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APPLICATION OF A HYPHENATED FACILITY FOR SIMULTANEOUS SPECIATION STUDIES OF TOXIC OXIDATION STATES [Cr^{3+}/Cr^{6+}] AND [As^{3+}/As^{5+}] IN PRODUCED WATER FROM CRUDE OIL

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ABSTRACT

Produced water is the aqueous component of crude oil and has not been previously characterized for noxious oxidation states: Cr^{3+}/Cr^{6+} and As^{3+} /As^{5+}. It is often returned to the environment where it could create an unwanted hazard. It remains unexplored in this context largely because standard HPLC techniques do not permit convenient simultaneous separation of Cr^{3+}/Cr^{6+} and As^{3+}/As^{5+} due to proximity of corresponding retention times. Our group has adapted a facile process for rapid elution and concurrent mass separation of all four species in an affiliated HPLC/ICP-MS system equipped with a dynamic reaction cell (DRC). Oxygen gas was circulated through the DRC to remove interferences and enhance detection of the eluted components, especially the arsenic constituents. The stationary phase consisted of a C8 deactivated silica based column (length 150 mm; internal diameter: 4.6 mm; particle size: 5 µm); and the mobile phase was composed of a mixture of TBAH/EDTA in 2% methanol/water, adjusted to a pH of 7.2. The rate of elution was 1 mL/min; and recorded retention times (min) were: As^{3+}: 1.81; As^{5+}: 5.50; Cr^{3+}: 1.83; and Cr^{6+}: 5.74. The oxygen flow rate in the DRC was 0.7 mL/min. The Cr^{3+}/ Cr^{6+} constituents were detected with m/z values of 52; the arsenic species coalesced with oxygen and were detected as adduct ions, AsO^{+}, m/z, 91. Standard reference materials were deployed to test the competency of the analytical system. Typical recorded levels in the samples were: Cr^{3+}: 0.5 – 20 mg/L; $Cr^{6+}/As^{3+}/As^{5+}$: 1-5 µg/L. Our results were evaluated in terms of the potential source of toxicity of produced water to the environment. The significance of the study to petroleum and environmental science is discussed.

Keywords: Cr^{3+}/Cr^{6+} and As^{3+} /As^{5+}, HPLC/ICP-MS, produced water, crude oil.

INTRODUCTION

The single most important advantage of a chemical speciation technique (Ball *et al*., 1998; Benramdane *et al*., 1999; Del Razo *et al*., 2001; Eary and Rai, 1987; Katz and Salem, 1993) is that it has the unique ability to accurately pinpoint constituent toxic agents in natural samples that pose an environmental threat (Korte and Fernando, 1991; Le *et al*., 2000; Burguera and Burguera, 1997; Le *et al*., 1996; Van Elteren *et al*., 2002). In this work a rapid procedure for toxic speciation of chromium and arsenic has been adapted (Nuebauer *et al*., 2004) for produced-water studies using a combined (hyphenated) high performance liquid chromatography DRC-ICP-MS system [dynamic reaction cell-inductively coupled plasma-mass spectrometry]. The affiliated DRC-ICP-MS arrangement is well known for its superior performance and high sensitivity. The facility was optimised with the express purpose of isolating these species in a single run, and is especially useful for low sample volumes (about 50 µL). When precious little sample is available, more than one isolation procedure may not be possible and complete separation in a single run is a great advantage. Other authors have used similar systems for individual speciation studies (Le *et al*., 1996; Van Elteren *et al*., 2002) but simultaneous speciation is conveniently accomplished with the HPLC-DRC-ICP-MS facility. Particularly low detection limits can be attained (ng/L); and the system is designed to produce results within minutes. A notable advantage of the technique is that there is no recourse to extensive sample pre-treatment or pre-concentration procedures.

Produced wastewater is the aqueous component separated from oil, and is usually returned to the environment. If such wastewater is disposed of in the environment, it could find its way into aquifers and pollute the water table. It could thus create an environmental hazard (Shearman, 1990; Robinson, 1993) especially if it contains noxious species such as Cr^{3+}/Cr^{6+} and As^{3+} /As^{5+}. According to the literature, produced water remains uncharacterised with regard to the species of interest, which are often present at levels beyond the reach of most modern techniques. Selected samples were subject to investigation to assay the species concerned and optimize the analytical performance of the system for routine studies of this nature. Our primary objective, therefore, was to conveniently adapt and optimize an HPLC-DRC-ICP-MS facility for rapid chromium and arsenic speciation studies in produced wastewater.

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MATERIALS AND METHODS

HPLC

Samples of produced water were collected from different sites and processed for analysis. Isolation of the species of interest was achieved with a Perkin Elmer quaternary LC pump and solvent manager. The stationary and mobile phases were prepared according to Perkin Elmer specifications (Neubauer *et al*., 2004) and were considered optimum for peak shape and retention time. The mobile phase was composed of 1 mM tetrabutyl ammonium hydroxide (TBAH) + 0.5 mM EDTA (potassium salt) + 2% methanol in water. The mixture was adjusted to a pH of 7.2 with dilute HNO_3. The stationary phase consisted of a C8 column, packed with base deactivated silica; column length: 150 mm; internal diameter: 4.6 mm; particle size: 5.0 µm; pore size 140 Å. The column was conditioned with the mobile phase prior to analysis and rinsed thoroughly with a methanol/water mixture at the end of each analysis to maintain its stability. The rate of elution was 1 mL/min. Certified standards containing appropriate levels of the species of interest were obtained from VHG Labs, UK.

DRC-ICP-MS

A Perkin Elmer SCIEX DRC-e ICP-MS was commissioned for mass separation of the eluted species. The nebulizer gas flow in the instrument was 0.80 L/min. The eluted solutions were conveyed to the core of the ICP-MS (Fig. 1) which was equipped with a dynamic reaction cell (DRC) for the suppression and elimination of interferences. In the DRC oxygen was chosen as the reaction gas as it subdued ArC^+ interferences with Cr^+ at m/z 52; and combined with As^+ to form an adduct ion, AsO^+, m/z 91 (Neubauer *et al*., 2004). The formation of this adduct conveniently avoids interferences with other undesirable species: $ArCl^+$ and $CaCl^+$ at m/z 75 (Neubauer *et al*., 2004). The oxygen flow rate was 0.7 mL/min. The instrument itself was standardized with a certified multiple standard (Fluka 70007; 10.00 ppb per element) and is linear over several orders or magnitude for aqueous samples.

The composition of samples and standards was the same as that of the mobile phase. Prior to each run, the instrument underwent linear calibration and background correction. Marginal drift in instrumental measurements was compensated for by use of an internal standard. To test the analytical competency of the system, the repeatability of the instrument was examined for a range of elements in the multiple-standard. Based on the relative standard deviation (RSD) the results showed that in general values <5% were attained demonstrating that the precision of the system for aqueous samples was satisfactory (Table 1).

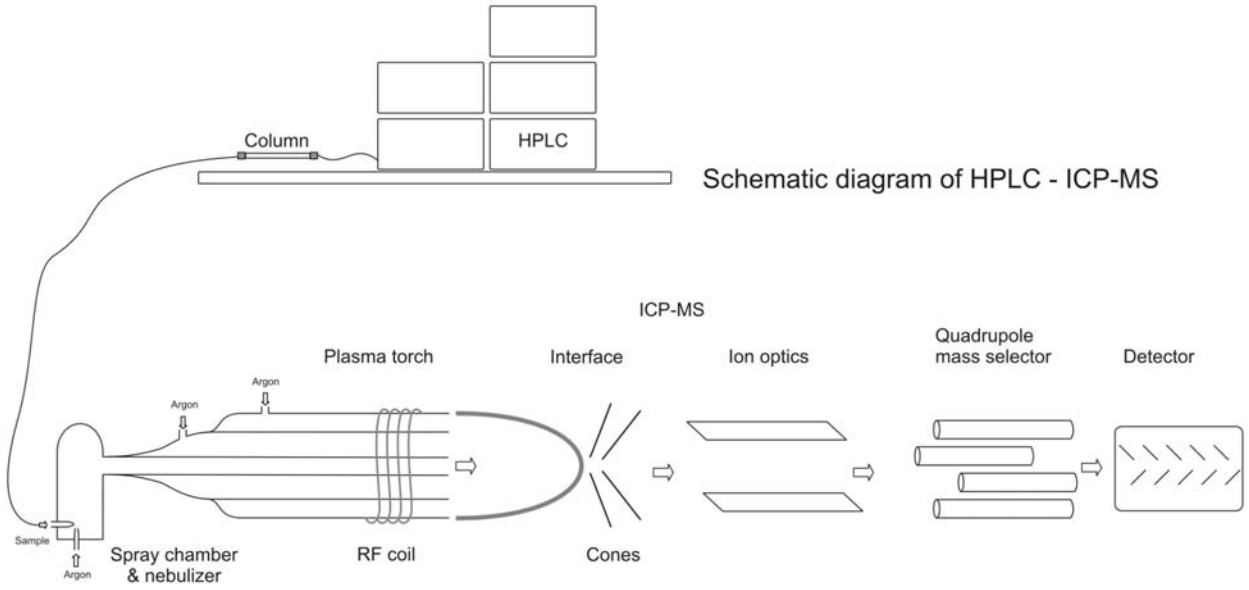

Fig. 1. Schematic of the HPLC/DRC-ICP-MS system.

RESULTS AND DISCUSSION

Speciation/Mass separation

Chemical speciation studies tend to be convoluted largely because of the complexities that accompany the isolation of the species. The primary difficulty encountered with standard HPLC techniques to isolate all four species (Cr^{3+}/Cr^{6+} and As^{3+}/As^{5+}) in a single run is the proximity of corresponding retention times. In this study the recorded retention times were: As^{3+}/As^{5+}: 1.81 and 5.50 min, respectively; and Cr^{3+}/ Cr^{6+}: 1.83 and 5.74 min, respectively. Clearly, in a conventional chromatographic separation overlap of these time intervals would hardly permit convenient collective separation of all four species – and would necessitate more than one isolation procedure. This is time consuming and presents difficulties, especially if sample sizes are limited to low volumes. The combination of chromatographic isolation followed by mass separation for all four oxidation states is unique and represents a marked attainment in instrumental analysis of this nature. Another noteworthy feature of the mass separation technique is its superior sensitivity.

The separation procedure itself was emulated from literature studies and adapted for our specific purpose (Neubauer *et al*., 2004). Baseline problems arose (Fig. 2) in cases where the use of oxygen in the DRC failed to completely eradicate the ArC^{+} interference associated with Cr^{+}. To resolve this situation the oxygen flow rate was carefully adjusted to optimize the signal to noise ratio.

Typical separation of the As^{3+} and As^{5+} species (standard) appears in figure 3. The peaks are distinct and clearly resolved, and the asymmetry factors (Dolan, 2003) relating to tailing are acceptable. The "hump" at about 7.8 min has not been identified, and it is not clear at this stage if this feature represents a constituent of the numerical analysis or is a minor perturbation due to slight aberrations in the solvent elution. However, it does not interfere with the overall analysis and could be an interesting subject of future investigation. The tailing factor is also satisfactory for the chromium species as delineated in the chromatogram in figure 4, which represents the Cr^{3+} component in produced water. The marginal shoulder on the peak (in Fig. 4) was attributed to

Table 1. Repeatability test of the ICP-MS for various elements (µg/L) in an aqueous standard.

Element	Run # 1	Run # 2	Run # 3	Run # 4	Mean	RSD %
V	9.51	9.74	9.90	9.51	9.67	1.97
Cr	9.82	9.61	9.39	9.82	9.66	2.13
Co	10.2	10.1	9.34	10.2	9.96	4.20
As	10.2	9.42	9.29	10.2	9.80	5.24
Mo	11.0	11.1	10.4	11.0	10.9	2.87
Cd	9.51	10.1	9.82	9.51	9.73	2.74
U	10.0	9.65	10.1	10.1	9.98	2.23

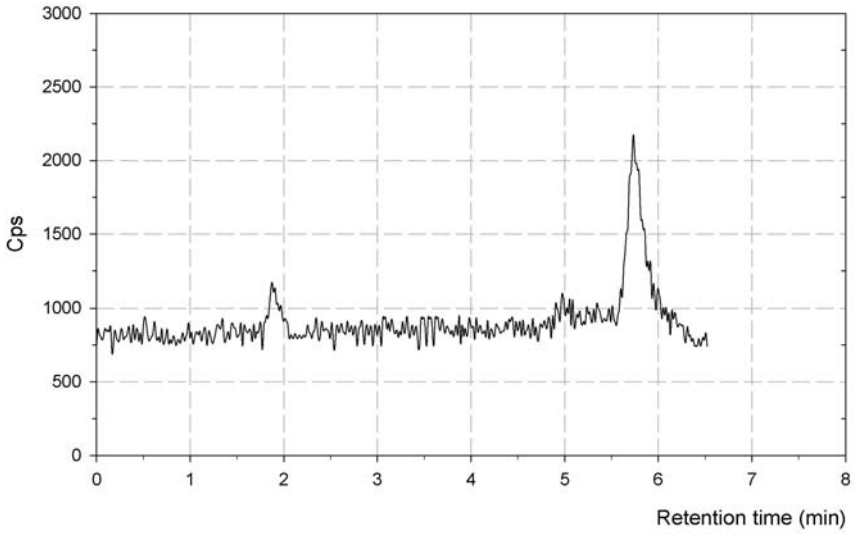

Fig. 2. Poor baseline in a typical chromatogram of chromium species due to interference from ArC^{+} .

Table 2. Levels of species of interest (µg/L) in produced water samples.

Species	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6	Sample #7	Sample #8	Sample #9	Sample #10
Cr 3+	434± 9	1816± 9	2275± 8	867± 9	1965± 9	1725± 8	622± 18	1209± 33	1023± 30	624± 23
Cr 6+	4.51± 0.13	4.94± 0.14	4.97± 0.10	7.63± 0.29	7.21± 0.14	6.77± 0.16	7.23± 1.30	6.55± 0.17	6.44± 0.19	4.39± 0.11
As 3+	2.36± 0.04	4.16± 0.14	5.36± 0.12	15.5± 0.4	3.33± 0.07	3.74± 0.05	11.5± 0.2	10.3± 0.2	9.86± 0.20	6.97± 0.17
As 5+	0.79± 0.02	1.30± 0.04	1.58± 0.05	2.68± 0.10	0.85± 0.02	0.78± 0.02	1.04± 0.03	0.99± 0.03	2.05± 0.04	1.26± 0.04

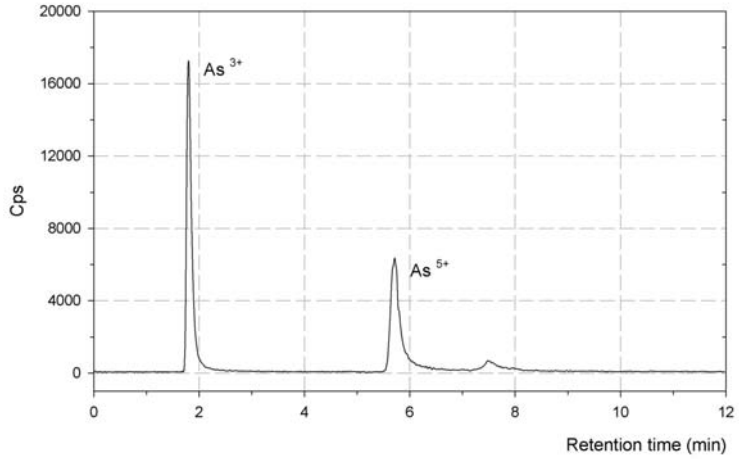

Fig. 3. Eluted arsenic species portraying distinct features of As^{3+} and As^{5+}

slight fluctuations in the elution rate. Table 2 presents typical concentrations of all species in produced water samples. The range of concentrations recorded in this study is as follows: Cr^{3+}: 0.5–20 mg/L; Cr^{6+}/As^{3+}/As^{5+}: 1-5 µg/L. To forecast produced water as a potential source of toxicity, it is necessary to consider acceptable levels in environmental/municipal waters (Neubauer *et al*., 2004): <1 µg/L for Cr^{3+}; <4 ug/L for Cr^{6+}; and <1 µg/L for As^{3+} /As^{5+}. From the perspective of a potential environmental threat to potable sources, the recorded values in table 2 show that Cr^{3+} levels are elevated, in some cases by a factor of more than 10. The levels of Cr^{6+}, As^{3+} and As^{5+} (in some samples) are also pronounced, indicating that produced water can be a significant source of toxicity. The toxic nature of these species to human health has been previously documented (Benramdane *et al*., 1999; Katz and Salem, 1993) and is discussed in more detail below.

Impact of the study

The primary significance of the study is that all four species can be conveniently eluted and detected in a single run (Fig. 5). Simultaneous separation of this nature is not conveniently achieved with other contemporary methods or with conventional HPLC systems because they are not as sensitive (Korte and Fernando, 1991). As aforementioned, a distinct advantage of accomplishing this isolation all at once is that if only small volumes of sample are available the determination is still practicable. The technology has implications for other studies such as biomedicine and immunology where only minimal volumes of body fluid are available for assay. The study also has environmental implications because it can be associated with sustainable development (Shearman, 1990; Robinson, 1993; Pillay *et al*., 2010). Produced waste water, if consigned to the environment, could affect subterranean sources. Many oil-bearing countries are arid regions, and depend on surface streams and underground supplies to feed livestock and for domestic purposes (Pillay *et al*., 2010). If such wastewater penetrates the water table, consequences could be serious. As a result, various components of the ecosystem could be affected leading to undesirable pollution. Wastewater extracted from oil, therefore, has the potential to become a significant source of ground water pollution, especially if it has elevated levels of chemical toxins (Benramdane *et al*., 1999; Korte and Fernando, 1991). The likely threat to sustainable development is therefore of material concern (Shearman, 1990; Robinson, 1993). The cytotoxic nature of chromium and arsenic species has grown in interest

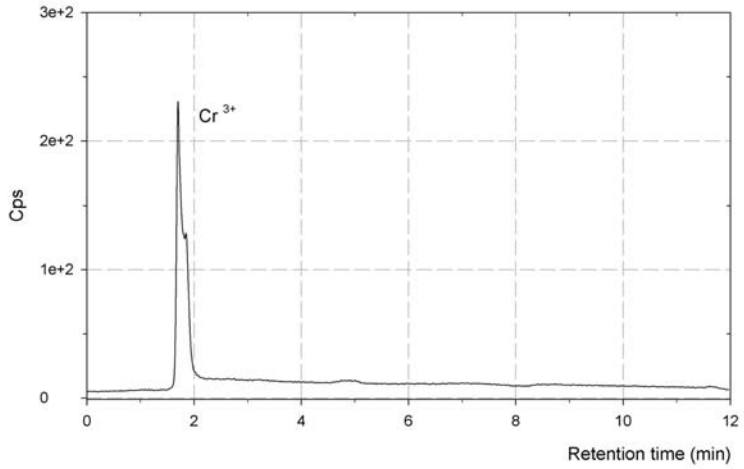

Fig. 4. Chromatogram of Cr^{3+} from produced water.

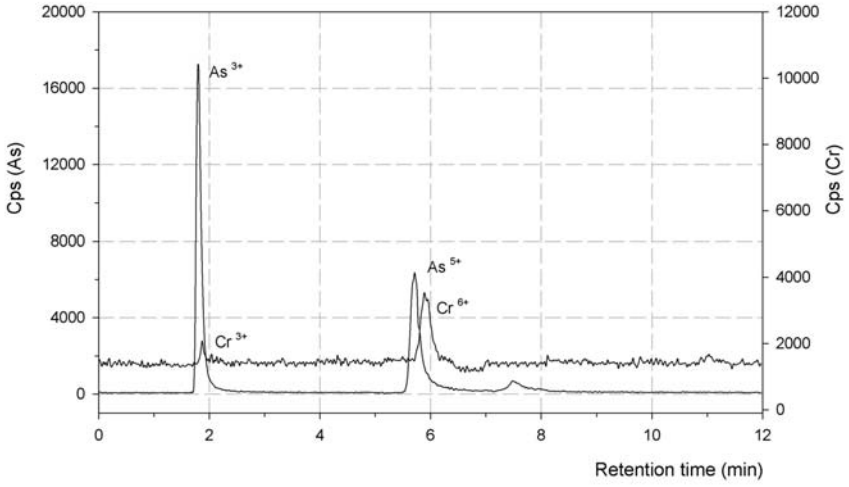

Fig. 5. All chromium and arsenic species in a single run.

(Benramdane *et al*., 1999; Katz and Salem, 1993). The hexavalent form of chromium (Cr^{6+}) is more toxic than its trivalent form, Cr^{3+} (Benramdane *et al*., 1999). However, elevated levels of Cr^{3+} in humans tend to inhibit iron uptake, which could lead to multiple disorders. On the other hand, trivalent arsenic (As^{3+}) is known to be more cytotoxic than the pentavalent species, As^{5+} (Katz and Salem, 1993). The presence of elevated levels of inorganic arsenic in humans leads to vascular diseases and cancer (Katz and Salem, 1993). Our results show Cr^{3+} concentrations represent a significant source of toxicity and could pose a hazard if produced water of this nature reaches potable water supplies. The $Cr^{6+}/As^{3+}/As^{5+}$ levels also appear menacing and remedial measures for removal of Cr and As species by chemical means would be apt prior to disposal of the produced water by-product. Another option would be either to immobilize the water by storing in vitreous slabs or in underground bunkers; or to convert it to a sludge using sand and aggregate, and subsequently constructing concrete blocks for storage in subterranean caverns (Pillay *et al*., 2010).

CONCLUSIONS

Our study provides significant speciation data (Cr^{3+}/Cr^{6+} and As^{3+} /As^{5+}) for produced water, which is of considerable practical interest to petroleum engineers and environmentalists. This essential information is not available in the documented literature and from this perspective our research breaks new ground. The fact that all four species can be isolated in a single run employing an HPLC/DRC-ICP-MS system implies the facility could be extended for rapid simultaneous assay of other toxic species including Se^{4+}/Se^{6+} and Hg^{2+}/Hg^{+}. The notable feature of this instrumental arrangement is that it caters for comparatively low sample volumes, which makes it useful for applications in other disciplines such as biomedicine and immunology. Our results were evaluated

in terms of the potential hazard to the environment that produced water could cause if it were a source of toxicity. The relevant levels recorded in our study were elevated suggesting they could pose a threat to potable water supplies if such wastewater is returned to the ecosystem. One suggested remedial measure is to immobilize the produced water in vitreous or concrete slabs for subterranean storage.

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