prove important from an analytical point of view. Clearly, higher light throughput is needed. A rotating variable interference filter [20] does provide higher light throughput but is limited in its wavelength range; and circular filters of a larger

range are, to our knowledge, not commercially available.

Rectangular filters, however, are. For this study, a 'variable wavelength selector' or 'filter monochromator' (see Ref. [21]) was built to hold a rectangular, variable interference filter of (nominally) 400 to 1000 nm range connected to a (modified) flame photometric detector. Also, a second light sensor [22] was installed, either to serve as a reference during spectral measurements, or to function as an FPD channel sui generis.

2. Experimental

A Shimadzu model GC-8APFp gas chromatograph with a single-channel flame photometric detector was used as the basic instrument. For the purpose of this study, its photomultiplier power supply was replaced by a laboratory-made −70 to −1270 V unit; its bucking range was extended by an exchange of resistors, and a simple three-pole analog filter, cf. [23], was added in order to provide ten time-constant settings in the RC (resistance×capacitance)=0.1 to 10 s range (though only the 1-s setting was regularly used). The flow resistors were removed from the gas supply lines and replaced by valves and rotameters.

In the case of hydrogen (which needed to be controlled to a very low flow), a pair of Nupro fine valves, B-SS2 and B-SS2-D-VH [24], was used, together with a coarse shut-off valve and a bypass arrangement, by virtue of which flow could be measured with a bubble flowmeter or even a pneumatic trough. (The measurements reported in this paper were, however, mostly done by sampling unignited jet effluent with a bubble flowmeter.) A PTFE ring (gasket) was added to the detector base to prevent outside air from being drawn into the flame area.

The detector jet was replaced with a more slender nozzle that would center the flame on the optical axis and allow it to be contained inside a 4 mm I.D., 6 mm O.D. quartz cylinder (chimney). A parabolic mirror with a focal length of 2.5 mm was machined from a 1-inch aluminum rod and doubly drilled; radially, to accommodate the chimney, and axially, to accept the second-channel light guide, cf. [22]. (In earlier, single-channel experiments, an Edmund no.

43 464 [25] first-surface mirror, with a diameter of 25 mm and a radius of 20 mm, was used both with or without the quartz chimney: it gave roughly comparable results.)

The detector was connected to the 'filter monochromator' channel via an aluminum cylinder, with cooling fins positioned in the air stream of a squirrel-cage blower. Light from the flame traversed a conventional quartz-window arrangement; it then proceeded through a highly polished thin aluminum cylinder (the purpose of which was to reflect light and, more importantly, to bar room light); the light then entered a biconvex lens with a focal length of 50 mm (Edmund no. 32 625), which focussed it onto the interference filter contained in the 'variable wavelength selector' box. A schematic diagram of the optical layout is shown in Fig. 1.

The variable wavelength selector ('filter monochromator') was a long, light-tight box with a vernier-controlled helical drive (Small Parts, item K-HELIX-1/45 [26]) that carried, with backstop, a frame holding the 20×2.5 cm variable interference filter (Oriel, item no. 57 481). The filter has been specified by the vendor to have a range of 400 to 1000 nm, a minimum transmission of 30%, and a maximum bandpass (in the middle of the filter) of 42.5 nm [21].

A pair of (non-coordinated) sliding slits could be controlled from the outside by two verniers. (For most measurements, the slits were left wide open and, in their stead, a piece of paper with a 6-mm aperture was positioned in front of and very close to the variable filter.) The backside port of the spectrometer allowed a photomultiplier tube (PMT) housing to approach the filter as close as the slit arrangement would allow. The PMT housing, which was made in the laboratory, carried a Hamamatsu R-1104 tube with a nominal wavelength range of 185 to 850 nm [27]. (An R-2228 tube, which nominally covers the 280–900 nm range, was sometimes used for spectral measurements.)

The (detached) variable-wavelength channel was roughly calibrated with the help of a tungsten (flashlight) lamp and a 1/4-m grating monochromator (Jarrell-Ash model 82-415 with a 1180 grooves/mm grating blazed for 500 nm, and 2 mm slits). The results are shown in Fig. 2.

For the initial series of optimization studies, the variable-wavelength channel was replaced by an R-1104 photomultiplier tube, which was held in a laboratory-made housing behind a (usually) 640-nm long-pass filter (Ditric). For measuring calibration curves and minimum detectable amounts, a 455-nm long-pass colored glass filter (Oriel no. 51 284) was
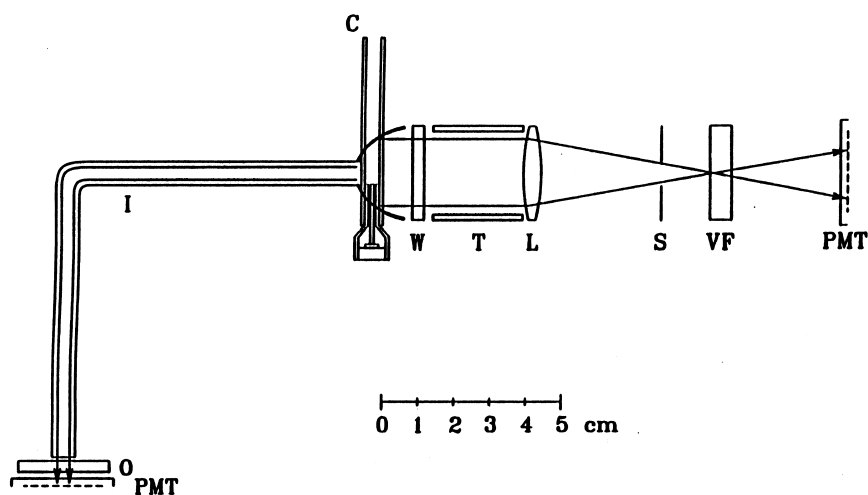

Fig. 1. Optical layout of dual-channel FPD arrangement. Reference channel on the left, wavelength-selective channel on the right. (The latter was replaced by a filter–photomultiplier combination for measuring calibration curves and minimum detectable amounts). PMT= photomultiplier tube, O=optical filter, I=image conduit, C=chimney, W=quartz window, T=reflecting light tunnel, L=biconvex lens, S=slit and VF=variable wavelength interference filter.
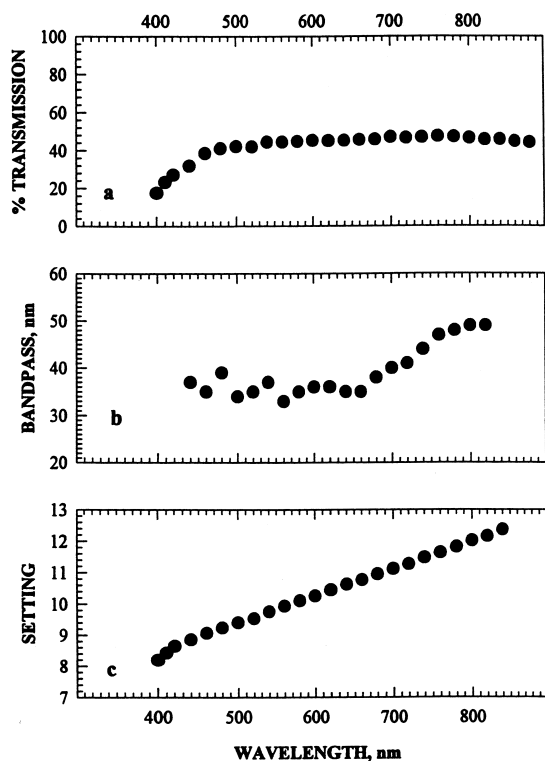
Fig. 2. Calibration curves of the variable interference filter (wavelength selector): (a) percentage monochromatic light transmission; (b) bandpass; (c) wavelength vs. helical-drive vernier setting.

substituted, primarily to minimize the baseline current.

To inspect the flame by (dark-adapted) eye, the detector was opened, i.e. the variable-wavelength channel was removed. A rough scale, drawn with luminescent paint (Small Parts, item K-YLP2), was then inserted behind the flame to allow the flame size in the pitch-dark room to be estimated.

For temperature estimates, a thin-wire thermocouple (0.2 mm diameter iron–constantan) was inserted from the top, and used with an Omega OMNI-AMP-II-A unit [28]. The approximate temperature distribution and the roughly spherical iron-group luminescence of a typical flame are depicted in Fig. 3.

The gas chromatographic column was a borosilicate tube, 100×0.3 cm I.D., packed with 5% OV-101 on Chromosorb W, AW, 100–120 mesh, and it was purged with about 20–25 ml/min of prepurified-
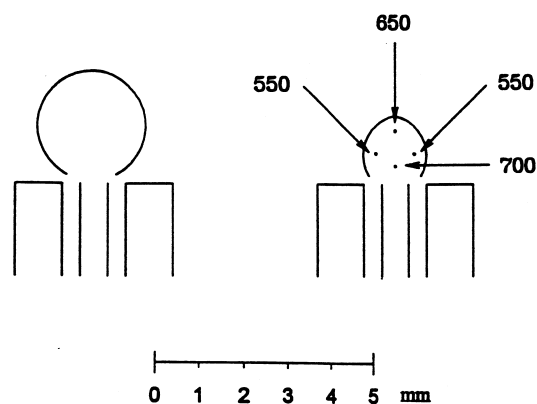

Fig. 3. Visual shapes of a typical metallocene luminescence (left) and the corresponding small, stoichiometric flame (right), with approximate thermocouple temperatures given in °C.

grade nitrogen. The bis(cyclopentadienyl) derivatives ferrocene, ruthenocene and osmocene (Strem [29]), were dissolved in acetone and injected, usually as 0.5 μl portions, with a Hamilton no. 7001 1 μl syringe.

3. Results and discussion

In conventional mode, the FPD uses a strongly hydrogen-rich flame. Such flame conditions did indeed obtain in earlier investigations of Fe [1], Ru [2] and Os [3]. In this study, however, interest focussed on continua. Since most observed continua extended into the red region, initial response optimizations were carried out with a 640-nm colored-glass long-pass filter installed in the light path.

The results were rather unexpected. All three elements reacted in a similar manner: the S/N maximum lay at, or very close to, the stoichiometric volume ratio (air–H_2=2.5) of the flame gases. Also, the S/N maximum was associated with very low total flow; a flow that was just short of extinguishing the flame. Most surprisingly for these conditions, the detection limits were roughly comparable to (or, as in the case of osmium, even significantly better than) those obtained under more conventional FPD circumstances [1–3]. Clearly, that strength of response invited scrutiny.

(It should be noted that optimum response for a given air flow characteristically prevailed if the baseline current was at its strongest and the dip

following the solvent peak at its weakest. Perhaps this indicates a direct mechanistic relationship between signal and background. If so, maximum response may correlate with minimum 'quenching', cf. [30], of baseline, solvent and analyte. This curious phenomenon has, however, not been fully investigated, although it has routinely served as an easy first step in the optimization protocol.)

Depending on the task at hand, the three metallocenes of the iron group were injected either together or singly. Fig. 4 shows a typical chromatogram obtained under temperature-programmed conditions. Note that the program does not disturb the baseline (flame), and that the 1-m column has no difficulty separating the three test compounds. This is important under the particular detector conditions
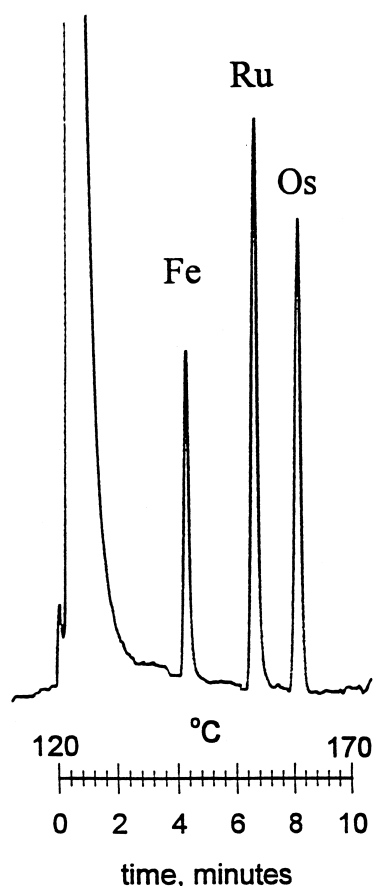
of this study: Since all three metals produce continua in roughly the same wavelength range with roughly comparable intensity, there is — in spectral, not chromatographic terms! — little that could distinguish between them.

Osmocene provided the biggest increase in sensitivity compared to an earlier study [3] and, perhaps not unrelatedly, displayed the most prominent and interesting spectral differences. It was, therefore, used preferentially as the test analyte.

For instance, Fig. 5 shows three calibration curves: two for osmocene and one for dodecane. The logarithmic ordinate presents the (analytically more meaningful) S/N ratio. Here, noise is defined as the peak-to-peak fluctuation of the baseline, with drift and spikes removed, over a time interval corresponding to about ten peak widths, and at an instrumental RC time constant of 1 s. Arrows indicate the approximate detectability level according to the two most commonly used criteria, cf. [31]. The logarithmic abscissa defines the molar flow of a
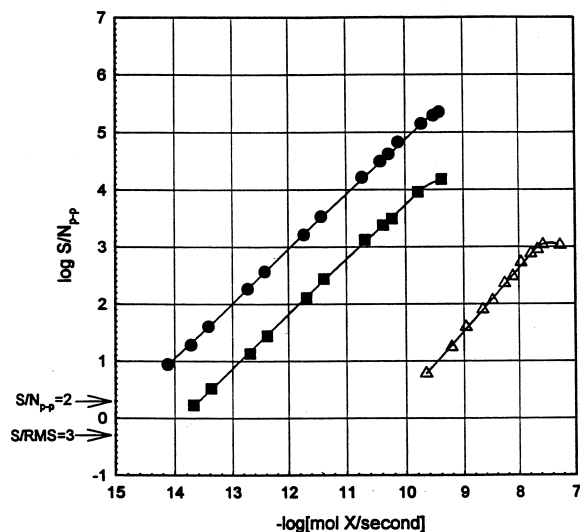

Fig. 4. Typical temperature-programmed, low-resolution separation of the iron-group metallocenes.

Fig. 5. Calibration curves, from left to right, for osmocene (X= Os), as seen through a 475-nm colored-glass long-pass filter (filled circles), or through the variable wavelength selector (filter monochromator) set at 610 nm (filled squares); and for dodecane (X=C), as seen through the 475-nm long-pass filter (empty triangles). Flow-rates (in ml/min): H_2, 16; air, 40; N_2 (from column), 20. R-1104 PMT at −540 V. N_{p-p} is the peak-to-peak noise of the baseline, with drifts and spikes disregarded, at an RC=1 s analog-filter time constant. Column temperature, 170°C (osmocene) or 130°C (dodecane).

characteristic element (X=Os for osmocene and C for dodecane).

As expected, the most sensitive performance was obtained in the 'holophotal' mode [32], i.e., with the photomultiplier tube (plus 455 nm long-pass filter) replacing the variable-wavelength channel and facing a parabolic mirror with the flame located at its focal point. The two types of detectabilities, through a filter monochromator vs. a holophotal channel, were $3 \cdot 10^{-14}$ vs. $1 \cdot 10^{-15}$ mol Os/s, respectively. The latter value is about two orders of magnitude better than the one obtained in the earlier study with a conventional FPD flame [3]. The atomic selectivity of Os/C and the linear range were extended to about 4.5 and five orders of magnitude, respectively.

These analytical figures of merit, together with those for Fe and Ru, are summarized in Table 1. [Honoring a request by one of our referees, we have included similar figures of merit for the most sensitive atomic spectroscopy technique, MIP–AED (microwave-induced plasma atomic emission detector), to allow a formal comparison to be made.]

The second (lower) calibration curve for osmocene was measured with the help of the variable wavelength selector set at 610 nm. While obviously less efficient than the holophotal one, this channel appears to be superior to what one might expect of a laboratory-made 'monochromator'. For analyses that do not require the ultimate in sensitivity, this os-

mocene calibration curve could in fact have been easily used (and probably with higher selectivity vis-a-vis other FPD-active elements). The efficient light transfer through the variable-filter channel suggests that similar optical arrangements could serve quite a variety of FPD tasks, most profitably those that must monitor a larger number of wavelengths.

One of the current tasks of this arrangement was to check for a possible change in the spectrum due to changes in the concentration of osmocene. Although the linearity of the calibration curve argued against such a change occurring, the formal possibility could not be ruled out (see later discussion of 'shifting' spectra). Experimental scrutiny was required, primarily because of the significant analytical and mechanistic implications. Fortunately, the spectral distribution remained invariant at all of the concentrations tested.

The response of osmium is now as strong as that of iron, and only slightly weaker than that of ruthenium. This is demonstrated by the calibration curves shown in Fig. 6. The minimum detectable amounts and flows were determined separately from chromatograms such as the ones shown in Fig. 7. (Note: for the purpose at hand, the analyte peaks were moved close to the solvent peak by choice of temperature, and given approximately the same 2-min retention time). Expressed as the molar flow of

Table 1

Analytical figures of merit for detection of Fe, Ru and Os by two types of GC–FPD, and by GC–MIP–AED[a]

Element	Instrument	Detection limit[b] (pg X/s)	Linear range	Molar X/C selectivity	Reference
Fe	FPD	3.0	10^4	$1.5 \cdot 10^4$	[1]
	FPD	0.14	10^5	$2.5 \cdot 10^4$	This study
	MIP–AED[c]	0.28	10^3	$2.8 \cdot 10^5$	[37]
Ru	FPD	0.10	10^4	$4.2 \cdot 10^5$	[2]
	FPD	0.040	10^5	$1.6 \cdot 10^5$	This study
	MIP–AED	7.8	10^3	$1.3 \cdot 10^5$	[37]
Os	FPD	29	10^3	$4.3 \cdot 10^4$	[3]
	FPD	0.25	10^5	$5.0 \cdot 10^4$	This study
	MIP–AED	6.3	10^3	$5.0 \cdot 10^4$	[37]

[a] MIP–AED data added, as per reviewer's request.
[b] At $S/N_{p-p}=2$.
[c] Three recent reviews [12–14] list a detection limit of 0.05 pg Fe/s for $S/N=3$ (*N* undefined), a linear range of >1000 and a selectivity vs. C of 3 500 000. Presumably, these data were measured on a Hewlett-Packard GG–AED (5921A), but no further documentation was given. Note: since this study was originally submitted, Fe and Ru have also been determined with a PFPD, with detection limits of 0.3 and 0.09 pg X/s, and with X/C selectivities of $2 \cdot 10^3$ and $5 \cdot 10^4$, respectively [38].

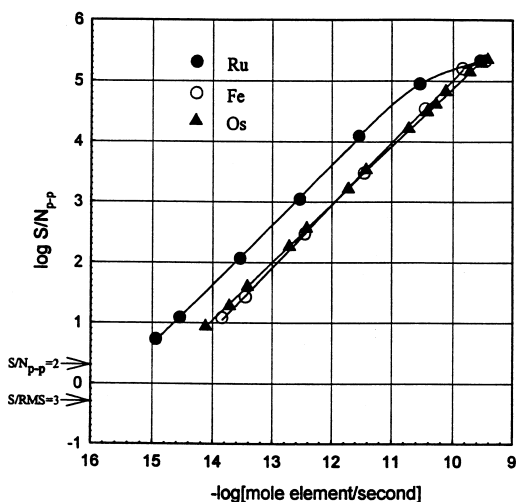*N.B. Lowery, W.A. Aue / J. Chromatogr. A 806 (1998) 305–316*

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Fig. 6. Calibration curves for ruthenocene (filled circles), ferrocene (empty circles) and osmocene (filled triangles) under conditions similar to those given in Fig. 5. A colored-glass long-pass filter was used at 455 nm for Ru and Fe, and at 475 nm for Os; R-1104 PMT was at −500 V (Ru) and −540 V (Fe and Os). Column temperatures: 160, 140 and 170°C for Ru, Fe and Os metallocenes, respectively.

metal per second that produced a signal twice the peak-to-peak noise of the baseline at a 1-s RC time constant, iron, ruthenium and osmium yielded detection limits of $2.5 \cdot 10^{-15}$, $4.0 \cdot 10^{-16}$ and $1.3 \cdot 10^{-15}$ mol/s; or $1.4 \cdot 10^{-13}$, $4.0 \cdot 10^{-14}$ and $2.5 \cdot 10^{-13}$ gram metal/s, respectively. (It is realized that detection limits admit only one significant digit; however, two digits were used here because of the otherwise awkward mol/mass conversion.) These data are in a similar range as our best conventional-FPD value for phosphorus, i.e. $8 \cdot 10^{-16}$ mol P/s.

(Under the conditions of this study, the detection limit for phosphorus, with a 475-nm long-pass filter, was close to $1 \cdot 10^{-15}$ mol P/s. The detection limit for sulfur, with a 385-nm long-pass filter and with 0.5 ng amounts of thionaphthene or di-*n*-butyldisulfide injected, was about $1 \cdot 10^{-12}$ mol S/s. In other words, phosphorus responds almost as well in the small, stoichiometric flame as in the conventional FPD flame, but sulfur does not. Since sulfur needs a rather hydrogen-rich flame to yield a good response, this comes as no surprise.)

The very small stoichiometric flame – close to extinction and typically supported by a mere 16

ml/min hydrogen and 40 ml/min air, with about 20 ml/min nitrogen coming from the column – thus produced excellent *S*/*N* ratios that, as demonstrated in Table 1, compare favorably with those of the most prominent of the high-powered hyphenated techniques, i.e. MIP–AED, for elements of the iron group. It is obvious that this flame differs radically, in principle as well as in performance, from the FPD flames previously used (which had H_2–air–N_2 flows of 370:60:55 ml/min for Fe [1], 300:80:42 for Ru [2] and 300:60:45 for Os [3]).

Since earlier studies produced mostly lines for iron [1], bands for ruthenium [2] and a continuum for osmium [3], a prime objective of this study was to map the present spectra of the three analytes. Does the now similar optimization and intensity behavior of the three metals also imply a similar type of spectrum?

Measuring such a spectrum proved a delicate operation, notwithstanding the fact that the very small, stoichiometric flame produced enough light. The problem was that even relatively small changes in flow, including nitrogen flow from the column, brought about optical changes. Certain experiments were therefore repeated several times in order to confirm spectra, substantiate trends and verify conclusions. (Note that the experimental difficulties apply mainly to exploring the spectral effect of flow changes. For routine analytical purposes, the flame can be easily set so as to provide reproducible quantitation as well as reliable stability vis-a-vis fast temperature programming and/or solvent injections up to 2 μl.)

The most carefully tested analyte, osmium, produced a continuum that appeared to shift in wavelength when flame conditions were changed. This potentially very interesting behavior (a true shift would imply a different type of mechanism, perhaps one based on small particles, cf. [4]) is illustrated in Figs. 8 and 9, with the air flow held approximately constant at two levels ('approximately' because detector resistance to the flow of one particular gas changes slightly when the flow rate of a co-emerging gas is altered).

Fig. 8 uses a higher-than-usual air flow (which, in turn, permits a wider range of hydrogen flow). It also uses a 'reference' compound, dirheniumdecacarbonyl, which elutes close to bis(cyclopentadienyl)os-

20 pg ferrocene
-log(mole Fe/s) = 14.6

2 pg ruthenocene
-log(mole Ru/s) = 15.4
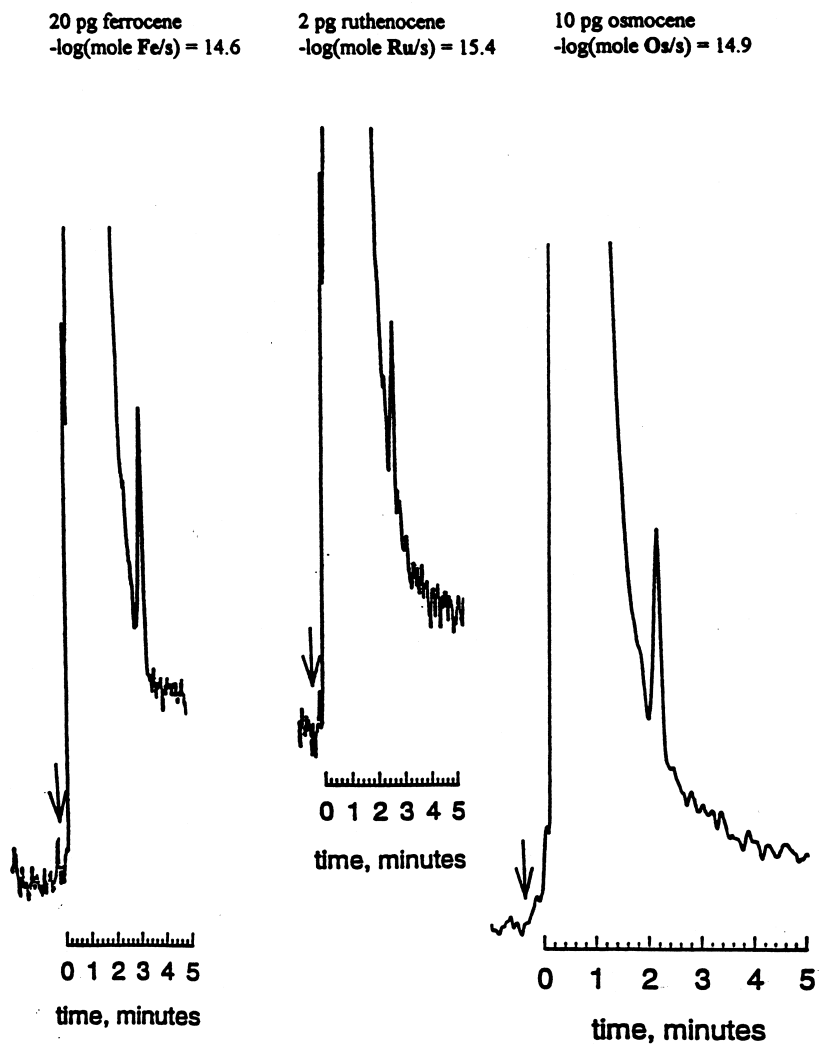
10 pg osmocene
-log(mole Os/s) = 14.9

Fig. 7. Metallocene peaks near their detection limits. Amounts injected: 20 pg of ferrocene, 2 pg of ruthenocene and 10 pg of osmocene. R-1104 PMT at −540 V behind a 455-nm colored-glass long-pass filter. (Note: the peaks are slightly quenched by the solvent tail, and individual temperatures differ: these were adjusted such that each analyte would elute at about the same retention time of 2 min.)

mium. The two compounds can thus be easily co-injected in order to appear together in an isothermal chromatogram. The rhenium compound also produces a continuum, although one of significantly lower intensity. The important point here is, however, that the rhenium-based continuum, while shifting in amplitude, does not shift in wavelength under the different conditions (hence its use as an optical 'reference'). In contrast, the continuum from the osmium compound appears to shift significantly ('appears' because the presence of more than one

emitter cannot be ruled out). It does so again in Fig. 9, over a more narrow range of hydrogen flow, but now with the 'typical' air flow of 40 ml/min.

In contrast, the apparent continuum that results when ferrocene is injected does not seem to shift to any significant degree with flow conditions. This is shown in Fig. 10. (The feature sporadically present at ca. 680 nm has not been investigated further.) Similarly, as shown in Fig. 11, ruthenocene produces a sizeable continuum under certain flow conditions. However, the appearance of the spectrum is too
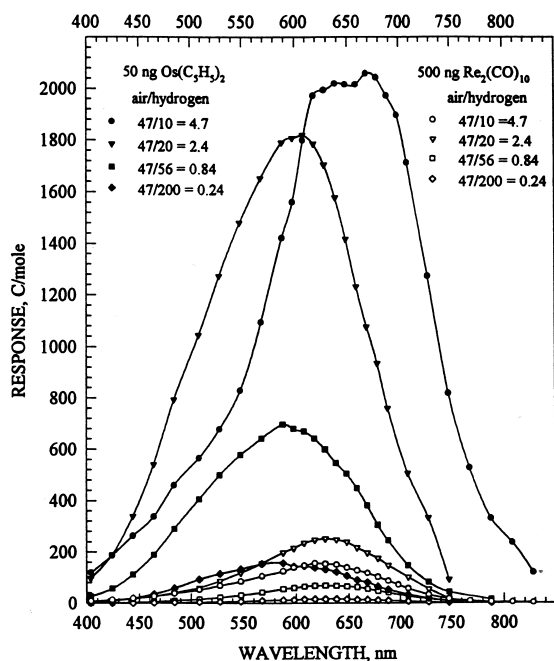
Fig. 8. Spectra from repeated injections of 50 ng of osmocene (filled symbols) with 500 ng of dirheniumdecacarbonyl (empty symbols) under different flame conditions. Air/hydrogen flow-rates in ml/min (volume ratio given in parenthesis; 2.5 = stoichiometric): 47/10 (4.7, circles), 47/20 (2.4, triangles), 47/56 (0.84, squares), and 47/200 (0.24, diamonds). Variable wavelength selector (see Fig. 2 for bandpass and percent transmission) with R-2228 PMT at −900 V. Column temperature, 190°C.
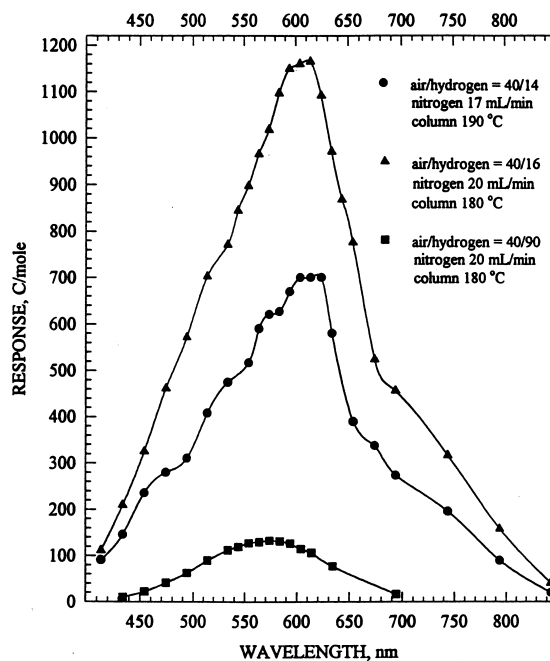
Fig. 9. Spectra from osmocene under different flow conditions. The results are similar to those of Fig. 7, but (from top to bottom) the air–hydrogen–nitrogen flow-rates (in ml/min) were 40:16:20 (air–H$_2$ volume ratio of 2.5; triangles; 180°C); 40:14:17 (ratio ca. 2.9; circles; 190°C); and 40:50:20 (ratio, 0.44; squares; 180°C). Note: the slightly different conditions for the smallest and air-rich flame (circles) were necessary to keep it alight.

cluttered, and the data too few, to draw a secure conclusion one way or the other.

Taking into consideration the fact that osmium is the only element examined so far [33] whose continuum appears to shift on the wavelength axis, proof positive would be required for authenticating this potentially very interesting phenomenon. Up to now, such proof has not been forthcoming.

Whether or not continua shift, the fact that they dominate the emission of the very small, stoichiometric flame demands attention. However, it could be argued that these emissions are not true continua but simply represent many lines/bands merged by low resolution. Although it would be unusual if many more lines/bands were to start emitting when the flame decreases in energy and approaches extinction, the formal argument does deserve an experimental answer.

There are limits to the extent resolution can be improved in a system that serves chromatography (as opposed to spectroscopy) and uses an emission source with a low absolute light flux. Obviously, the FPD is not the best device on which to conduct spectrochemical investigations. On the other hand, the FPD must be used if the data are to be trusted to correctly characterize the spectral processes occurring during FPD-based analyses. Spectral analogy between the FPD flame and typical 'spectroscopic' flames is sometimes tacitly assumed. However, as several articles in the literature and the current study cogently demonstrate, this assumption is often seriously at odds with reality.

Fig. 12 shows spectra obtained with a Jarrell-Ash quarter-meter grating monochromator at a bandpass of 6.7 nm. Note that these were done with a different photomultiplier tube than that used for Figs. 8–11, that they extended into the near UV, and that
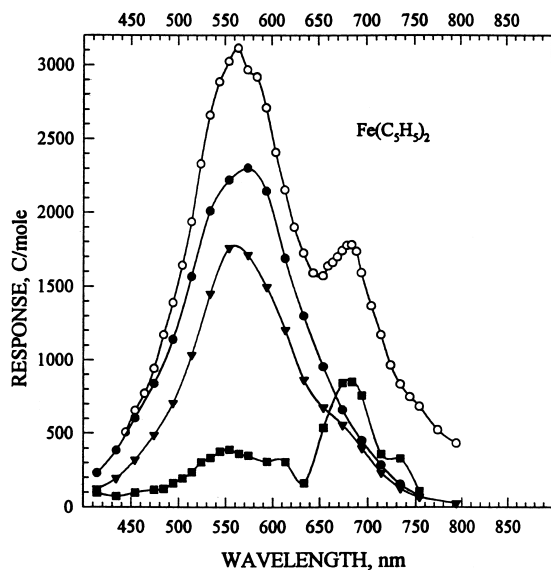
Fig. 10. Spectra from ferrocene taken under different conditions and at different times. Variable wavelength selector (see Fig. 2 for bandpass and percent transmission) with R-2228 PMT at −900 V. The lowest curve (filled squares) has been amplified five times for clarity. Air–hydrogen–nitrogen flow-rates (in ml/min), and column temperature, from top to bottom: 34:15:25, 140°C (empty circles); 47:10:20, 170°C (filled circles); 47:20:20, 170°C (filled triangles) and 47:46:20, 170°C (filled squares, ×5).

Fig. 11. Spectra from ruthenocene taken under different flow conditions; the results are comparable to those of Fig. 10. Column temperature, 170°C; column nitrogen flow-rate, 20 ml/min. Air–hydrogen flow-rates (in ml/min): 47:20 (circles), 47:46 (triangles) and 47:10 (squares).

colored-glass long-pass filters were used in reruns (open circles) to block second-order signals. Note also that the grating suffered from a pronounced Wood's anomaly [21] at around 700 nm, whose visual effects are disregarded in the following spectral discussion.

The visible iron spectrum displays what we believe to be only very minor emissions superimposed on the large central continuum. The UV contribution is probably due to the 353–358 and 363–367 nm FeOH system [34]: This system is best discerned in its second order, appearing at ca. 710 and 730 nm. This flame behavior contrasts with that of the earlier, hydrogen-rich system, whose strongest feature was the resonance line at ca. 344 nm [1]. Evidence for this as well as for another normally strong line at ca. 372 nm is (if these lines are present at all) decidedly minor in Fig. 12. It may be remembered that iron does show strong, orange FeO emissions in conventional flames; however, their pattern [34] does not fit the present spectrum.
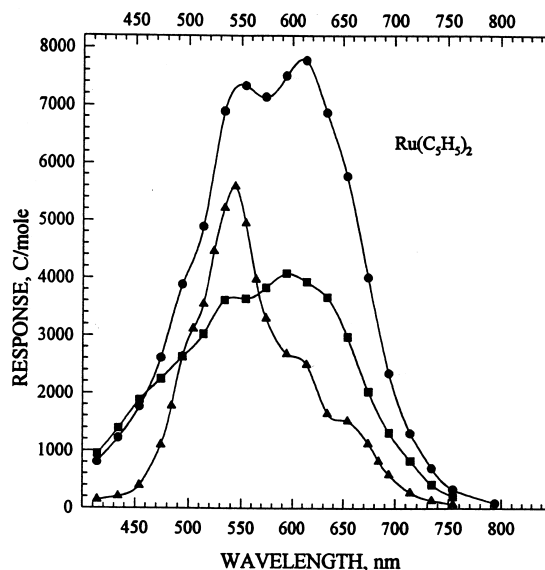
The spectrum from ruthenocene shows merely remnants of the earlier-noted bands, centered at 484 and 528 nm (RuH?), which dominated the spectrum obtained from a much stronger, hydrogen-rich flame [2]; otherwise, no clear features emerge. A similar assessment can be made of the spectrum from osmocene. Both spectra show strongly the optical anomaly of the grating around 700 nm. Overall, all three spectra appear to be remarkably similar, with dominant continua appearing in the visible region.

These continua are not restricted to the iron group. A rhenium continuum is included in Fig. 8. More examples of continua have been found among other metals [33] – including some that, like tungsten, had not produced a significant response (then defined as more than ten times the expected carbon response) in a conventional FPD [35]. What is interesting here is not so much the existence of continua as (at least for some of them) their strength in an exceedingly weak flame.

The small, stoichiometric FPD flame can thus be conveniently used to determine volatile compounds (or derivatives) of members of the iron group, and do so with unusual, and unexpected, sensitivity.
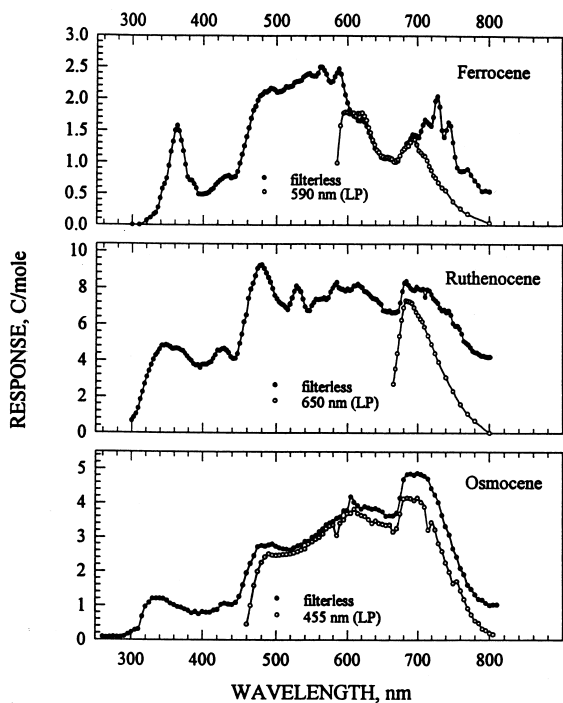
Fig. 12. Spectra from ferrocene (top), ruthenocene (middle) and osmocene (bottom). Quarter-meter grating monochromator at 6.7 nm bandpass, with R-1104 PMT (-540 V). Air, 40 ml/min; H_2, 16 ml/min and column nitrogen, 20 ml/min.

4. Note added in revision

In the context of the final paragraph, and of a request by one of our referees, we should add that this determination of members of the iron group is not restricted to ready-made ferrocenes, ruthenocenes and osmocenes. In a recent study, analytical amounts of simple nitrate or chloride salts of Fe, Ru and Os were derivatized with sodium cyclopentadienylide in tetrahydrofuran to produce the metallocenes whose detection behavior is described in this manuscript. The derivatization can also be carried out (with butylmagnesium chloride added) to produce easily chromatographed organometallic derivatives from a simple test mixture containing Fe, Ru, Os, Ge, Sn and Pb ions [36].

Acknowledgements

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