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Coupling of a gas chromatograph to a simultaneous-detection inductively coupled plasma mass spectrograph for speciation of organohalide and organometallic compounds

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Received 17th September 2003, Accepted 1st April 2004
First published as an Advance Article on the web 18th May 2004

A gas chromatograph (GC) has been coupled to an inductively coupled plasma Mattauch–Herzog geometry mass spectrograph (ICP-MHMS) equipped with a novel detector array. In its current state of development the detector array, termed the focal plane camera (FPC), permits the simultaneous monitoring of up to 15 *m*/*z* values. A heated line was used to transfer the capillary-column effluent from the GC to the ICP torch, though due to instrument operating conditions, the transfer line was terminated 50 mm ahead of the ICP torch. Minimal tailing was observed, with the most severe effect seen for high-boiling analytes. With this coupling, absolute limits of detection are in the tens to hundreds of femtogram regime for organometallic species and in the single picogram regime for halogenated hydrocarbons.

Introduction

An ever-increasing need in elemental analysis is to know not only the concentration of an analyte, but also its chemical form. Often, the toxicity or bioavailability of an inorganic element is governed more by its chemical state than by its concentration. The process of obtaining this information, know as speciation, is often accomplished by introducing a separation step prior to atomic mass-spectrometric analysis. Typically, a chromatographic separation, such as gas chromatography (GC),[1] liquid chromatography (LC)[2,3] or capillary electrophoresis (CE)[4] is utilized, though other methods are possible. Applications of electrothermal vaporization,[5] X-ray spectroscopy,[6] and electrochemical analysis[7] to elemental speciation have been made. The majority of elemental speciation research has been performed on organometallic compounds, redox systems and metal-containing biological molecules, with elements such as arsenic, selenium, chromium, tin, mercury, and lead being the main targets.

Inductively coupled plasma mass spectrometry (ICP-MS) is a proven method for high-sensitivity elemental analysis. Therefore, it is not surprising that many speciation methods utilize ICP-MS to determine the elemental composition of the target compounds. The ICP is admirably suited for coupling to separation techniques because of its robustness, its broad dynamic range, and its ability to provide multielement information on a continuous basis. The rapidly changing sample load associated with chromatographic separations causes little perturbation to the ICP. Additionally, the ICP provides nearly uniform ionization of many elements,[8] simplifying quantification.

Though elemental speciation by ICP-MS has demonstrated considerable utility, several limitations still exist. The ICP is an inherently noisy ionization source, which can compromise reproducibility. Moreover, the majority of ICP mass spectrometers are scanning instruments with low duty cycle for multielement detection. Scanning instruments also cannot accurately monitor rapidly changing transient signals on a multielement or multi-isotope basis. This limitation, known as spectral skew, results from the finite length of time required to measure each *m*/*z* ratio, during which the signal level can change.

All of the aforementioned shortcomings can be addressed through simultaneous detection. The majority of ICP source noise is correlated or multiplicative in nature. By simultaneous detection of two *m*/*z* values, the correlated noise associated with each signal can be minimized or eliminated through ratioing. Further, with simultaneous detection, the need to scan a mass spectrum is obviated, so duty cycle increases and spectral skew is eliminated. An additional benefit of improved duty cycle is better absolute detection limits for a given analysis time.

Two types of commercially available ICP-MS instruments approximate simultaneous detection, and therefore offer the foregoing benefits. Time-of-flight mass spectrometers (TOFMS) simultaneously extract packets of ions but sequentially detect the time required for each ion to traverse a flight tube. With simultaneous extraction, spectral skew is eliminated, though the duty cycle is not raised to unity. Additionally, through ratioing, ICP source noise can be eliminated, but correlated noise affecting the mass analyzer and detector will remain uncorrected. Sector-field mass spectrometers employing multiple collectors (MC-SFMS) also simultaneously detect several *m*/*z* ratios with near-unity duty cycle. In addition, they can use ratioing to eliminate correlated noise sources. These instruments, though, suffer from the limited number and range of *m*/*z* values that can be simultaneously detected. Typically, fewer than six *m*/*z* ratios can be simultaneously measured, and over a mass window covering only approximately 5% of the total elemental mass range. Therefore, although these instruments can provide improved results over scan-based mass spectrometers, a need exists for a truly simultaneous detection mass spectrometer.

At Indiana University, a Mattauch–Herzog geometry mass spectrograph (MHMS)[9,10] has recently been equipped with a novel detector array, termed the focal plane camera (FPC).[11,12] Though in an early stage of development, the FPC employs 31 discrete detector elements, and when coupled to the MHMS provides the ability to monitor up to 15 *m*/*z* ratios

DOI: 10.1039/b311353a

simultaneously. The utility of this coupling has been demonstrated with both glow discharge (GD)[11] and ICP ionization sources,[13] with results comparable to or better than those obtainable with a conventional single-channel mass spectrometry detector. With ICP ionization, the instrument has demonstrated limits of detection in the single to sub-pptr regime, isotope ratio precision of better than 0.01% RSD, and a linear dynamic range of 10^7. Moreover, the FPC response is mass-independent, unlike traditional electron multipliers.[13] In order to further demonstrate the promise of this new instrument, a GC has been coupled to the ICP-MHMS-FPC for speciation analysis.

Presented here are the results for the coupling of a GC to the ICP-MHMS-FPC for the determination of halogenated hydrocarbons and organometallic species. The ability of the instrument to separate species based on both elemental composition and chemical form is demonstrated. Finally, the absolute detection ability of the instrument is evaluated.

Experimental

Gas chromatograph

A Shimadzu gas chromatograph (GC-9A, Kyoto, Japan) with a non-polar column (DB-5MS, 30 m length, 0.25 mm id, J&W Scientific, Folsum, CA, USA) was used in all experimentation. The GC was equipped with a split injector with a measured split ratio of 70 : 1. Helium (99.999%, Air Gas, Radnor, PA, USA) was supplied to the GC column at a flow rate of 5 mL min^{-1}. A heated transfer line, consisting of heated copper tubing (1 m length, 3.175 mm od) wrapped in Heat Tape (Glas-Co, Terre Haute, IN, USA) and insulated with glass wool, was used to couple the GC to the ICP-MHMS-FPC. This transfer line was maintained at a temperature of 150 °C and extended from the GC oven to a location approximately 50 mm ahead of the ICP torch. The remaining distance was bridged by a length of polyethylene tubing, used to prevent a discharge from forming between the heating tape and the electrically floating mass-spectrometer interface on the MHMS. The transfer line served also to heat the argon used for the central channel of the ICP. This gas was additionally warmed before the transfer line by a length of heated copper tubing (1 m length, 3.175 mm od), as shown in Fig. 1.

Inductively coupled plasma mass spectrograph

Since the ICP-MHMS has been described previously in the literature,[10] only the parameters relevant to the present study will be given. The ICP was maintained at a forward power of 1.3 kW with central, intermediate, and coolant gas flows of 1.15, 1.25, and 16.0 L min^{-1}, respectively. Ions were extracted into the MHMS through a three-stage differentially pumped interface held at 1 kV above the instrument. Sampler, skimmer and third-stage apertures of 0.7, 0.7, and 1 mm were used, resulting in a third-stage pressure of 5×10^{-6} Torr. Other pertinent operating conditions of the instrument are detailed in Table 1.

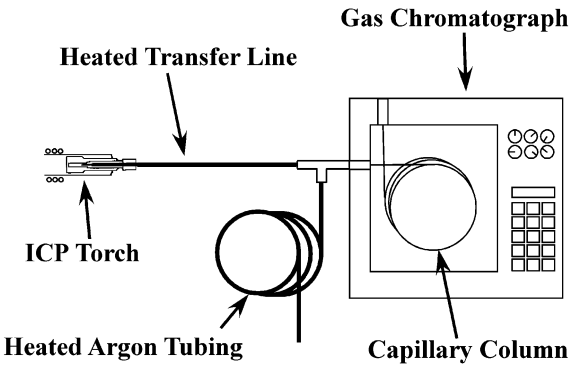

Fig. 1 Heated transfer line used with the GC-ICP-MHMS-FPC. The transfer line consists of copper tubing wrapped with Heat Tape and insulated with glass wool.

Focal plane camera

The FPC was developed at the University of Arizona by Knight, *et al.*, in conjunction with Spectral Instruments (Tucson, AZ), Pacific Northwest National Laboratory and Indiana University.[12] The prototype FPC used in the present study utilizes for detection an array of 31 Faraday cups spaced 175 μm on center and separated by 10-μm wide ground wires with 10-μm spacing between the pixels and ground wires. The FPC was refrigerated to −40 °C by a Peltier cooler to reduce detector noise and improve performance. Integration time can be varied between 1 ms and 20 s, with either destructive or non-destructive readout-mode data acquisition. Further information regarding the FPC can be found elsewhere,[11,12] though the important operating parameters associated with the FPC are summarized in Table 1.

Reagents

Reagent-grade methanol (Fisher Scientific, Pittsburgh, PA) was used for all sample preparation and dilution. Single-component stock solutions of 1 mg g^{-1} metal or halogen were prepared from tetramethyltin (TMT, Acros, Pittsburgh, PA), tetraethyltin (TET, Aldrich, St. Louis, MO), ferrocene (Aldrich), methylcyclopentadienyl manganese tricarbonyl (MMT, Aldrich), cyclopentadienyl cobalt dicarbonyl (CCD, Aldrich), 1-chloropropane (Mallinckrodt, Phillipsburg, NJ), 2-chlorobutane (Aldrich), dichloroethane (Mallinckrodt), trichloroethylene (Mallinckrodt), 1-chloropentane (Aldrich), 1-chlorohexane (Aldrich), chlorocyclohexane (Mallinckrodt), 1-chloroheptane (Aldrich), 1-bromopropane (Aldrich), 1-bromobutane (Acros), 1,2-dibromoethane (Aldrich), bromoform (Acros), bromobenzene (Mallinckrodt), and bromocyclohexane (Aldrich). These solutions were further diluted for calibration.

By using the aforementioned chemicals, three test systems were devised to demonstrate the capabilities of the instrument. The first system, consisting of TMT and TET, was designed to

Table 1 Operating conditions for the GC-ICP-MHMS-FPC

Gas chromatograph	
Injector temperature	200 °C
Split ratio	70 : 1
Injected sample volume	1 μL
Helium carrier gas flow	5 mL min^{-1}
Transfer line temperature	150 °C
Transfer line length	1 m
Inductively coupled plasma	
Central argon flow	1.15 L min^{-1}
Intermediate argon flow	1.25 L min^{-1}
Outer argon flow	16.0 L min^{-1}
Sampling depth	12 mm
Forward power	1.3 kW
Reflected power	<5 W
Mattauch–Herzog mass spectrograph	
Sampling-cone aperture diameter	0.7 mm
Skimmer-cone aperture diameter	0.7 mm
Third-stage aperture diameter	1.0 mm
First-stage pressure	1–2 Torr
Second-stage pressure	5×10^{-3} Torr
Third-stage pressure	5×10^{-6} Torr
Acceleration potential	1000 V
Focal plane camera	
Detector element width	145 μm
Detector element height	1.6 mm
Center-to-center cup spacing	175 μm
Operating temperature	−40 °C
Number of detector elements	31

be simple to separate, so the multi-isotope detection capability of the GC-ICP-MHMS-FPC could be tested. Although a conventional single-detector mass spectrometer could be used with this system to detect a single tin isotope, the FPC can monitor all tin isotopes simultaneously. The second system, consisting of ferrocene, MMT, and CCD, was used to demonstrate the multi-element detection ability of the FPC with fast transient signals. The final system, comprised of brominated and chlorinated hydrocarbons, was devised to test the detection performance of the FPC in the presence of intense background species.

Results and discussion

GC-ICP-MHMS-FPC coupling

Of immediate concern was the effectiveness of the locally fabricated transfer line linking the GC capillary column and the ICP. Ordinarily, a heated tube can simply be used to house the column between the oven and the ICP torch. Unfortunately, the interface and ICP in the MHMS are held at a potential 1 kV above ground. With a transfer line that contacts the ICP torch, a discharge forms between the ICP and the heating element of the transfer line, which rapidly destroys the capillary column. Additionally, with this interface, it is possible to capacitively couple the rf power from the ICP into any conductors near the torch. The coupling of the interface potential to the heating element could be eliminated with the use a non-conductive material for the transfer line. This solution, though, will not eliminate the capacitive coupling of the rf power into the heating element of the transfer line. A straightforward solution to both these problems is to terminate the transfer line short of the ICP torch and to use unheated polymer tubing to traverse the distance. The undesirable consequence of this solution is peak broadening and tailing caused by the relatively large volume in the transfer tubing compared with the capillary column. Despite this consequence, the transfer line was terminated 50 mm before the ICP torch. Minimal peak tailing was observed, with the most severe effect seen with higher boiling-point analytes. This minimal effect can be attributed to several factors. The heated argon makeup gas slows the condensation process significantly. Moreover, at the flow rates utilized in this experiment, the analyte resides in the unheated portion of the transfer tube for less than 0.5 s. These factors combine to ensure that the analyte is successfully transferred into the ICP without any significant loss in the transfer line, as is evident from the lack of memory effects or increased background signal.

Optimization of chromatographic conditions

Temperature programming is commonly used with GC separations to reduce analysis time and improve separation efficiency. Although shorter chromatographic runs can then be realized, one must wait between successive injections for the column oven to return to its initial temperature. A consequence of this requirement can be a greater time period between injections than with an isothermal separation. This effect arose with the first chromatographic system. Baseline separation of TMT and TET required 90 s with a constant column temperature of 100 °C, whereas the same separation could be accomplished in 75 s with a temperature program of 100 °C to 150 °C at 25 °C min^{-1}. However, the latter run required over 2 min after the separation was complete before the oven was ready for the next injection. The separation of TMT and TET was therefore performed isothermally at 100 °C. The benefits of temperature programming were utilized for the other two chromatographic systems. For these systems, the oven temperature was increased at a rate of 25 °C min^{-1} over two minutes from 150 °C to 200 °C. Under these conditions injections could be made every 5 min. A summary of the separation conditions is given in Table 2.

Table 2 Temperature program used for the separation of the synthetic samples

	System A[a]	System B[b]	System C[c]
Temperature program	100 °C isothermal	150 °C, 25 °C min^{-1} to 200 °C	150 °C, 25 °C min^{-1} to 200 °C

[a] TMT and TET. [b] Ferrocene, MMT, and CCD. [c] Chlorinated and brominated hydrocarbons.

FPC response and limits of detection

Fig. 2 shows the simultaneously detected mass window from $m/z = 113$ to $m/z = 125$ for the separation of the first sample mixture containing TMT and TET. The channel-summed FPC response is shown in Fig. 2a. This chromatogram depicts what would be obtained by a conventional single-channel detection system, such as a UV–Visible detector or a single-channel mass spectrometer. Use of the FPC provides an added dimension to the separation, as shown in Fig. 2b. The isotopic distribution of the tin isotopes in both TMT and TET can be clearly distinguished across the detector elements of the FPC. Although not necessary for this simple sample mixture, the added m/z dimension could prove useful for the identification of unknown species.

The separation of the second sample system containing ferrocene, MMT and CCD is shown in Fig. 3. As with the previous system, the total FPC response and the m/z window from $m/z = 55$ to $m/z = 60$ are depicted in Figs. 3a and 3b, respectively. The adverse effect of the section of unheated tubing between the heated transfer line and the ICP torch is most pronounced for the severely tailed ferrocene peak. Note that under these operating conditions, the background signal from $^{40}Ar^{16}O$ is negligible. With this sample mixture, a conventional single-channel mass spectrometer could not record the entire chromatogram without the use of m/z scanning. Regrettably, when scanning is employed, the detection duty cycle drops in proportion to the number of m/z values that must be monitored, leading to the likelihood of spectral skew in the measurement. In contrast, the FPC monitors the entire mass window continuously so quantification is more straightforward.

The final sample system consisted of chlorinated and brominated hydrocarbons. These compounds were chosen because chlorine and bromine are found in mass windows that contain intrinsic plasma background species, and are therefore difficult to quantify by ICP-MS. A major ICP background species,

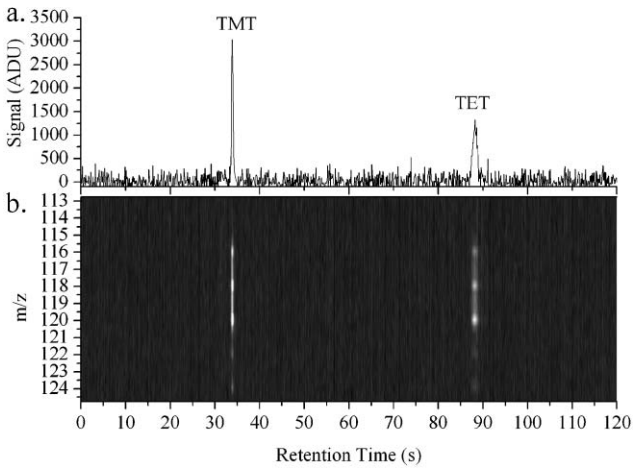

Fig. 2 Chromatograms for the injection of 140 pg of TMT and TET shown as (a) total FPC response and (b) m/z-dependent response.

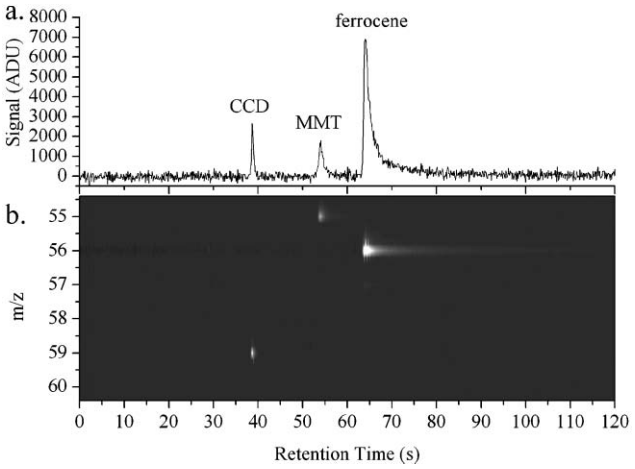

Fig. 3 Chromatograms for the injection of 140 pg of ferrocene and CCD and 14 pg of MMT with (a) total FPC response and (b) *m*/*z*-dependent response. The tailing observed on the ferrocene peak can be attributed to the length of unheated transfer tubing between the chromatograph oven and the ICP torch.

$^{40}Ar_2^+$, lies between the two isotopes of bromine, while the isotopes of chlorine are found in a mass window containing the minor isotopes of argon at $m/z = 36$ and $m/z = 38$ as well as their hydrides. It is therefore important to have a detection system capable of correcting for the background peaks. The separation of six brominated hydrocarbons is shown in Fig. 4. The conventional and two-dimensional chromatograms are shown in Figs. 4a and 4b before any background correction has been applied. To perform a background correction, a blank injection of methanol was performed immediately following the sample run and the detector response was mathematically subtracted from the detector response for the analyte injection, as shown in Figs. 4c and 4d. Although a background correction could be performed without a second injection, simply by measuring the detector response after the analyte peaks returned to baseline, the blank injection was used to account for any fluctuations in the plasma-related background species caused by the introduction of the large plug of organic material. Even though the solvent peak elutes prior to the analyte peaks, the effect of the solvent on the plasma persists for tens of seconds. Therefore, in order to accurately perform a background correction, a blank injection is preferable. The same procedure was performed for a series of eight chlorinated hydrocarbons, and is displayed in Figs. 5 a–d. It is important to note that due to the high loading of hydrocarbons that are being introduced into the ICP, the majority of the argon background is in the form of argon hydride.

The aforementioned sample systems have been designed to be simple, thus allowing the characteristics of the FPC to be tested. With such systems, a single-channel mass spectrometer,

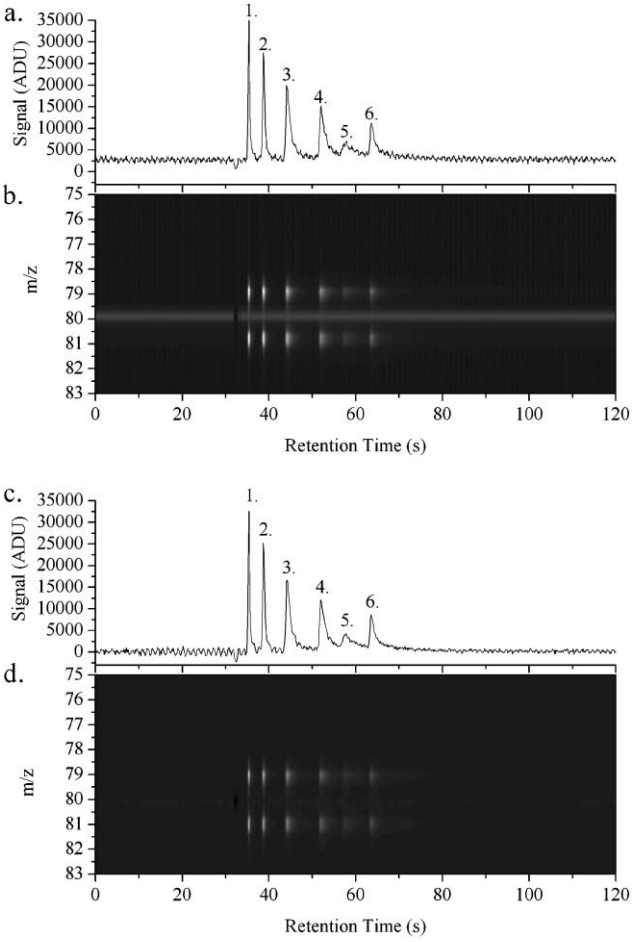

Fig. 4 Chromatograms for the injection of 1.4 ng of six brominated hydrocarbons with (a) total FPC response and (b) *m*/*z*-dependent response. Due to the presence of $^{40}Ar_2^+$, a background correction must be made. A blank injection of methanol has been mathematically subtracted from the (c) total FPC response and (d) *m*/*z*-dependent response to remove the plasma-related background. Peaks: 1, 1-bromopropane; 2, 1-bromobutane; 3, 1,2-dibromoethane; 4, bromoform; 5, bromobenzene; 6, bromocyclohexane.

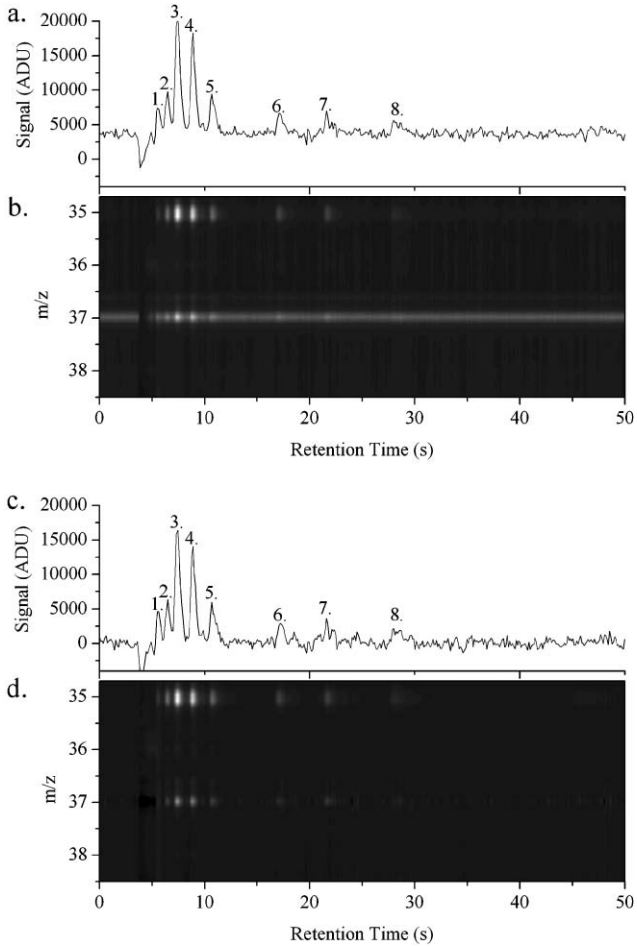

Fig. 5 Chromatograms for the injection of 1.4 ng of eight chlorinated hydrocarbons with (a) total FPC response and (b) *m*/*z*-dependent response. Due to the presence of $^{36}Ar^+$, $^{36}Ar^1H^+$, and $^{38}Ar^+$, a background correction must be made. A blank injection of methanol has been mathematically subtracted from the (c) total FPC response and (d) *m*/*z*-dependent response to remove the plasma-related background. Peaks: 1, 1-chloropropane; 2, 2-chlorobutane; 3, dichloroethylene; 4, trichloroethylene; 5, 1-chloropentane; 6, 1-chlorohexane; 7, chlorocyclohexane; 8, 1-chloroheptane.

Table 3 Absolute limits of detection[a] reported at a 3σ level above background

Analyte	Limit of detection/fg
TMT	34
TET	85
Ferrocene	134
MMT	104
CCD	850
1-Chloropropane	4900
2-Chlorobutane	2300
Dichloroethylene	1300
Trichloroethylene	1100
1-Chloropentane	1500
1-Chlorohexane	2200
Chlorocyclohexane	2300
1-Chloroheptane	3400
1-Bromopropane	1300
1-Bromobutane	870
1,2-Dibromoethane	1100
Bromoform	1300
Bromobenzene	1200
Bromocyclohexane	960

[a] Values given in terms of metal or halogen mass.

such as a quadrupole instrument, could easily monitor one *m*/*z* value or peak hop to record the chromatogram. Since the transient signals produced by these separations are in the second time regime, little spectral skew will be observed. The true benefit of simultaneous detection will be realized with more complex or unknown systems, where many more *m*/*z* values must be monitored. Under these circumstances, the concentration information obtained from scan-based instruments will be increasingly degraded by spectral skew as the number of required *m*/*z* values increases.

For all the sample systems that were examined, absolute limits of detection are in the tens to hundreds of femtogram regime for organometallic species and in the single picogram regime for halogenated hydrocarbons. Limits of detection have been calculated at a 3σ level and have been corrected for the isotopic abundance of the detected elements. The values obtained in this study are comparable to those commonly obtained by other GC-ICPMS techniques. These values are summarize in Table 3 and are listed in femtograms of the detected element.

Isotope ratio accuracy and precision

A significant disadvantage of scan-based mass spectrometers is the negative effect of spectral skew on isotopic abundance measurements. Since analyte concentration changes with time during chromatographic separations, the finite amount of time required to move between *m*/*z* values will result in a misrepresentation of the *m*/*z* signal levels, and therefore of the isotopic abundances. With simultaneous detection, this problem is eliminated, since all *m*/*z* values are recorded in unison.

Table 5 Isotope-ratio accuracy and precision obtained for the separation of CCD, MMT and ferrocene

		m/*z*			
		55	56	57	58
CCD	Total signal				9832
MMT	Total signal	11922			
Ferrocene	Total signal		60631	1239	
	Calculated abundance		92.0	1.88	
	Natural abundance		91.8	2.12	
	Error (%)		0.3	11.3	
	Precision (% RSD)		0.3	14.5	

This benefit has been demonstrated here through the separation of the three sample systems. Reported in Tables 4–6 are the signal levels for each analyte *m*/*z* value for the three sample systems. From these values, the elemental isotopic abundances of the analytes have been calculated and compared to the naturally occurring abundances. Additionally, the precision of the isotopic abundances has been reported.

For the first sample system (*cf*., Table 4), the calculated and naturally occurring abundances of the isotopes of tin were in close agreement, with typical deviations near or less than 1% error for both TMT and TET. Only three isotopes, ^{117}Sn, ^{122}Sn, and ^{124}Sn, deviated greatly from the expected abundance. All three isotopes are of low abundance (below 8%) and ^{117}Sn fell across multiple detector elements, resulting in increased error. The isotope-ratio precision that was obtained varied from 3.5% to 43% RSD, with the best values obtained for the most abundant isotopes of tin. These accuracy and precision levels are comparable to those obtainable with other GC-MS techniques. Moreover, since the FPC responds to individual charges, the isotope-ratio precision can be improved simply by increasing the sample concentration, as demonstrated in ref. 13. Accuracy and precision values were both obtained with a single injection, consuming only 140 pg of each analyte.

With the second sample system, isotope-ratio accuracy and precision were calculated for two isotopes of iron (^{56}Fe and ^{57}Fe) in ferrocene and can be found in Table 5. For ^{56}Fe, the calculated and natural abundances differed by only 0.3%, while for ^{57}Fe, the difference was 11%. The precisions of the calculated abundance for ^{56}Fe and ^{57}Fe were 0.3% and 14.5% RSD for a single injection. Again, these accuracy and precision values were obtained from a single injection, consuming only 14 pg of MMT and 140 pg of CCD and ferrocene.

The agreement between the calculated and natural isotopic abundances for the brominated hydrocarbons was excellent (Table 6), with errors ranging from 2.8% to 3.9% for the ratio ^{79}Br : ^{81}Br. Additionally, a high level of precision was obtainable for this ratio for a single injection, ranging from 1.7% to 2.9% RSD for all the analytes. This demonstrates that little or no adverse effects result from the intense signal at $m/z = 80$, indicating that the background-subtraction process does not

Table 4 Isotope-ratio accuracy and precision for the isotopes of tin obtained for the separation of TMT and TET

		m/*z*						
		116	117	118	119	120	122	124
TMT	Total signal	1062	433	1815	617	2358	354	391
	Calculated abundance	14.8	6.04	25.3	8.61	32.9	4.93	5.45
	Natural abundance	14.5	7.68	24.2	8.59	32.6	4.63	5.79
	Error (%)	1.8	21.3	4.4	0.3	0.9	6.6	5.8
	Precision (% RSD)	3.5	24.2	8.8	9.1	4.0	34.3	41.9
TET	Total signal	1120	455	1860	655	2457	403	525
	Calculated abundance	14.7	5.97	24.4	8.58	32.2	5.29	6.89
	Natural abundance	14.5	7.68	24.2	8.59	32.6	4.63	5.79
	Error (%)	1.1	22.3	0.7	0.0	1.1	14.3	19.0
	Precision (% RSD)	17.7	29.9	9.8	11.6	8.1	43.2	37.5

Table 6 Isotope-ratio accuracy and precision obtained for the separation of brominated and chlorinated hydrocarbons

	Total signal					
Brominated hydrocarbons	$m/z = 79$	$m/z = 81$	Experimental ratio	Expected ratio	Error (%)	Precision (% RSD)
1-Bromopropane	49120	49401	0.994	1.028	3.3	2.5
1-Bromobutane	49365	49427	0.999	1.028	2.8	2.7
1,2-Dibromoethane	70280	70847	0.992	1.028	3.5	2.9
Bromoform	59688	60258	0.991	1.028	3.6	1.7
Bromobenzene	30644	30922	0.991	1.028	3.6	2.8
Bromocyclohexane	38562	39044	0.988	1.028	3.9	1.8
	Total signal					
Chlorinated hydrocarbons	$m/z = 35$	$m/z = 37$	Experimental ratio	Expected ratio	Error (%)	Precision (% RSD)
1-Chloropropane	4376	1676	2.610	3.127	−16.5	21.2
2-Chlorobutane	13324	3883	3.432	3.127	9.7	9.3
Dichloroethylene	45653	14111	3.235	3.127	3.5	28.2
Trichloroethylene	39780	12704	3.131	3.127	0.1	16.5
1-Chloropentane	16888	5593	3.019	3.127	−3.5	23.8
1-Chlorohexane	9883	3353	2.948	3.127	−5.7	22.7
Chlorocyclohexane	9607	4690	2.048	3.127	−34.5	15.5
1-Chloroheptane	6565	2735	2.401	3.127	−23.2	48.7

affect adjacent m/z values. Poorer performance was obtained for ^{35}Cl and ^{37}Cl from the chlorinated hydrocarbons. For these analytes, isotope-ratio accuracy ranged from 0.1% to 34.5% and isotope-ratio precision varied from 9.3% to 48.7% RSD. This high level of error and variation results from the strong $^{36}Ar^{1}H$ background peak at $m/z = 37$, demonstrating that the subtraction process cannot completely eliminate background completely. Accuracy and precision values were obtained from a single injection, consuming only 1.4 ng of each analyte.

Conclusions

The coupling of a GC to a sector-field ICP-MS fitted with a novel array detector has been successfully demonstrated. Minimal peak tailing was observed despite the use of unheated tubing between the heated transfer line and the ICP torch. A major benefit of this coupling is the ability to obtain m/z information for the analytes without the need for mass-spectral scanning. With this capability, spectral skew is eliminated and detection duty cycle is increased.

Acknowledgements

Support for this work was provided by the U.S. Department of Energy, Office of Nonproliferation Research and Engineering. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the Department of Energy under contract DE-AC06-76RLO-1830.

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