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CAPABILITIES OF ON-LINE ELEMENT-SPECIFIC DETECTION IN HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY USING AN INDUCTIVELY COUPLED ARGON PLASMA EMISSION SOURCE DETECTOR

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SUMMARY

The applicability of the inductively coupled argon plasma (ICAP) as a detector in high-performance liquid chromatography (HPLC) was investigated. The influence of the flow-rate and the nature of the mobile phase on the operation of the ICAP source, and on peak broadening, sensitivity, linearity and detection limits was determined. At the flow-rates and mobile phase compositions normally applied in reversed-phase chromatography the ICAP proved to be a highly valuable HPLC detector.

In straight-phase chromatography troublesome limitations in the choice of the mobile phase were observed.

Peak broadening effects are acceptable; detection limits are in the nanograms per millilitre range while the linear range covers about four orders of magnitude. The sensitivity is essentially independent of the molecular form.

The usefulness of ICAP-HPLC is illustrated by the separation of iron carbonyl and molybdenum carbonyl complexes and of ferrocene, organoarsenic, organomercury and organolead compounds.

INTRODUCTION

Conventional methods in atomic spectrometry, using arcs, furnaces, sparks or flames, are not suitable for coupling to high-performance liquid chromatographic (HPLC) systems because arc and furnace¹ techniques require batchwise operation, and flames²⁻⁴ and sparks⁵ present serious limitations due to either restricted sensitivity or lack of precision⁶.

With the introduction of commercial versions of the inductively coupled plasma (ICP) emission source, an element-specific detection system, suitable for HPLC coupling, has become available. An ICP can be considered as an "electrical flame". The plasma, *i.e.*, the flame, is generated by induction heating of a flowing conducting gas ("fuel" gas) by inducing a magnetic field around the top of an assembly of coaxial silica tubes which constitutes the burner or "torch". Via the torch, test solutions are introduced into the plasma by means of a pneumatic nebulizer. When argon (A) is used as the "fuel" gas and as the nebulizing gas, the technique is referred to as ICAP.

The property that makes the plasma most suitable as an excitation source is its high temperature. Depending on the quantities of electrical energy transferred to the plasma, the temperature is between about 6000 and 10,000°K. As a consequence of this high temperature, the ICP offers two distinct advantages over combustion flames, *viz.*, excitation of elements the spectral lines of which have high excitation energies and elimination or considerable depression of compound formation.

The characteristics of the combination of this technique with HPLC appear to be very attractive: continuous monitoring, low detection limits for a large number of elements and the possibility of simultaneous multi-element monitoring. Two major drawbacks remain, *viz.* high investment costs and insensitivity towards most of the non-metallic elements. Despite these disadvantages, an HPLC-ICAP combination seems to be a highly valuable analytical asset, practically unique in its capability to distinguish different molecular forms of metallic elements at low concentration levels, with easy and reliable calibration because the calibration factor is generally independent of the molecular form. Areas of application of such a system can easily be found in the field of pollution studies, where valency and complex states of trace amounts of heavy metals are to be determined, in biomedical studies of metal intoxication and in the field of metal-organic covalently bound complexes.

This paper presents the results of a study undertaken in order to assess the capabilities of the ICAP as a detector in HPLC. General characteristics, such as the contribution to the chromatographic peak width, sensitivity, linearity and detection limits for various elements are reported. The influence of the specific nature of the mobile phase and of the flow-rate on these parameters has been investigated. Attention is also given to the influence of the molecular form of the element on the sensitivity.

EXPERIMENTAL

Spectrometric equipment

The ICAP instrumentation consisted of a Plasma Atomcomp Model 96-975 (Jarrell Ash, Waltham, Mass., U.S.A.). The specifications of the relevant components are presented in Table I. A Model 126 lock-in amplifier (PAR, Princeton, N.Y., U.S.A.) in combination with a Model 7501 mechanical 400-Hz chopper (Fairlight, Amsterdam, The Netherlands), placed in front of the entrance slit, and a linear potentiometric recorder (Servogor RE 511; Goerz, Vienna, Austria) were applied for signal readout of the photomultiplier. The wavelengths of the emission lines used are summarized in Table II.

Chromatographic equipment

For testing the ICAP under chromatographic conditions, a constant flow pump (Model 8500; Varian, Palo Alto, Calif., U.S.A.), a syringe injection device (custom built), an injection valve (HPSV 20; Chromatronix, Berkeley, Calif., U.S.A.) and stainless-steel connecting tubes were used. No special minimal dead volume connection between the HPLC equipment and the nebulizer was applied. The outlet of the injection device or column consisted of Teflon capillary tubing (1.65 mm O.D., 0.3 mm I.D., 10 cm long) and was merely connected to the inlet side of the nebulizer by using a piece of silicone rubber tubing (1.5 mm I.D.) as a collar, taking care to obtain immediate contact between the connected capillaries.

TABLE I
SPECIFICATIONS OF THE ICAP INSTRUMENTATION

System	Components and parameters Specification	
RF generator	Generator	Plasma-Therm (Kresson, N.Y., U.S.A.), Model HFS-2000 D
	Frequency	27.12 MHz (stability $\pm 0.05\%$)
Torch assembly	Power output	0.5-2.0 kW (nominal)
	Plasma gas tube	I.D. 18 mm
	Auxiliary gas tube	I.D. 13 mm
	Sample introduction tube	O.D. 7 mm tapered to 3.3 mm, I.D. 1 mm, length 200 mm
Sample introduction system	Tube material	Clear fused quartz, General Electric Type 204
	Nebulizer	Cross-flow
	Nebulizer capillaries	Glass, length 77 mm, I.D. 0.7 mm, with an orifice diameter of 0.22 mm
Readout system	Spray chamber	length 150 mm, I.D. 30 mm
	Monochromator	0.5-m Mark V (Jarrell Ash); Ebert mounting; reciprocal linear dispersion 8.5 Å/mm
	Photomultiplier	Hamamatsu R 456, 450-950 V

TABLE II
WAVELENGTHS OF THE EMISSION LINES USED IN THIS STUDY

I = atomic line, II = ionic line.

Element	Spectral line (Å)
As I	2780.22
Cu I	3247.54
Fe II	2599.40
Fe I	3734.87
Hg I	2536.52
Mo II	2816.15
Pb II	2203.53
Pb I	2833.06
Sn I	2839.99

Peak-area measurements were performed with an electronic integrator (Autolab System I; Spectra Physics, Santa Clara, Calif., U.S.A.).

In chromatographic applications, a gradient elution pumping system (Series 3; Perkin-Elmer, Norwalk, Conn., U.S.A.), stainless-steel columns and a variable-wavelength UV detector (SF 770 Spectro Flow; Schoeffel, Westwood, N.Y., U.S.A.) in series with the ICAP were used.

Titration procedure

To determine the iron content of several iron compounds, a back-titration procedure was applied. After complexation of iron with excess of EDTA, this excess was titrated photometrically with bismuth at pH 1.5, using 4-(2-pyridylazo)resorcinol (PAR) as an indicator.

Chemicals

Analytical-reagent grade solvents and doubly distilled water were used. All

ionic iron-containing solutions were acidified to pH 2 with nitric acid. The iron carbonyl and molybdenum carbonyl compounds were chromatographically pure; the other chemicals were of analytical-reagent grade.

RESULTS AND DISCUSSION

The ICAP was operated under the conditions specified in Table III. These are compromise conditions for simultaneous multi-element analysis.

TABLE III
ICAP OPERATING CONDITIONS

<i>Parameter</i>	<i>Aqueous solutions</i>	<i>Organics</i>
Forward power at generator	1.05 kW	1.90 kW
Reflected power at generator	<10 W	<30 W
Observation height in plasma	17 mm above coil	17 mm above coil
Plasma gas flow-rate	20 l/min	24 l/min
Auxiliary gas flow-rate	0 l/min	0 l/min
Sample carrier gas-flow rate	0.8 l/min	0.8 l/min

The use of the ICAP appears to place few restrictions on the choice of the mobile phase in reversed-phase separations with modified silica. Plasma ignition problems appeared to arise when using methanol or tetrahydrofuran (THF). Concentrations higher than 40% methanol or 10% THF prevented the ignition of the plasma. This problem can be easily overcome by ignition of the plasma with an ethanol-water mixture. Once the plasma is ignited, switching to a methanol-water mixture of the required composition can be carried out. Up to 90% (v/v) methanol in water can be used this way, although at higher methanol concentrations [80%–90% (v/v)] the reflected power increases to 50–100 W. With 100% methanol the plasma is very unstable.

Acetonitrile, ethanol and higher alcohols can be applied up to 100% without serious problems. In straight-phase adsorption chromatography the choice of the mobile phase appeared to be very restricted. Only with xylene and toluene was a stable plasma obtained, whereas the use of hexane and 2,2,4-trimethylpentane produced plasmas that were stable for only a short time.

Test of the ICAP as HPLC detector

Peak broadening. In order to preserve the resolution created by the HPLC column, the peak broadening caused by the detector must be small compared with the peak broadening caused by the column. To determine the contribution to the peak broadening of the complete measuring system, *viz.*, the connecting tube, the nebulizer, the spray chamber, the plasma torch and the signal readout devices, 1- μ l samples of an $\text{FeNH}_4(\text{SO}_4)_2$ solution (50 μg Fe/ml) were injected by means of a precision syringe injection device⁷. The peak broadening, determined by measuring half the peak width at 60% of the maximum height of the peak and using a time constant of 0.03 sec in the amplifier, corresponded to about 25 μl .

In order to prevent the nebulizer from becoming clogged with septum material and to permit convenient and reproducible injections, a sampling valve was preferred to the syringe injection device in later experiments. The value of 25 μl permitted an injection volume of 15 μl (loop plus internal volume), without a severe injection contribution to the total peak broadening.

The influence exerted by the flow-rate and the nature of the mobile phase on the peak broadening was determined using $\text{FeNH}_4(\text{SO}_4)_2$ solutions (50 $\mu\text{g Fe/ml}$), observing the Fe II line.

The results in Fig. 1 indicate that the peak broadening ranges between 20 and 30 μl and does not show a strong dependence on either the flow-rate or the mobile phase composition.

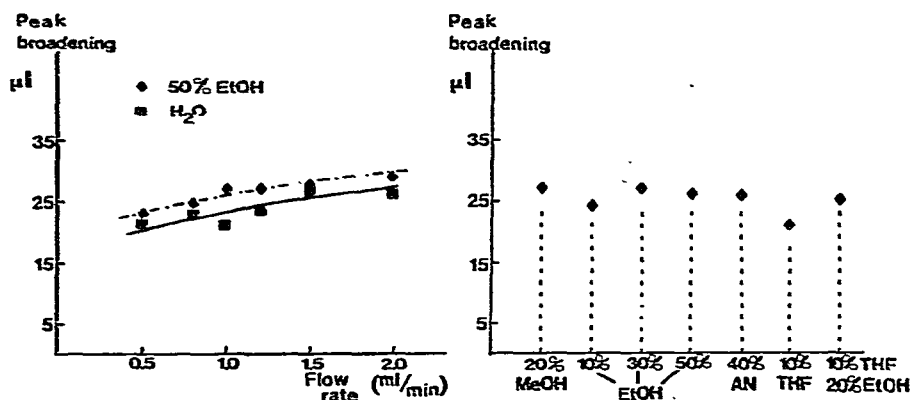


Fig. 1. Influence of the flow-rate and the mobile phase composition (at a flow-rate of 1.2 ml/min) on the peak broadening. Emission line, Fe II; eluent, water (pH 2).

Sensitivity. The sensitivity (S) was determined dynamically by applying the equation

$$S = \frac{W}{Q} \int \Delta V dt \quad (1)$$

where W = ($\mu\text{l/sec}$) is the flow-rate, Q = (ng) the sample amount, $\int \Delta V/dt$ ($\mu\text{V} \cdot \text{sec}$) represents the area of a chromatographic peak and S ($\text{mV} \cdot \text{ml}/\mu\text{g}$) is the sensitivity. The sensitivity was determined in this way for several emission lines (Fe I, Fe II, Cu I, Pb II) at various flow-rates (Fig 2), and the influence of the mobile phase composition on the sensitivity was investigated for the Fe II emission line (Fig 3).

The results in Fig. 2 show that the sensitivity for these four emission lines is essentially independent of the flow-rate, especially in the range 0.8–2.0 ml/min. Therefore, in this flow-rate range, the ICAP can be considered as a concentration-sensitive detector. This is also confirmed by plotting the peak areas, obtained from equal injections at different flow-rates, versus the reciprocal of the flow-rate. A linear relationship is observed in the flow-rate range 0.8–2.0 ml/min. At lower flow-rates the ICAP changes to a mass-flow-sensitive detector.

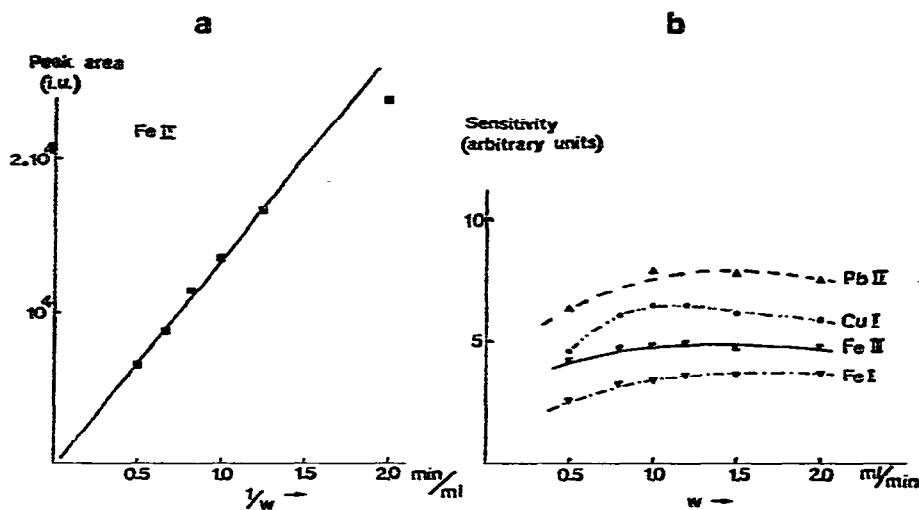


Fig. 2. (a) Peak area versus reciprocal of flow-rate. Emission line, Fe II; eluent, water (pH 2). (b) Sensitivity for the Fe I, Fe II, Cu I and Pb II emission lines at various flow-rate; using water (pH 2) as eluent.

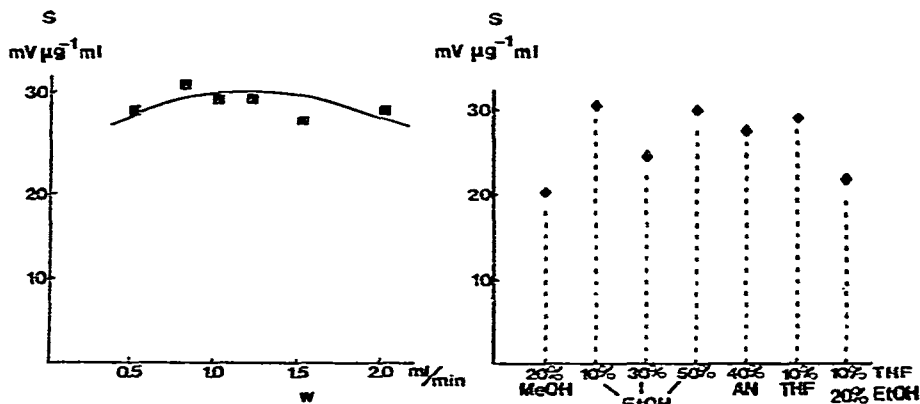


Fig. 3. Sensitivity for the Fe II emission line at different flow-rates (eluent 50% ethanol) and at different mobile phase compositions (flow-rate 1.2 ml/min).

A similar result is obtained when 50% (v/v) ethanol in water is used as the eluent (Fig. 3). Fig. 3 also shows that the nature and concentration of the organic solvent has only a minor influence on the sensitivity, measured at 1.2 ml/min

Linearity. One of the characteristics of the ICAP emission source is a large linear dynamic range, permitting analyses covering a concentration range of about four orders of magnitude. This feature did not deteriorate under the experimental conditions applied here: in testing the applicability of the ICAP as an HPLC detector.

Injection of 15- μl samples of $\text{FeNH}_4(\text{SO}_4)_2$ solutions, ranging from 0.5 to 5000 $\mu\text{g Fe/ml}$, indicated that, for all flow-rates and mobile phase compositions

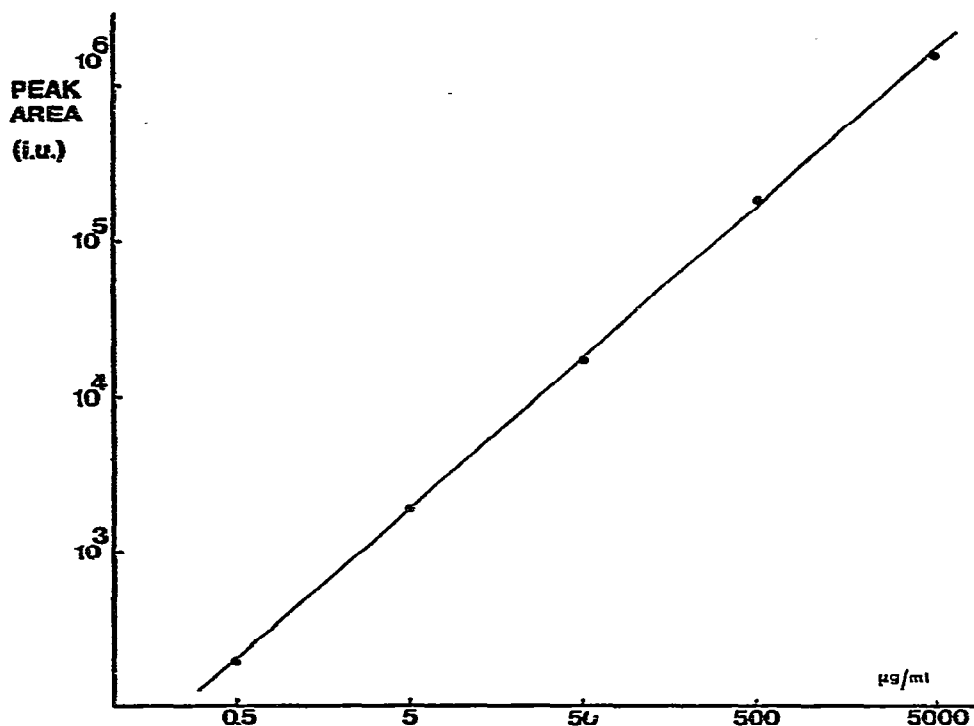


Fig. 4. Double-logarithmic calibration graph. Emission line, Fe II; eluent, 30% (v/v) ethanol; flow-rate, 1.2 ml/min.

tested, the calibration graphs were linear within this concentration range (Fig. 4). The slopes of the double-logarithmic calibration graphs are slightly less than 1.00 in all instances (Table IV). Considering the concentration range of four orders of magnitude, this slight non-linearity is of minor importance.

Noise and detection limit. As the peak area in chromatography is often taken as representing the amount of analyte, the integrated baseline noise must be determined⁸. The standard deviation of the integrals was calculated for different integration times. This calculation was performed with respect to a straight line fitted through these integrals with a least-squares programme. Results obtained by this method are shown in Table V. The standard deviations of the integrals were transformed into equivalent standard deviations of the signal by dividing by the integration time. The results are representative of the standard deviation in concentration units. From these figures, 2σ detection limits were calculated, and Table VI lists the 2σ detection limits for several elements and under various conditions.

The quantitative precision using the ICAP is affected by proportional noise. Replicate analyses with peak-area measurements yielded a standard deviation of about 3%, also at those high concentration levels where baseline noise has a negligible effect. The proportional noise is also visible as an irregular peak shape in a chromatogram (Fig. 5). A study of the cause of and the remedies for this effect is in progress in our laboratory⁹.

TABLE IV
DETECTOR LINEARITY

<i>Mobile phase</i>	<i>Flow-rate (ml/min)</i>	<i>Emission line</i>	<i>Concentration range ($\mu\text{g/ml}$)</i>	<i>Slope of double-logarithmic calibration graph</i>
Water (pH 2)	0.5	Fe I	0.5-5000	0.98
Water (pH 2)	0.8	Fe I	0.5-5000	1.00
Water (pH 2)	1.0	Fe I	0.5-5000	0.98
Water (pH 2)	1.2	Fe I	0.5-5000	0.98
Water (pH 2)	1.5	Fe I	0.5-5000	0.99
Water (pH 2)	2.0	Fe I	0.5-5000	0.98
Water (pH 2)	0.5	Fe II	0.5-5000	0.94
Water (pH 2)	0.8	Fe II	0.5-5000	0.94
Water (pH 2)	1.0	Fe II	0.5-5000	0.95
Water (pH 2)	1.2	Fe II	0.5-5000	0.95
Water (pH 2)	1.5	Fe II	0.5-5000	0.98
Water (pH 2)	2.0	Fe II	0.5-5000	0.94
20% Methanol	1.2	Fe II	0.5-5000	0.95
10% Ethanol	1.2	Fe II	0.5-5000	0.96
30% Ethanol	1.2	Fe II	0.5-5000	0.97
50% Ethanol	1.2	Fe II	0.5-1000	0.98
40% Acetonitrile	1.2	Fe II	0.5-1000	0.98
10% Tetrahydrofuran	1.2	Fe II	0.5-1000	0.96
10% Tetrahydrofuran, 20% ethanol	1.2	Fe II	0.5-1000	0.95

TABLE V

NOISE AND DETECTION LIMITS

Emission line: Fe II. Flow-rate: 1.2 ml/min. Eluent: water.

<i>Integration time, ΔT (sec)</i>	<i>Standard deviation integral, s_1 (V. sec.)</i>	<i>Corresponding minimal detectable amount, $2s_0$ (ng)</i>	<i>Standard deviation of voltage, s_V (ΔT) (V)</i>	<i>Corresponding minimal detectable concentration, $2s_C$ (ΔT) (ng/ml)</i>
10	$39.7 \cdot 10^{-5}$	0.18	$43.9 \cdot 10^{-6}$	1.0
30	$139 \cdot 10^{-5}$	0.62	$46.5 \cdot 10^{-6}$	1.0
100	$524 \cdot 10^{-5}$	2.34	$58.2 \cdot 10^{-6}$	1.3

TABLE VI

DETECTION LIMITS FOR VARIOUS ELEMENTS AND UNDER VARIOUS CONDITIONS WITH AN INTEGRATION TIME OF 30 SEC

<i>Emission line</i>	<i>Flow-rate (ml/min)</i>	<i>Eluent</i>	<i>Minimal detectable concentration, $2s_C$ (ΔT) (ng/ml)</i>
Fe II	0.5	Water	0.7
Fe II	1.2	Water	1.0
Fe II	2.0	Water	0.9
Mn II	1.2	Water	0.3
Cu I	1.2	Water	0.6
Sn II	1.2	Water	10.8
Pb I	1.2	Water	10.9
Fe II	1.2	20% Ethanol	6.1
Fe II	1.2	50% Ethanol	0.8
Fe II	1.2	80% Ethanol	1.0

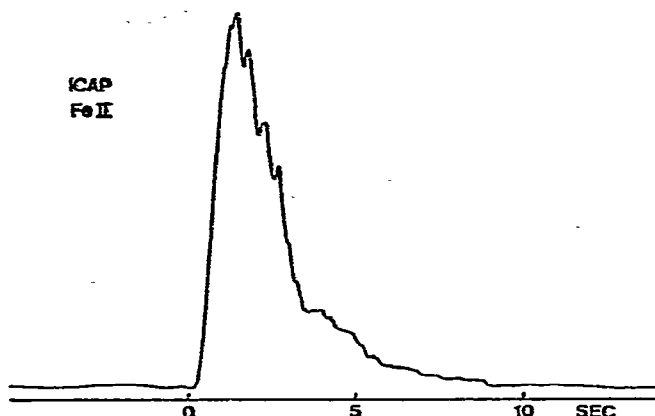


Fig. 5. Irregular peak shape due to proportional noise. Emission line, Fe II; eluent, water (pH 2); flow-rate, 2.0 ml/min; concentration, 50 μg Fe/ml.

Response factors for different iron compounds

Efficient use of the ICAP in the quantitative analysis of different organometallic complexes is facilitated when the sensitivity of the ICAP is independent of the molecular form of a certain element. This was investigated for a number of different iron compounds. Aqueous solutions of several iron salts and solutions of iron complexes in ethanol were analysed with the ICAP, observing the Fe II line. The iron content was verified by a titration method. With iron complexes a wet destruction with concentrated perchloric acid-concentrated nitric acid (4:1) plus a few drops of 30% hydrogen peroxide preceded the titration. Response factors were calculated as the detector response per gram of iron present, relative to iron ammonium sulphate (aqueous solutions) or iron acetylacetonate (ethanolic solutions) (Table VII).

The results in Table VII indicate that the detector response is not entirely independent of the molecular form. However, large differences in the response factors, as occur for example with UV detection, were not observed. In order to obtain a better

TABLE VII
RESPONSE FACTORS FOR DIFFERENT IRON COMPOUNDS

Iron compound	Solvent	Response factor
$\text{NH}_4\text{Fe}(\text{SO}_4)_2$	Water	1.00
$\text{Fe}(\text{NO}_3)_3$	Water	1.01
FeCl_3	Water	1.01
$\text{K}_3\text{Fe}(\text{CN})_6$	Water	0.95
$\text{K}_4\text{Fe}(\text{CN})_6$	Water	0.96
$\text{Fe}(\text{acetylacetonate})_3$	Ethanol	1.00
Ferrocene	Ethanol	0.83
1-Acetylferrocene	Ethanol	0.91
1,1'-Diacylferrocene	Ethanol	1.13
$\text{Fe}_2(\text{CO})_9$ -di-(<i>tert.</i> -butyl-diazabutadiene)	Ethanol	1.10
$\text{Fe}_2(\text{CO})_9$ -di-(cyclohexyl-diazabutadiene)	Ethanol	1.41
$\text{Fe}_3(\text{CO})_9$ -p-tolyl-NS	Ethanol	0.71

relative to
 $\text{NH}_4\text{Fe}(\text{SO}_4)_2$

relative to
 $\text{Fe}(\text{acetylacetonate})_3$

understanding of the (possible) influence of the molecular form on the detector response, a more extensive study is required.

Application to chemical analysis

The use of an ICAP as a detector for liquid chromatography offers the advantages of element-specific detection combined with low detection limits for a large number of elements. The element specificity appears to be very helpful in organometallic chemistry. The analysis of a reaction mixture containing several iron carbonyl complexes, resulting from the reaction of iron nanocarbonyl $[\text{Fe}_2(\text{CO})_9]$ and di-*tert.*-butylsulfurdiimine ($\text{R}-\text{N}=\text{S}=\text{N}-\text{R}$) showed a large number of components^{10,11}.

As can be seen from Figs. 6 and 7 even minor constituents can be identified as iron complexes. Fig. 6 illustrates the large linear dynamic range, while Fig. 7 gives an example of the use of 90% (v/v) methanol as the mobile phase. In the latter instance gradient elution was applied in order to achieve an almost complete separation of the components in one run. Another application in organometallic chemistry is the separation of five molybdenum carbonyl complexes (Fig. 8). A gradient of 55 to 80% (v/v) ethanol within 5 min is possible without impairing the detector performance.

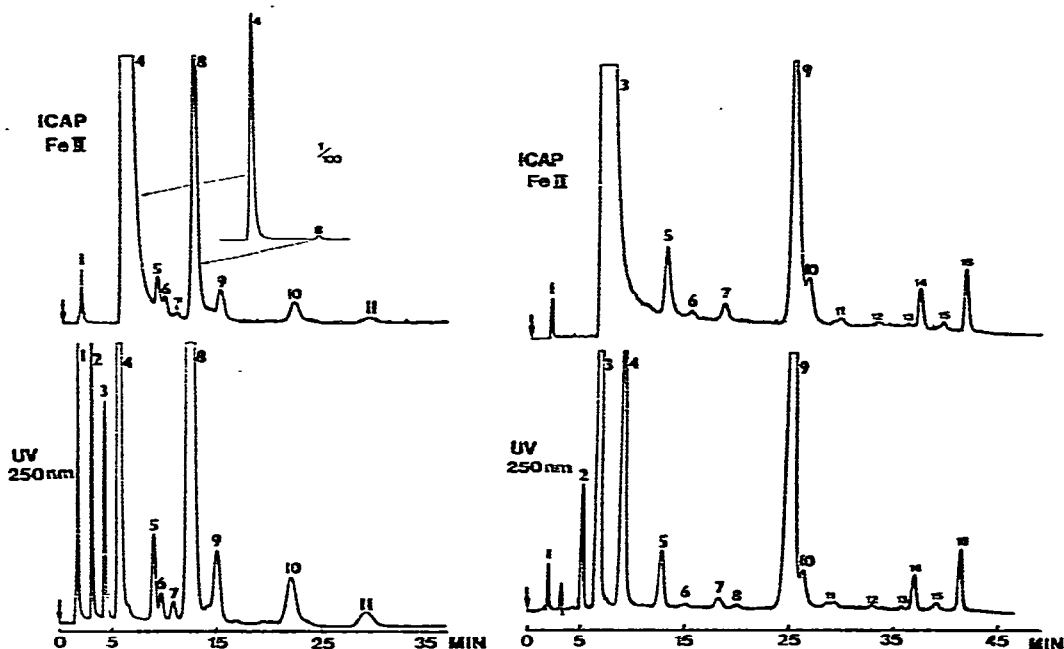


Fig. 6. Separation of iron carbonyl complexes, resulting from the reaction of $\text{Fe}_2(\text{CO})_9$ and di-*tert.*-butylsulfurdiimine. Column, 250×4.6 mm I.D.; mobile phase, 70% (v/v) ethanol; stationary phase, Zorbax-C8; flow-rate, 1 ml/min; UV detection, 250 nm; ICAP detection, Fe II; injection, $5 \mu\text{l}$ of reaction mixture in toluene.

Fig. 7. Separation of iron carbonyl complexes using gradient elution. Gradient conditions: 80% (v/v) methanol for 15 min, 20 min linear gradient of 80% (v/v) to 90% (v/v) methanol. Other conditions as in Fig. 6.

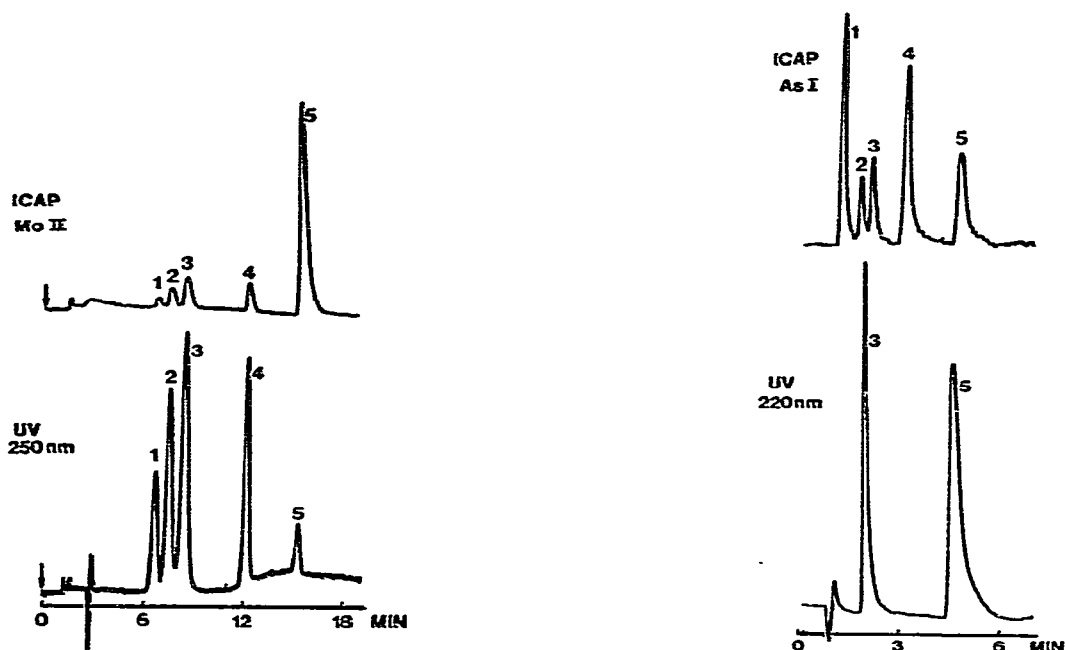


Fig. 8. Separation of a test mixture of molybdenum carbonyl complexes using gradient elution. Gradient conditions: 5 min linear gradient of 50 to 55% (v/v) ethanol, 5 min linear gradient of 55% (v/v) to 80% (v/v) ethanol. ICAP detection: Mo II. Injection: 20 μ l of test mixture. Other conditions as in Fig. 6. Peaks: 1 = molybdenum tetracarbonyl bipyridyl; 2 = molybdenum tetracarbonyl pyridinecarbaldehyde-2-isopropylimine; 3 = molybdenum tetracarbonyl pyridinecarbaldehyde-phenylimine; 4 = molybdenum tetracarbonyl di-*tert*-butyldiazabutadiene; 5 = molybdenum hexacarbonyl.

Fig. 9. Separation of a test mixture of arsenic compounds using dynamic ion exchange. Mobile phase: 30% (v/v) methanol, 1% (w/w) *n*-hexadecyltrimethylammonium bromide, $[\text{PO}_4] = 0.08 \text{ M}$, pH = 5. Stationary phase: Hypersil (6 μ m). Column, 100 \times 4.6 mm I.D.; flow-rate, 1.2 ml/min; UV detection, 220 nm; ICAP detection, As I. Peaks: 1 = dimethylarsinic acid, monosodium salt; 2 = disodium methylarsenate; 3 = *p*-arsanilic acid; 4 = sodium arsenate; 5 = phenylarsonic acid.

The analysis of trace amounts of heavy metals of different valencies or complex states is of interest in pollution or toxicity studies. Examples of such analyses are shown in Figs. 9–11.

The separation of some arsenic compounds was performed with dynamic ion-exchange chromatography, using a quaternary ammonium salt as an ion exchanger. Separation systems suitable for the analysis of organomercury compounds have been described elsewhere¹². In these cases (Figs. 9 and 10), the ICAP, when compared with UV detection, shows a strongly enhanced sensitivity for alkyl-metal complexes. The mercury compounds give rise to extra peak broadening in the ICAP, presumably due to adsorption in the nebulizing system. Possibly this effect is connected with so far unspecified problems met in the ICAP analysis of mercury.

In Fig. 11 the analysis of a petrol sample for lead compounds is shown. Use of the UV detector results in a chromatogram with a large number of unseparated components, whereas the ICAP detects only the four lead-containing compounds in this chromatogram.

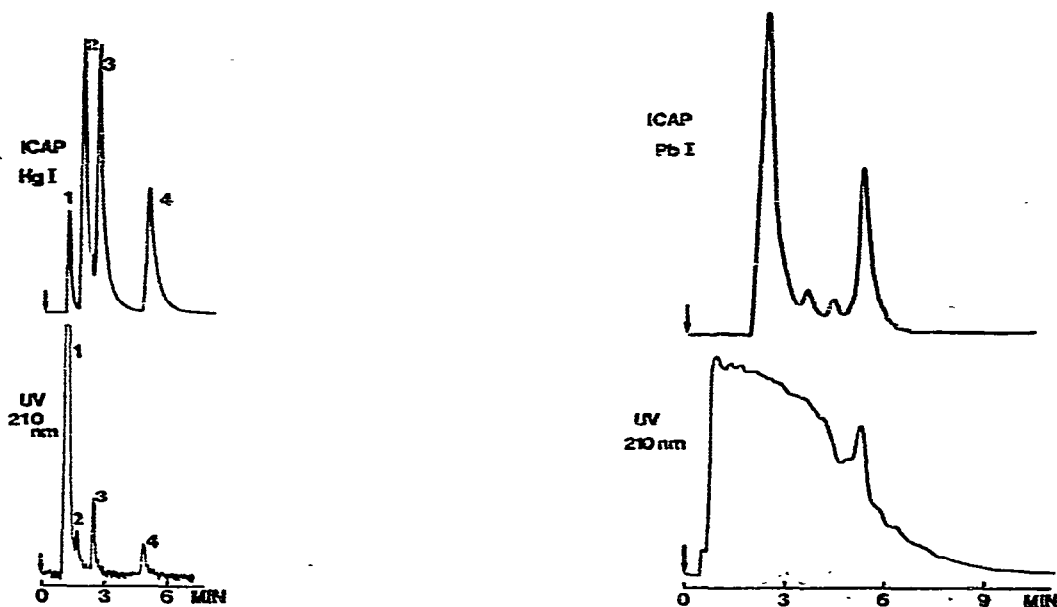


Fig. 10. Separation of a test mixture of mercury compounds. Mobile phase: ethanol-0.05 *M* NaBr (1:2), pH = 3. UV detection, 210 nm; ICAP detection, Hg I. Other conditions as in Fig. 9. Peaks: 1 = mercury(II) chloride; 2 = methylmercury; 3 = ethylmercury; 4 = propylmercury.

Fig. 11. Analysis of a petrol sample. Mobile phase, 75% ethanol; flow-rate, 1.4 ml/min; UV-detection 210 nm; ICAP detection, Pb I; injection, 30 μ l of petrol. Other conditions as in Fig. 6.

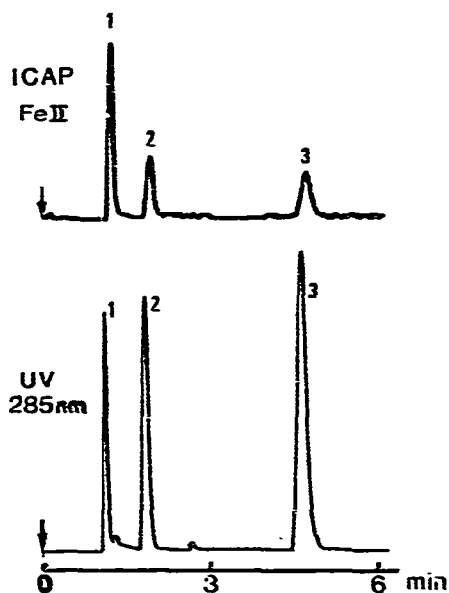


Fig. 12. Separation of a test mixture of ferrocene compounds using straight-phase adsorption chromatography. Column, 250 \times 3 mm I.D.; stationary phase, silica gel Si 60 (8 μ m); mobile phase, toluene; flow-rate, 1.4 ml/min; UV detection, 285 nm; ICAP detection, Fe II. Peaks: 1 = ferrocene; 2 = monoacetylferrocene; 3 = diacetylferrocene.

Applications with straight-phase adsorption chromatography are less comprehensive because of the limitations in the choice of the eluent. The separation of three ferrocene derivatives is an example of straight-phase adsorption chromatography in which toluene was applied as the eluent (Fig. 12).

CONCLUSION

The ICAP can easily be applied as a detector in HPLC. Element specificity is combined with low detection limits for a large number of elements and with a wide linear dynamic range. No serious restrictions on the flow-rate or on the mobile phase composition in reversed-phase separations were found. Without a special design of a minimal dead volume connection or modification of the nebulizer system, a contribution to the peak broadening of only 25 μ l was found. Adaptation of the nebulizer for chromatographic purposes may yield a smaller peak broadening. A drawback encountered in this work, with the equipment described, is the limitation to aromatic hydrocarbons as the mobile phase in straight-phase adsorption chromatography.

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