Journal of Chromatography A, 622 (1994) 329–340
Elsevier Science B.V., Amsterdam

CHROM. 25 697

Chromium determination by supercritical fluid chromatography with inductively coupled plasma mass spectrometric and flame ionization detection

Jeffrey M. Carey[☆], Nohora P. Vela and Joseph A. Caruso*

University of Cincinnati, Department of Chemistry, Cincinnati, OH 45221-0172 (USA)

(First received July 2nd, 1993; revised manuscript received October 26th, 1993)

ABSTRACT

Supercritical fluid chromatography (SFC) has been investigated for the separation of a pair of β-ketonate chromium compounds and a thermally labile organochromium dimer. A limited comparison between flame ionization detection (FID) and inductively coupled plasma mass spectrometric (ICP-MS) detection of these compounds is presented. The β-ketonate complexes were observed with both detectors, while the thermally labile dimer was not observed with ICP-MS detection. Detection limits for these compounds with ICP-MS were in the range of 0.9 to 3 pg with FID giving values between 10 and 250 pg. Reproducibility of the method is between 1 and 4% relative standard deviation (R.S.D.). The technique provided a linear response over approximately three orders of magnitude. The effect of two mobile phases (nitrous oxide and carbon dioxide) on the detection by each of the detectors are presented in a qualitative manner. Finally, the SFC–ICP interface heating method and the manner in which the restrictor is heated in the FID system are compared and there effect on the chromatography discussed.

INTRODUCTION

Coupling supercritical fluid chromatography (SFC), as well as other chromatographic methods, to inductively coupled plasma mass spectrometry (ICP-MS) has received increasing interest in recent years as the need for speciation information on a particular sample begins to rival the need to achieve ultra-trace level detection [1–3]. This increasing demand comes from the dependence of the chemical form or environment of a given element on its toxicity. An important example of such an element is chromium. Chromium(III) is an essential element for good nutrition and health while chromium(VI) is a known carcinogen; therefore, a total chromium level determination for a given sample is not sufficient. In order to accurately assess the toxicological concern of the sample, a determination of the chromium form is required for an accurate assessment of the toxicological and environmental concern.

While the trivalent form of chromium is the most innocuous and common form, the hexavalent form is the most industrially important. Sodium chromate and dichromate are principal materials in the production of all chromium containing chemicals. These chromates are produced by a smelting, roasting, and extraction process from chromite ore. The major uses of chromium, and therefore, environmental sources, are: the production of stainless steel; leather tanning; pigment production; wood preservatives; and anti-corrosives in cooking systems and boilers [4].

A number of different liquid chromatographic

* Corresponding author.
☆ Present address: The Lubrizol Corporation, 29400 Lakeland Boulevard, Wickliffe, OH 44092, USA.

0021-9673/94/$07.00
SSDI 0021-9673(93)E1144-O

methods have been employed for speciation of the different chromium oxidation states and different complexed forms of chromium [5–10]. Because of the limitations in the analysis of highly polar compounds via SFC, for analysis of ionic compounds, it may be necessary to complex the chromium prior to injection into the SFC system. For these reasons, β-ketonate compounds were chosen for this study. Chromium β-ketonate complexes have previously been used with reversed-phase LC to provide chromophores for the UV detector [5,6].

Reports have appeared on the use of supercritical fluid chromatography for the separation of metal β-ketonate complexes using ICP atomic emission spectroscopy and UV absorption spectrometric detection [11–13]. These reports, however, use packed column SFC instruments which may not be the most advantageous for ICP detection. The higher flow rates, relative to capillary systems, of mobile phase may cause severe perturbations in the plasma relative to those found with capillary SFC sample introduction. A review of SFC–plasma spectrometry has appeared [14], and the coupling of capillary SFC to ICP-MS has been performed successfully previously in our laboratory and been reported [15–17].

When using a new detector for a chromatographic method (such as ICP-MS) it is important to have a grasp on the detector's effect on the separation. Flame ionization detection (FID) was chosen as the detection method for comparison to ICP-MS due to its preferred usage for capillary SFC. The work presented in this report will investigate the effect of pressure programming with both ICP-MS and FID, the effect of mobile phase, and the effect of the SFC–ICP interface on the analysis.

EXPERIMENTAL

SFC Instrumentation

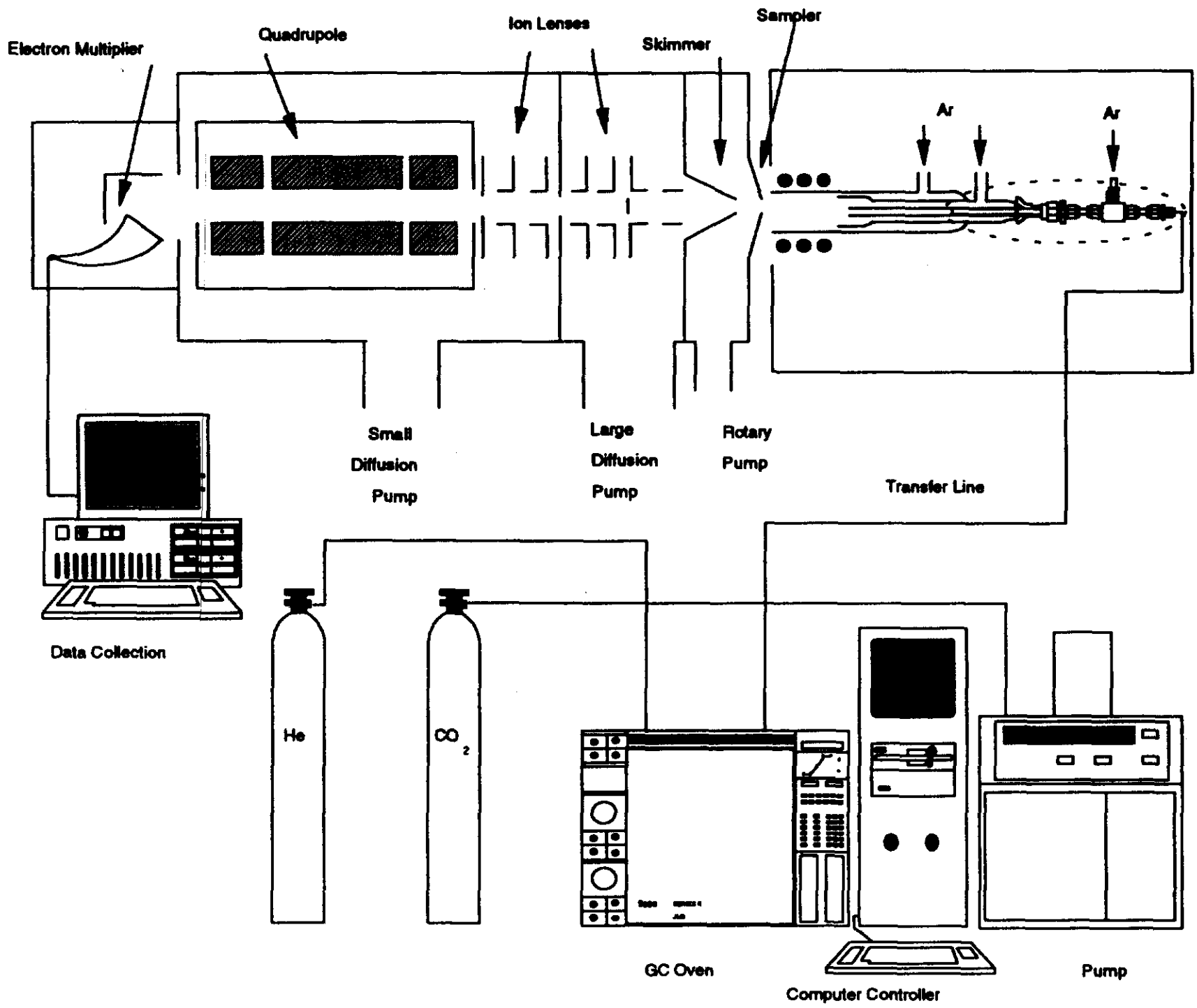
The supercritical fluid chromatograph used has been described in detail previously [15] (Fig. 1). It consisted of a Hewlett-Packard 5890 Series II gas chromatograph (Hewlett-Packard, Avondale, PA, USA) and a Lee Scientific Series 600 supercritical fluid pump (Lee Scientific Division of Dionex, Salt Lake City, UT, USA) controlled by an XT-clone computer. Mobile phases used were supercritical fluid grade liquid carbon dioxide and supercritical fluid-grade liquid nitrous oxide (Scott Specialty Gases, Plumsteadville, PA, USA). The column used was a 4 m long capillary which had an internal diameter of 50 μm. The stationary phase, which had a film thickness of 0.25 μm, was SB-biphenyl-30 (Dionex). A 1.5 cm/s linear velocity frit restrictor was used which had a length of 1.5 m (Dionex). The SFC–ICP interface has also been described previously [15] and differed only in that the interface was constructed from brass, rather than stainless steel; to avoid chromium contamination. The injector and pump were cooled, through the use of a recirculating chiller, to approximately 0°C.

FID

The chromatographic conditions to be compared to those obtained with ICP-MS were obtained with FID (Hewlett-Packard). The FID signal obtained was collected using a Hewlett-Packard 3396 Series II integrator. The integrator data were then collected by a 386SX computer, equipped with Hewlett-Packard's Peak96 software.

ICP-MS Instrument

The inductively coupled plasma mass spectrometer used in this study was a VG PlasmaQuad II STE (Fisons Instruments, Winsford, UK). SFC was coupled to ICP-MS by removing the pneumatic nebulizer and spray chamber, and replacing them with the SFC–ICP interface. No other modifications to the instrument were necessary. The ICP-MS operating conditions are shown in Table I. It is important to note that since the SFC sample introduction method produces a "dry plasma", it is necessary to tune on either a background spectral feature (such as the peak at $m/z = 56$ resulting from ArO^+) or an element which has a high vapor pressure and can be introduced into the dry plasma (such as mercury).



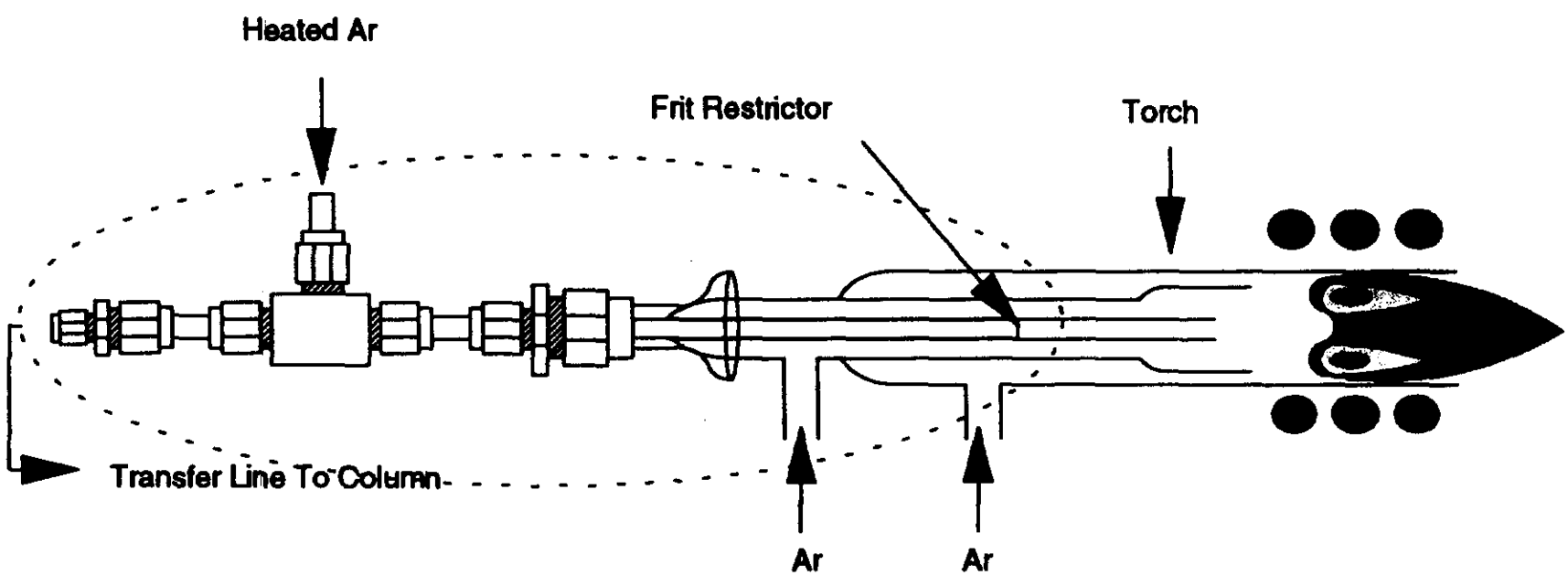


Fig. 1. SFC–ICP-MS instrument diagram showing the SFC–ICP interface.

TABLE I

FID AND ICP-MS OPERATING CONDITIONS

FID Conditions		
Temperature[a]	375°C	
Nitrogen flow	31 ml/s	
Hydrogen flow	50 ml/s	
Air flow	400 ml/s	
ICP-MS Conditions		
Interface temperature[a]	300°C	
Transfer line temperature[a]	80°C	
Injector gas flow	0.9 l/min	
Auxillary gas flow	1.5 l/min	
Coolant gas flow	15 l/min	
Forward power	1.35 kW	
Reflected power	Less than 5 W	
Ion lens tuning	m/z 56 (ArO^+)	
Expansion pressure	Less than 2 mbar	
Intermediate pressure	Less than 10^{-4} mbar	
Analyzer pressure	Approximately $5 \cdot 10^{-6}$ mbar	
SFC Conditions		
Ramp rate[a]	30 atm/min (FID) or	70 atm/min (ICP-MS)
Initial pressure[a]	85 atm	
Initial hold time[a]	4 min	
Oven temperature[a]	70°C	

[a] Optimized condition.

Reagents

Chromium(III) 2,4-pentanedionate [$Cr(C_5H_7O_2)_3$, PDC, M_r 349] was purchased from Alfa Products (Ward Hill, MA, USA) and was used without further purification. Chromium(III), 2,2,6,6-tetramethyl-3,5-heptanedionate [$Cr(C_{11}H_{19}O_2)_3$, MHDC, M_r 602] and pentamethylcyclopentadienylchromium dicarbonyl dimer {$[(CH_3)_5C_5Cr(CO)_2]_2$, MCCD, M_r 757, decomposes at 200°C} were obtained from Strem Chemicals (Newburyport, MA, USA) and were also used without further purification. All solutions were prepared in optima-grade methylene chloride (Fisher Scientific, Fairlawn, NJ, USA).

RESULTS AND DISCUSSION

FID Separation optimization

The chromatographic conditions, initial hold time, initial pressure, ramp rate, oven temperature and FID temperature, for these compounds were optimized using FID. A univariate optimization approach was used for the investigation. The parameters studied were the initial hold time, initial pressure, ramp rate, oven temperature and detector temperature. The optimum conditions found for the optimized parameters are shown in Table I. Optimum conditions were chosen to allow for the shortest analysis time with the best separation.

When no hold time was initially used (no period of constant pressure) the first eluting peak (MHDC) was not observed and was assumed to be co-eluting with the solvent peak. This assumption was based on the expected elution order due to the relative polarities and sizes of the compounds in question. Therefore, in order to effectively resolve the relatively non-polar MHDC from the solvent peak it was necessary to utilize a period of constant pressure prior to the start of any pressure ramp (times of 3.5 to 6 min were investigated). The four-minute hold time was chosen for the separation of MHDC from the solvent peak, and allowed for good resolution of the latter eluting PDC and MCCD peaks.

The next parameter investigated was the initial pressure. As previously stated, the initial hold time used was 4 min while each of the other parameters had the same values as used in the preceeding optimization. While holding these parameters constant, the initial pressure was varied between 70 and 120 atm (1 atm = 101 325 Pa). At pressures below 85 atm, the two later eluting peaks are not observed during the time the signal was acquired. At pressures above 110 atm, the MHDC peak is not observed and is assumed to be co-eluting with the solvent peak. Both sets of peaks (MHDC/solvent and PDC/MCCD) are nearly baseline resolved at 85 atm, and therefore this pressure was chosen for future use.

The ramp rate was also optimized in a univariate manner by varying the rate from 10 to 60 atm/min. Each of the previously optimized parameters were used (initial hold time of 4 min and an 85 atm initial pressure) and the other variables were also held constant. Unlike the previous optimizations, all three of the com-

pounds were observed under each of the conditions. When both analysis time considerations and resolution of the peaks were considered, the optimal condition for the ramp rate was chosen to be 30 atm/min. This value was chosen due to the increased resolution over faster ramp rates, compared to the improvement in analysis times.

An important parameter with SFC (besides the pressure) is the temperature of the supercritical fluid. The previously determined conditions were used for the optimization, along with a FID temperature of 325°C. As the oven temperature is increased, the density is decreased, and, therefore, the capacity factor for each of the compounds in question increases. Another aspect is that the solvent is not affected to as large an extent as the three compounds due to the decreased mobile phase densities at higher temperatures and the less volatile nature of the compounds.

From an analysis of the capacity factors alone, it might be assumed that for these compounds, the lower temperatures might be optimal. However, the separation between PDC and MCCD is greatly affected by the oven temperature. This is probably due to the more polar nature of these compounds. Since they are more polar, they have a greater affinity for the induced dipoles of the stationary phase. Therefore, a stronger solubilizing ability of the mobile phase is required to elute these compounds, leading to larger differences in elution at lower densities (and longer retention times). Given that PDC and MCCD are nearly baseline resolved and that the resolution between the solvent peak and MHDC is not overly large at 70°C, this was chosen as the optimum condition for the separation.

FID Temperature optimization

Previous work has shown that the temperature of the restrictor may have a marked effect on the chromatographic performance of the system [19]. This has been particularly observed with the previously described SFC–ICP interface. These effects have included losses in signal, particularly for less volatile compounds, changes in retention times, and freezing of the restrictor tip. In this study, the effect of the restrictor temperature, through the FID temperature, on the peak areas of the three compounds and on the capacity factors for each of the three compounds was investigated. This will allow a clearer determination of whether or not the restirctor is being heated in the same manner with the SFC–ICP interface, as it is with a well-defined detection method such as FID.

Fig. 2 illustrates the effect of different FID temperatures on each of the three compounds. Fig. 2A shows a decreasing trend for the capacity factors as the FID temperature is increased. This is to be expected because as the FID temperature is increased the frit in the restrictor expands, causing further restriction of the flow of carbon dioxide. This has the effect of increasing the analysis times with increasing FID temperature. Fig. 2B illustrates the effect of the FID

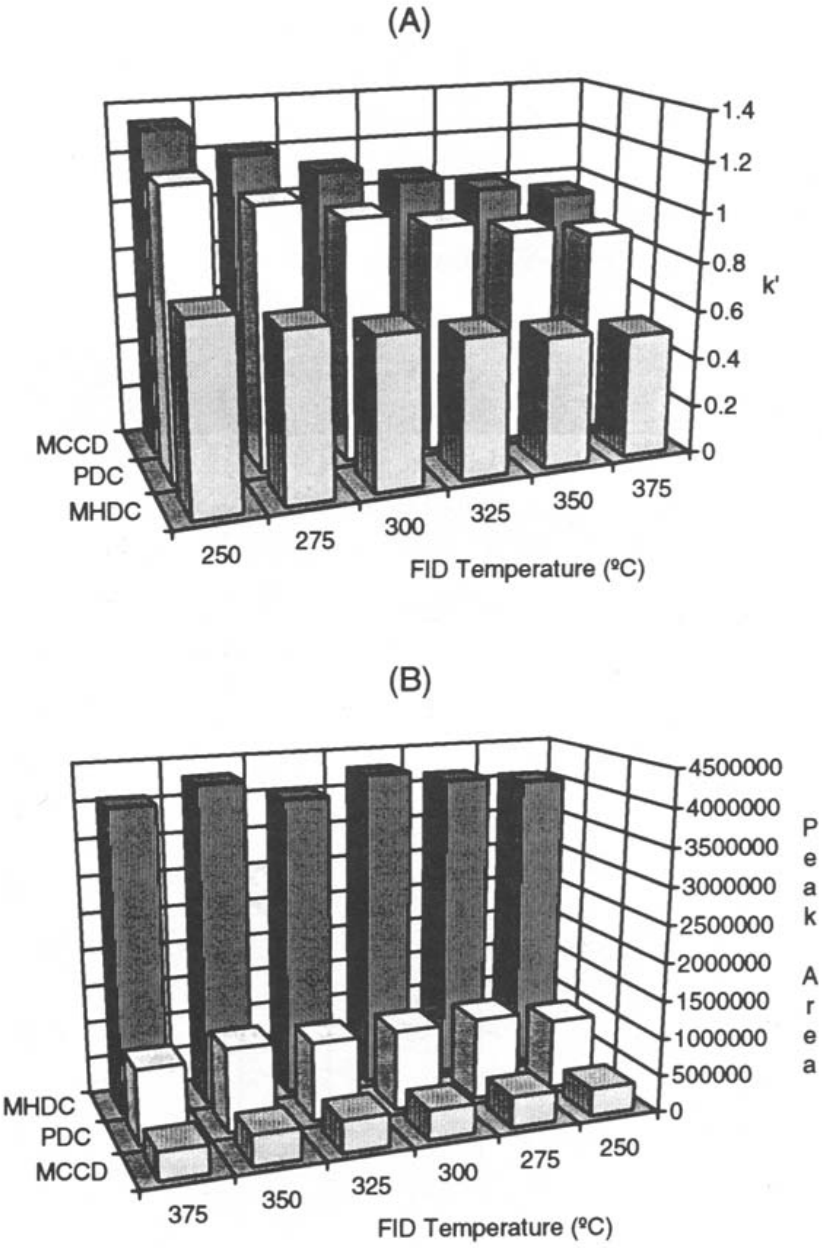


Fig. 2. SFC–FID detector temperature optimization: (A) indicates the capacity factors for each of the three compounds (MHDC, PDC and MCCD) and (B) indicates the peak areas for each of the compounds.

temperature on the area of each of the peaks. It is interesting to note that the detector temperature seems to have no effect on the peak areas obtained. This result is important since a different result was expected using the SFC–ICP interface [19]; indicating that if this is indeed the case, the restrictor is heated in a different manner with the SFC–ICP interface requiring further study of the interface fundamentals. Because the FID temperature seemed to have little effect on the analysis, and 375°C gave the fastest analysis times, it was decided that this temperature would be used as the optimal.

SFC–FID Mobile phase considerations

The chromatograms found using the conditions described previously are shown in Fig. 3 for a carbon dioxide mobile phase and Fig. 4 for a nitrous oxide mobile phase. Carbon dioxide is, by far, the most commonly used mobile phase for SFC due to its non-toxic nature, availability in highly purified forms, and relative low cost. An additional factor in the favorable nature of carbon dioxide as a SFC mobile phase is that it produces minimal FID signal, the most common detection method for reasons previously described. Indeed, as is shown in Fig. 3, a good separation for the compounds was achieved with minimal background signal. The peaks shown, in order of increasing retention time, are methylene chloride, MHDC, PDC, and MCCD.

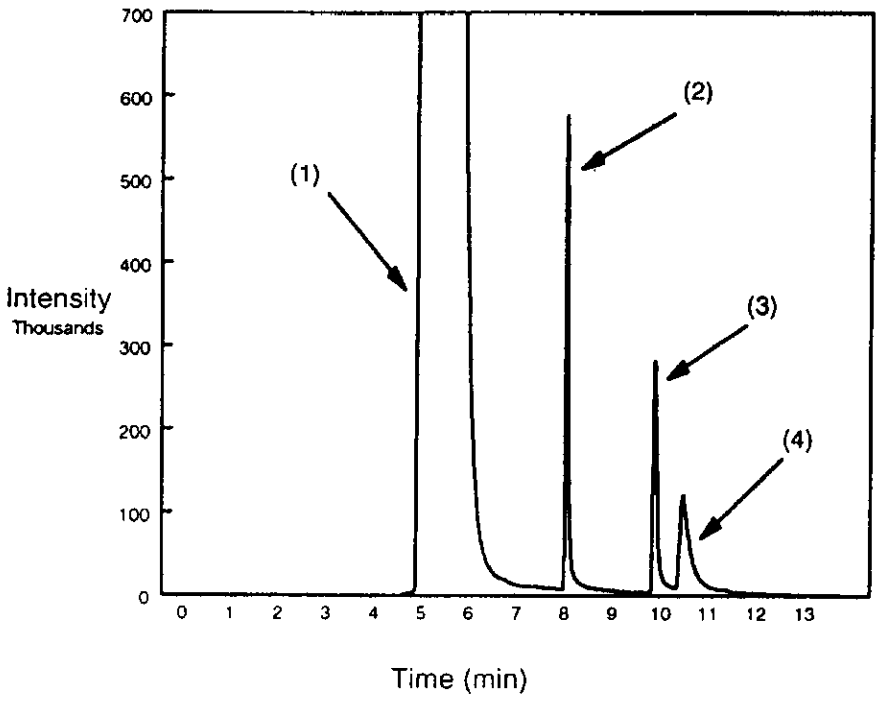


Fig. 3. SFC–FID chromatogram using a carbon dioxide mobile phase for a 10 ng mixture of MHDC (2), PDC (3) and MCCD (4) in methylene chloride (1).

Despite the successful separation of the compounds with the flame ionization detector using a carbon dioxide mobile phase, there were expected difficulties with the use of carbon dioxide for ICP-MS detection. These difficulties result from an expected isobaric interference at m/z 52 (the major isotope of chromium) from the polyatomic species $^{40}Ar^{12}C^{+}$. For this reason, the use of an alternative mobile phase, nitrous oxide, was investigated. Nitrous oxide was chosen due to its similar solvating properties to those of supercritical carbon dioxide. The main difference between the two fluids is that nitrous oxide has a slight dipole moment, making it somewhat polar.

As can be observed in Fig. 4, this mobile phase is not ideal for FID, as sufficient ionization of the nitrous oxide occurs to cause a fairly intense background signal. The background signal mirrors the pressure program, as a greater amount of nitrous oxide is introduced into the flame ionization detector at higher pressures. This background signal obscures the detection of the later eluting compounds at lower concentrations. It can be observed, however, in Fig. 4 that for a 100 ng mixture, the chromatographic separation is maintained.

SFC–ICP-MS Mobile phase backgrounds

When switching of ICP-MS detection, it was hoped that minimal differences in the chromato-

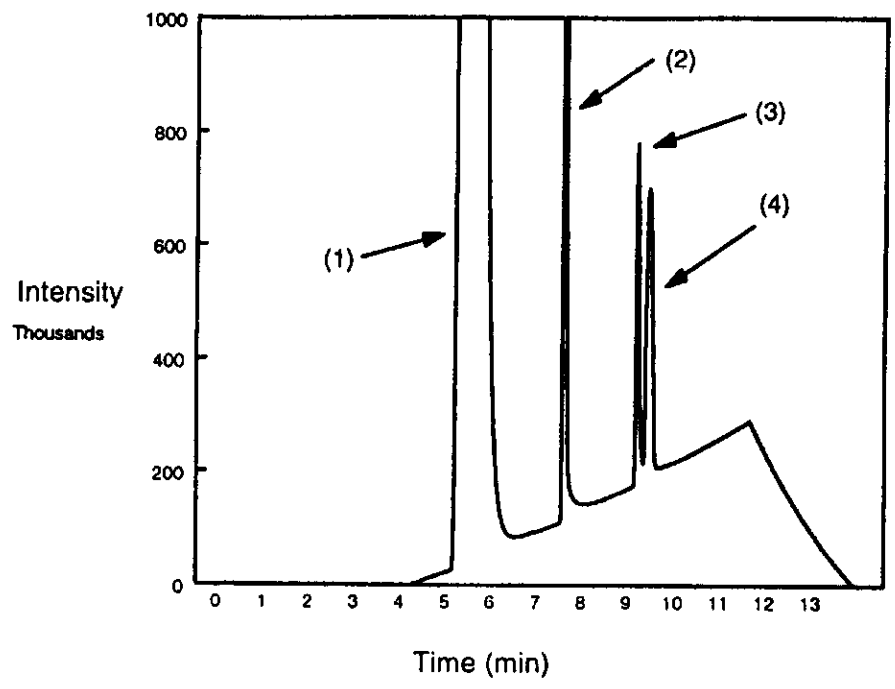


Fig. 4. SFC–FID chromatogram using a nitrous oxide mobile phase for a 100 ng mixture of MHDC (2), PDC (3) and MCCD (4) in methylene chloride (1). The large baseline increase is due to ionization of the nitrous oxide mobile phase.

graphic conditions would be observed. Therefore, it would be desirable to use the same mobile phase as is most favorable for FID. However, as previously mentioned, this was not believed to be possible. In order to determine the feasibility of using both carbon dioxide and nitrous oxide mobile phases, background scans of the plasma while introducing each of the mobile phases at a given pressure were acquired. These scans are shown in Fig. 5 for the introduction, from an isobaric pressure program at 100 atm, of carbon dioxide (A) and nitrous oxide (B). Fig. 5A clearly shows that the detection of chromium at the major isotope (m/z 52) would be extremely difficult due to the large background signal at this mass from ArC^+. In addition, large argon oxygen polyatomic species are observed which may interfere with the determination of iron at m/z 56. A large peak is also observed at m/z 59 which corresponds to cobalt. However, a cobalt contamination source was not found, and this peak is believed to be resulting from an unknown carbon dioxide related polyatomic (possibly $HNCO_2^+$).

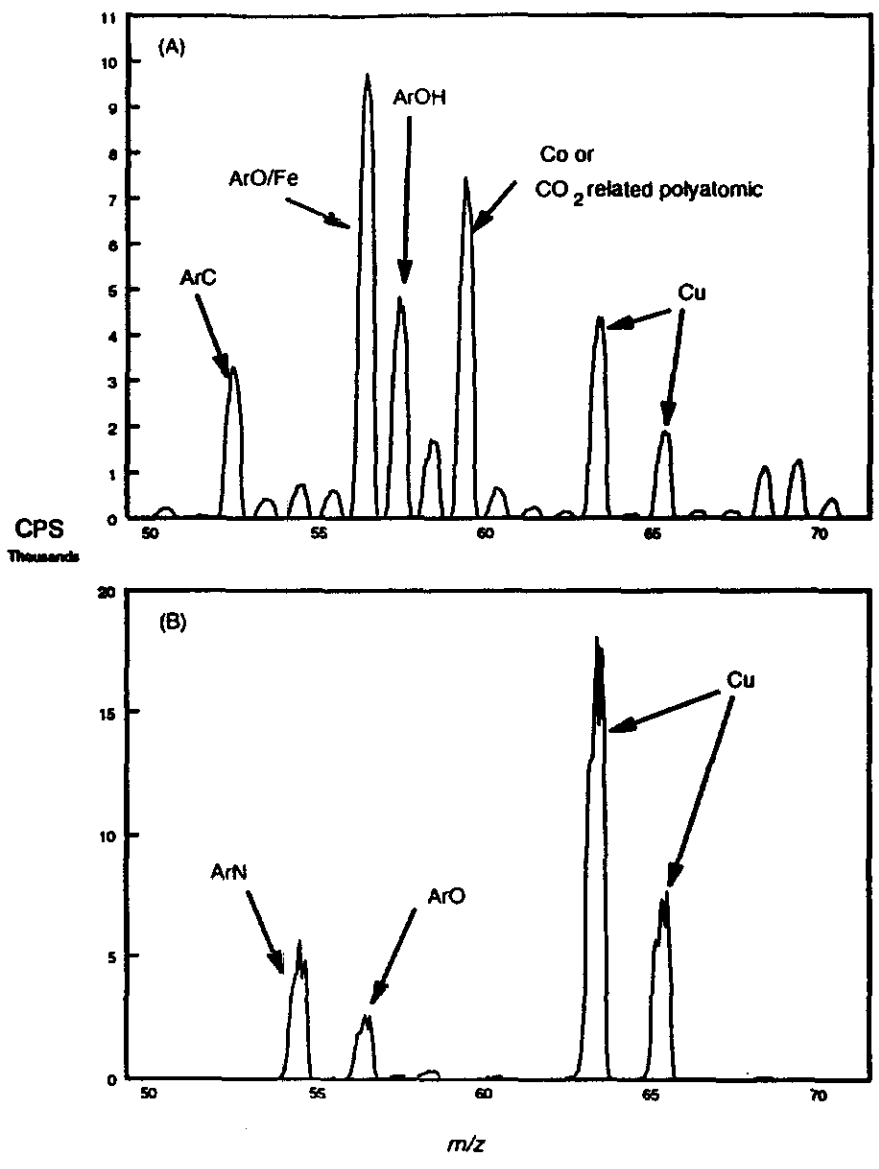


Fig. 5. ICP-MS background scans: (A) is the resulting background from introducing carbon dioxide from a constant pressure program at 100 atm; (B) is the resulting background from introducing nitrous oxide from a constant pressure program at 100 atm.

From Fig. 5B it is observed that with nitrous oxide a much simpler background spectrum is observed. The main peak of note occurs at m/z 54 corresponding to $^{40}Ar^{14}N^+$. This particular mass to charge ratio does not correspond to the major isotope of any elements. Despite not interfering with the major isotope of any elements, this background feature may interfere with isotope ratio determinations for both iron and chromium. Large peaks associated with copper in both of the scans are from the brass SFC–ICP interface. The peaks for the copper in the nitrous oxide scan are larger because the interface was brand new. As the interface ages and is heated for a period of time this signal begins to decrease as the copper surface is oxidized. The carbon dioxide scan shown in Fig. 5A was acquired after the interface had been used for several days.

Problems with thermally labile MCCD

Once it was determined that a nitrous oxide mobile phase would be necessary for ICP-MS detection, each of the three compounds were injected to determine what changes, if any, were observed with their elution. Both of the β-ketonate complexes were found to elute with similar characteristics to FID (with slightly shorter retention times); however, no peak was observed for the MCCD compound. This was unexpected since the compound was easily observed with FID, and peak identification could be made based on retention time. There are several possible causes for the "loss" of this compound including thermal decomposition of the compound in the restrictor followed by irreversible binding to the capillary tube walls and an oxidatively driven decomposition of the compound (using a N_2O mobile phase) with irreversible binding to the capillary walls.

The second of these possibilities is the most unlikely, primarily due to the observation of the compound (albeit in high concentrations) on FID with the nitrous oxide mobile phase. This conclusion is based on the fact that MCCD is known to

decompose at 200°C. Since the interface is heated for a length of nearly 30 cm, the compound is exposed to the high temperatures for a longer period of time than in the FID detector (approximately 8 cm). This will most likely cause the decomposition of the compound, and the chromium is then in an inorganic, or highly polar organic, form which irreversibly binds to the deactivated fused silica capillary tubing walls. The supercritical nitrous oxide then does not have sufficient solvating power to elute the remaining chromium.

A further possibility for the loss of the MCCD is that the interface temperature is too low and the compound is freezing in the restrictor. This type of behavior has been observed previously with non-volatile tin compounds [19]. Because of this possibility, the interface temperature was optimized while injecting the MCCD. However, the compound was not observed at any of the temperatures investigated, reducing the possibility of this being the cause of the loss.

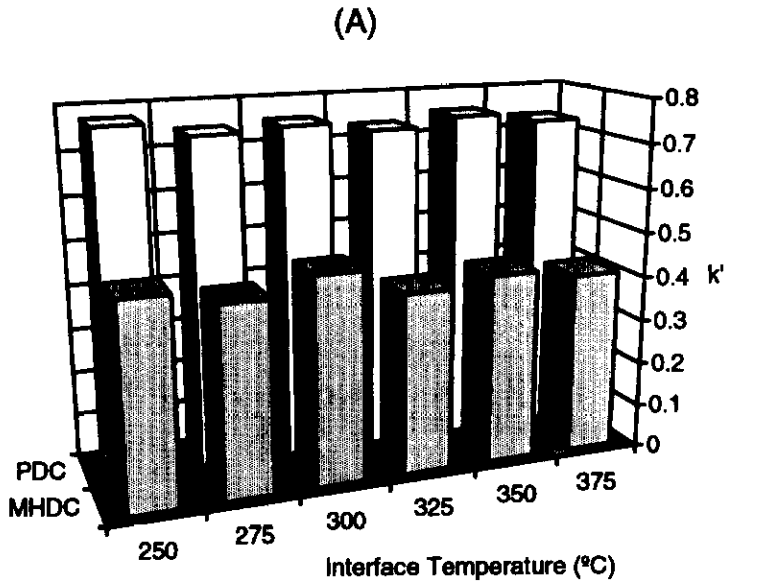


Fig. 6. SFC–ICP interface temperature optimization: (A) indicates the capacity factors for both of the detected compounds (MHDC and PDC); (B) indicates the peak areas obtained for the compounds.

SFC–ICP Interface temperature optimization

Despite the loss of the MCCD compound, it was necessary to optimize the interface temperature, to achieve optimum sensitivity, for the pair of β-ketonate complexes. Fig. 6 illustrates the effect of this parameter on both PDC and MHDC. Since the solvent is a carbon-containing compound, it gives an ArC^+ signal in the ICP-MS allowing the determination of capacity factors. It is interesting that the trends observed are not at all the same as those observed for FID. The capacity factors, Fig. 6A, increased on FID with increasing frit temperature, (the interface and FID temperatures are both essentially the temperature of the frit restrictor) while with ICP-MS detection there is no effect with increasing restrictor temperature on the capacity factor. The retention times were observed to increase; however, the void volume time (solvent peak) increased accordingly. A further difference is that for the more polar PDC, the peak widths were larger at higher temperatures than those observed with FID. Clearly the restrictor in the ICP-MS interface is being heated in a manner different from that in the FID system.

This conclusion is further illuminated by the results shown in Fig. 6B. The peak areas, particularly for the PDC compound, are affected by the SFC–ICP interface temperature. At higher temperatures the PDC compound gives a much smaller peak than at temperatures less than about 325°C. The reason for the significant effect on the signal from PDC is the more polar nature of the compound requiring greater solvating power of the nitrous oxide, which is not available at the higher temperatures (PDC is slightly soluble in water while MHDC is only soluble in relatively non-polar organic solvents).

Since the MCCD compound was not observed with the ICP-MS and no immediate solution to this problem was found, the ramp rate was re-optimized to improve the analysis time. At a ramp rate of 70 atm/min good resolution was found with a sufficiently fast separation (less

than 7 min) and, therefore, this value was chosen as optimal. The chromatographic conditions chosen for the SFC–ICP-MS analyses are shown in Table I.

SFC–ICP-MS Chromatogram and figures of merit

Fig. 7 shows the chromatogram achieved for a 10 ng injection of MHDC and PDC in methylene chloride. This chromatogram was acquired using a nitrous oxide mobile phase and the conditions listed in Table I for ICP-MS, while monitoring m/z 52. Analytical figures of merit for these compounds are listed in Table II. The detection limit for MHDC was less tan one picogram while the detection limit for the PDC was approximately three picograms. These detection limits were calculated using three times the standard deviation of the blank and dividing by the slope of the calibration curve. The linearity of the calibration curves was tested between 0.1 and 100 ng and was found to be quite linear for both compounds. Linearity of the curves was confirmed through the correlation coefficient (R^2) values and the slope of the log–log calibration curve being near one. Finally, the reproducibility of the measurements was tested for five replicate injections of 1 ng of each of the compounds (as chromium). The relative standard deviation (R.S.D.) was found to be less than 3% for the peak area of both compounds.

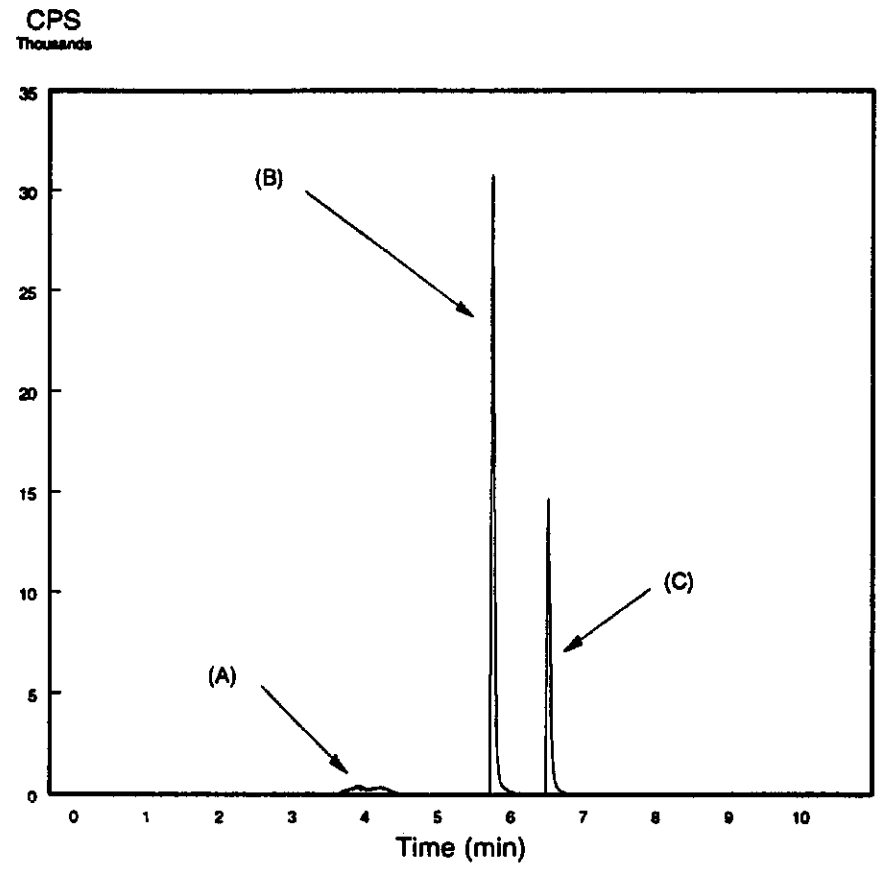


Fig. 7. SFC–ICP-MS chromatogram at m/z 52 using the optimal conditions and a 10 ng mixture. A = Solvent; B = MHDC; C = PDC.

Peak shape analysis

A measure of comparison between the chromatographic efficiency of the two methods is the extra-column variance (or peak broadening in the interface). As can be seen in Table III the expected peak broadening in the SFC–ICP interface was not observed for either MHDC or PDC. The variance was analyzed by normalizing the signal intensity and time scale, while measur-

TABLE II

SFC–ICP-MS ANALYTICAL FIGURES OF MERIT

Detection limits based on 3σ calculations.

	Chromium(III) 2,2,6,6-tetramethyl-3,5-heptanedionate	Chromium(III) 2,4-pentanedionate
Detection limit	0.9 pg	3 pg
Relative standard deviation (%)	1.4	2.6
Linear range	0.1–100 ng	0.1–100 ng
Log–log slope	0.99	0.98
Correlation coefficient	0.999	0.999

TABLE III

PEAK SHAPE INFORMATION FOR FID AND ICP-MS DETECTION OF SFC

Peak shape factor	FID	ICP-MS
MHDC		
Asymmetry factor	1.1	1.5
Total system variance (σ^2)	22 mm^2	15 mm^2
Variance difference (σ_{ex})	2.7 mm	N/A[a]
PDC		
Asymmetry factor	1.4	1.8
Total system variance (σ^2)	31 mm^2	24 mm^2
Variance difference (σ_{ex})	2.6 mm	N/A

[a] N/A = Not applicable.

ing the peak widths at half maximum (see Fig. 8). The differences in the system variance result from differences in analysis times and from differences in the heating of the restrictor. A result such as this probably means that the observed differences in peak widths are due to an increase in the variance from the analytical column (increased retention time) rather than any extra column effects, *per se*.

A final measure of the quality of the chromatogram is the deviation from a Gaussian peak, the asymmetry factor. Table III clearly indicates a difference in the peak shape for PDC and MHDC with FID and ICP-MS. This conclusion is further born-out by a visual inspection of the peaks shown in Fig. 8 for MHDC and PDC. The skewed peak shapes for ICP-MS may result from the use of the carrier gas to sweep the analyte from the restrictor into the plasma.

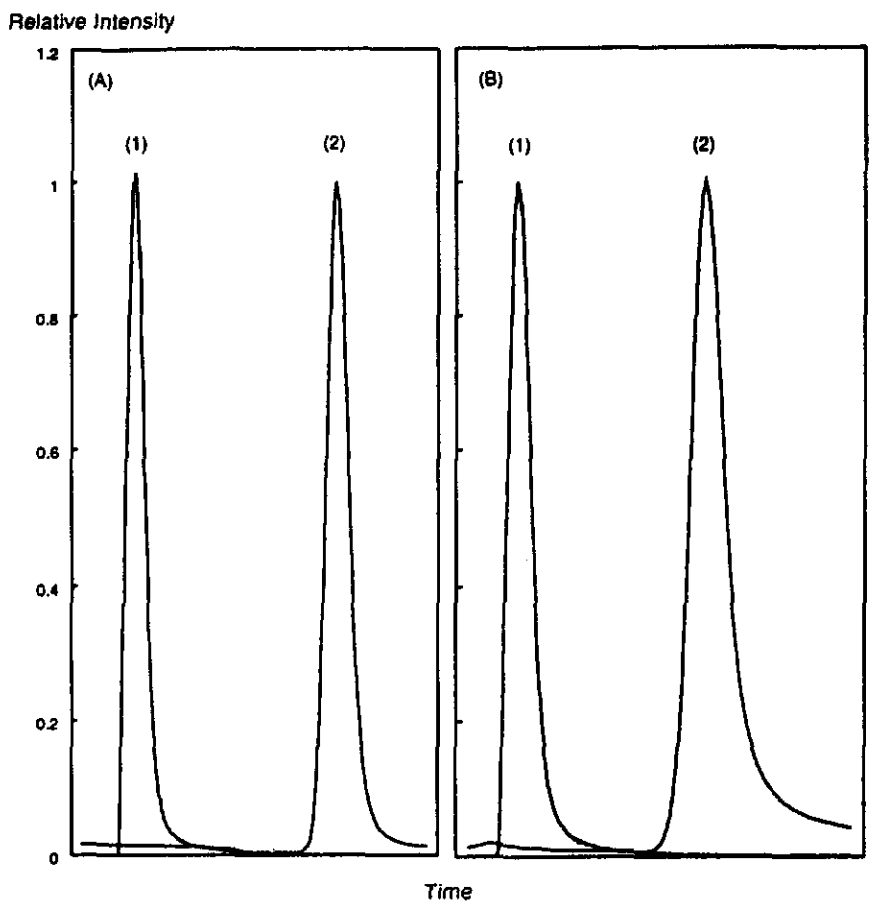


Fig. 8. Peaks for MHDC (A) and PDC (B) using both ICP-MS (1) and FID (2); note that the intensities have been normalized for comparison purposes.

Comparison to other methods

A brief comparison of the figures of merit obtained with this method, to those achieved with other methods is listed in Table IV. The chromatographic methods listed are for β-ketonate chromium complexes. The detection limits shown for FID are the range for the three compounds used in this study. The large difference in reported retention times is due to the slower pressure ramp used for FID. It is clear that the nitrous oxide is not a desirable mobile phase for FID and that ICP-MS provides for better detectability in both cases. Although the retention times for the chromium compounds are somewhat less for the other SFC reports, they are for a packed column, which may not be the most advantageous for plasma detection. In addition, in these analyses a methanol modifier was added to the carbon dioxide, while with the current investigation pure carbon dioxide and nitrous oxide were used. Finally, the use of MS allows for greater detectability compared to the ICP-AES and UV detectors described although no detection limits were presented in these reports.

When compared to liquid chromatographic methods, the advantages of SFC for these compounds, if ICP-MS detection were used, is found in the mobile phase. Upon decompression, the supercritical fluid is a gas which causes minimal plasma perturbations, while HPLC mobile phases can cause problems with plasma quenching, low nebulizer transport efficiency, and clogging of the nebulizer, skimmer and/or sampler cone orifices. Finally, a comparison of the detection limits to another dry plasma, transient signal sample introduction method (electrothermal vaporization, ETV) is provided. It can be seen that the detection limits are improved for the ETV

TABLE IV

COMPARISON OF SFC–FID AND SFC–ICP-MS TO OTHER METHODS

AES = Atomic emission spectroscopy; ETV = electrothermal vaporization; MIP = microwave induced plasma.

Technique	Detector	Detection limit	Retention time (min)	Ref.
SFC (capillary, N_2O)	ICP-MS	0.9–3 pg	6–7	This work
SFC (capillary, N_2O)	FID	50–250 pg	8–11	This work
SFC (capillary, CO_2)	FID	10–70 pg	8–11	This work
SFC (packed)	UV and ICP-AES	N.R.[a]	9	14
SFC (packed)	UV	N.R.	1–4	12
HPLC	UV	N.R.	6–14	5
HPLC	UV	N.R.	6–12	6
ETV	ICP-MS	0.2 pg	N.A.[b]	18
ETV	MIP-AES	1.5–4.2 ng	N.A.	18
ETV	ICP-AES	0.009–1.0 ng	N.A.	18

[a] N.R. = Not reported.
[b] N.A. = Not applicable.

measurements; however, electrothermal vaporization is a total element analysis method, not a speciation method. This is not desirable since as previously indicated; chromium is an element whose concern is highly species dependent.

CONCLUSIONS

The ability to analyze organochromium compounds by SFC–ICP-MS has been demonstrated. However, the technique does not allow for the use of the most common SFC mobile phase, carbon dioxide, due to an isobaric interference in the mass spectrometer resulting from the formation of ArC^+ at m/z 52. This mass to charge ratio corresponds to the major isotope of chromium so detection is severely limited when sufficiently high levels of carbon containing materials are used. The use of ICP-MS detection does not change the optimal chromatographic conditions to any considerable extent. However, the interface heating method does degrade the peak shapes to some degree. Perhaps the most severe limitation of the SFC–ICP interface is that the restrictor is heated over a relatively long distance which may hinder the analysis of thermally labile compounds such as MCCD.

Further investigations are needed into the ability to analyze ionic chromium and speciate the different oxidation states. This should be feasible through complexation of the chromium with a common organic ligand such as the β-ketonates illustrated here. In addition, the method in which the restrictor is heated, with the interface, needs to be investigated on a fundamental level so a better understanding of the processes which are occurring can be gained. Studies such as these may lead to an interface with a more efficient method of heating the restrictor, which also may possess better chromatographic compatibility with other detectors and better chromatographic performance.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Dr. Jiangsheng Wang, Dr. G. Paul Sutton, Mr. Jeffrey J. Giglio and Ms. Sandra L. Cleland for their assistance in the preparation of this manuscript. In addition the financial support of the United States Environmental Protection Agency, under grant RP-2963, the National Institute of Environmental Health Sciences under grants ES03221 and ES04908 are greatly appreciated.

REFERENCES

1 D.T. Heitkemper and J.A. Caruso, in I.S. Krull (Editor), *Trace Metal Analysis and Speciation*, Elsevier, Amsterdam, New York, 1992, Ch. 3.
2 L.K. Olson, D.T. Heitkemper and J.A. Caruso, in P. Uden (Editor), *Element-Specific Chromatographic Detection by Atomic Emission Spectroscopy*, American Chemical Society, Washington, DC, 1992, Ch. 17.
3 J.M. Carey, F.A. Byrdy and J.A. Caruso, *J. Chromatogr. Sci.*, 31 (1993) 330.
4 C.D. Klaassen, M.O. Amdur and J. Doull, *Toxicology: The Basic Science of Poisons*, MacMillan, New York, 1986.
5 R.C. Gurira and P.W. Carr, *J. Chromatogr. Sci.*, 20 (1982) 461.
6 W. Mastowska and S. Starzynski, *Chromatographia*, 9/10 (1989) 519.
7 L.H. Lajunen, E. Eijarvi and T. Kenakkala, *Analyst*, 109 (1984) 699.
8 B. Maiti and S.R. Desai, *Analyst*, 111 (1986) 809.
9 J.J. Thompson and R.S. Houk, *Anal. Chem.*, 58 (1986) 2541.
10 I.S. Krull, D. Bushee, R.N. Savage, R.G. Schleicher and S.B. Smith, *Anal. Lett.*, 15 (1982) 267.
11 M. Ashraf-Khorassani, J.W. Hellgeth and L.T. Taylor, *Anal. Chem.*, 59 (1987) 2077.
12 C. Fujimoto, H. Yoshida and K. Jinno, *J. Microcol. Sep.*, 2 (1990) 146.
13 K. Jinno, H. Mae and C. Fujimoto, *J. High Resolut. Chromatogr.*, 13 (1990) 13.
14 J.M. Carey and J.A. Caruso, *Trends Anal. Chem.*, 11 (1992) 287.
15 J.M. Carey, N.P. Vela and J.A. Caruso, *J. Anal. At. Spectrom.*, 7 (1992) 1173.
16 N.P. Vela and J.A. Caruso, *J. Anal. At. Spectrom.*, 7 (1992) 971.
17 W.L. Shen, N.P. Vela, B.S. Sheppard and J.A. Caruso, *Anal. Chem.*, 63 (1991) 1491.
18 J.M. Carey and J.A. Caruso, *Crit. Rev. Anal. Chem.*, 23 (1992) 397.