Setting standards in analytical science

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Chromium Speciation in LGC 6177 Landfill Leachates Initial identification

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Analyst	John Entwisle
Our reference No.	AT20/10/3210-3214

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Aim

To develop a protocol, which ensures compatibility of the landfill leachate (LGC 6177, certified for total Cr content 0.18 ± 0.02 mg/L) matrix with the previously developed and well established ion pairing chromatographic method with ICP-MS detection, enabling the tentative identification of chromium species in this material.

Method

Chemicals and standards

Ethylenediaminetetraacetic acid (EDTA, 99.995%), tetrapropyl ammonium hydroxide (TPAOH, 1.0 mol L^{-1} aqueous solution), tetrapropyl ammonium bromide (TPABr, >99%), ammonium hydroxide solution (28-30% m/v) and chromium(III) chloride hexahydrate (98%) were obtained from Sigma-Aldrich (Poole, Dorset, UK).

Potassium dichromate standard reference material NIST SRM 136f, certified for mass fraction of $K_2Cr_2O_7$ (99.9954 % ± 0.0044 %), was supplied by LGC Standards (Teddington, Middlesex, UK).

Preparation of diluent and mobile phase

The *diluent* (2.8 mM TPABr, 4 mM EDTA, pH 8.5) is prepared by dissolving TPABr (0.745 g) in 1 L deionised water, then adding EDTA (1.16 g) and sonicating the mixture. The pH is adjusted to 8.5 with aqueous ammonia solution. EDTA has a low solubility at pH less than 8 and therefore repeated sonication and pH adjustment is required to dissolve all the EDTA. The *mobile phase* (0.18 mM TPABr, 1 mM EDTA, pH 8.5) is prepared in a similar manner as the diluent by dissolving TPABr (0.0478 g) and EDTA (0.29 g) in 1 L deionised water.

Preparation of standards

Standard solutions were gravimetrically prepared from chromium salts by dissolving 0.1g in 150g of water in a plastic bottle. Further dilutions were prepared immediately using *diluent*. Prior to injection, the standards were heated (75°C for 30 minutes) in a similar manner to the samples to ensure entire complexation of Cr(III) with EDTA.

Sample collection and preparation

Five sample bottles of the landfill leachate (LGC 6177 bottles 1133, 1152, 1158, 1164 and 1166) were received on the 6th September 2010 (internal reference

AT20/10/3210-3214) and subsequently stored at 4°C for the initial purpose of identifying and quantifying arsenic species under a previous Government Chemist project. Further analysis was requested to add tentative chromium species identification by ion pairing HPLC-ICP-MS. The bottles were found to contain a light brown liquid with a small amount of dark brown particulate matter. The samples were homogenised by inversion and shaking before subsamples were taken. These units were stored in a similar manner to the distributer (LGC Standards, Teddington, UK) and therefore species transformation during storage is unlikely. The landfill leachate solution has been acidified (pH ≈ 1.8) to ensure metal ion stability and to act as a preservative. In order to ensure sample compatibility with the chromatography system a pH adjustment and complexation of Cr(VI) and Cr(III) with EDTA / TPA ions is required. Therefore, sample aliquots require the addition of a quantity of ammonia solution to neutralise the acid followed by dilution with the *diluent* (2.8 mM tetrapropylammonium bromide, 4 mM EDTA, pH 8.5).

Special care has to be taken to adjust the sample pH; if the sample is adjusted to alkaline pH directly there is the possibility of Cr hydroxide precipitation thus making a proportion of the Cr(III) unavailable for complexation resulting in a reduction of the observed Cr(III) peak area. If the sample is directly diluted with the *diluent* there is the possibility of EDTA precipitation due to the drop in pH. Therefore, the addition of a predetermined volume of ammonia solution to a volume of *diluent* before addition of a predetermined volume of sample avoids these issues. Bottle 1152 was selected and a pH monitored titration performed. It was established that 41 µL of 0.62 M ammonia solution were required to neutralise 0.5 mL of sample. Therefore, for subsequent dilution of the sample the *diluent* was preloaded with 41 µL of 0.62 M ammonia solution before the addition of 0.5 mL aliquot of the sample. To ensure that all the available Cr(III) complexes with EDTA the solutions were heated to 75°C in a hot block for 30 minutes prior to injection onto the ion-pairing HPLC system.

Instrumentation

Ion-pairing reversed phase HPLC online with ICP-MS

The chromatographic separation was carried out using an Agilent Technologies 1100 Series HPLC. Ion pair HPLC was performed using an Agilent PLRP-S 100Å in PEEK column (150 mm x 4.6 mm, 3 µm) directly coupled to an Agilent 7700x ICP-MS

operating in Helium mode (4.3 ml/min) to minimise $^{40}Ar^{12}C^{+}$ interferences for element-specific detection at ^{52}Cr and ^{53}Cr. The HPLC eluant was introduced into the plasma *via* a microflow quartz concentric nebuliser and a cooled Scott type double pass spray chamber. Each analysis comprised of a 20 minute isocratic chromatographic run using 0.18 mM tetrapropylammonium bromide, 1 mM EDTA (pH 8.5) as the mobile phase. Baseline separation of the Cr species was achieved within 15 minutes, at a flow rate of 0.8 mL/min using an injection volume of 30 µL. Chromatograms of a mixed standard and a reagent blank are shown in Figures 1 and 2, respectively.

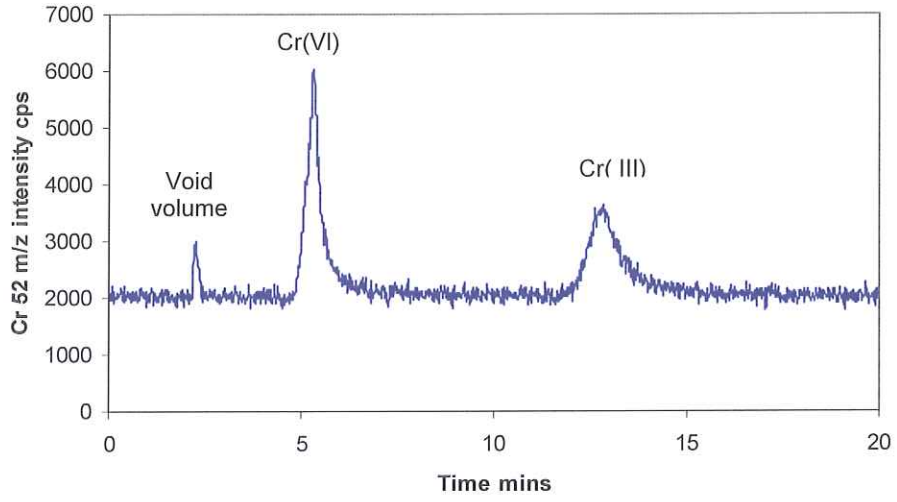

Figure 1: Standard containing Cr(VI) and Cr(III) ≈ 2 ng g^{-1} prepared in *diluent*.

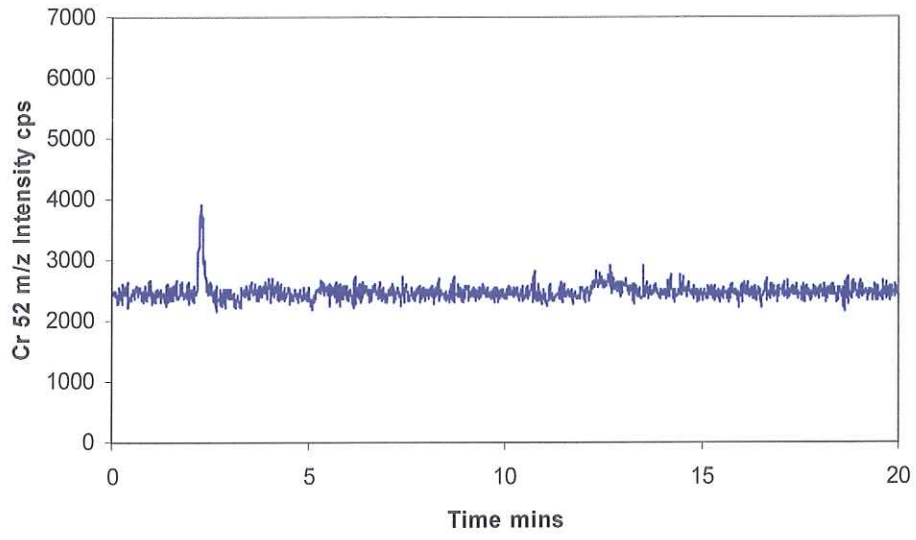

Figure 2: Reagent blank prepared in *diluent*

Results and discussion

A Cr(III) standard solution was prepared from a commercial Cr(III) stock solution (1000 μg g^{-1} in 0.5 M nitric acid). An unknown peak was observed (see chromatogram of **Figure 3**) at a retention time of 8 minutes, apart from the main Cr(III) peak. Formation of this compound was initially thought to be due to incomplete complexation of Cr(III) with EDTA so the standard solution was subjected to an extended heating time. This did not have an effect on the Cr and the identity of the peak at 8 mins remains unknown. An alternative Cr(III) standard was prepared by dissolution of solid chromium(III) chloride. To avoid transformation of the standard solution prior to analysis, a fresh Cr(III) stock standard solution was prepared and immediately diluted to working concentrations with minimal delay. The chromatogram of this standard solution showed a single Cr peak corresponding to Cr(III). This standard was selected for further work.

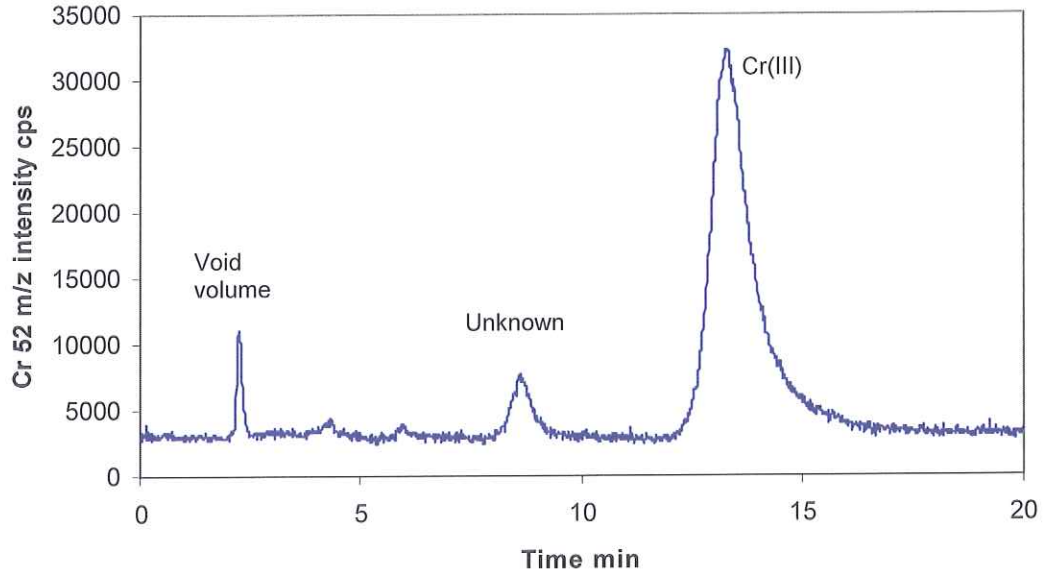

Figure 3: Standard containing Cr(III) ≈ 14 ng g^{-1} prepared from 1000 μg g^{-1} commercial Cr(III) stock solution diluted in *diluent*.

Investigation into optimal sample loading of the chromatographic system.

The leachate sample is expected to contain trace concentrations of Cr(VI), in the presence of a significant concentration of Cr(III). Therefore, it is important to optimise sample dilution in order to achieve the lowest limit of detection for Cr(VI) in the sample matrix without compromising the chromatographic separation. 2.5 mL of

diluent was dispensed into individual 15 mL falcon tubes followed by 41 µL of 0.62 M ammonia solution. 0.5 mL of sample 1152 was dispensed into each tube and the solutions mixed. The solutions were further diluted to 3, 4, 5, 6, 7, 8, 9, or 10 mLs with *diluent* before heat treatment at 75˚C for 30 minutes. The solutions were individually injected onto the system interspersed with a mixed species standard. It was found that no significant adverse affects occurred to the chromatographic separation even at the maximum loading of 1:6 (0.5 mL to 3 mL). Therefore, it was decided to adopt this ratio.

Analysis of leachate samples

The optimised conditions were used for the analysis of the units 1133, 1152, 1158, 1164, and 1166 (see **Figure 4** for example chromatogram of 1133). For all these samples peak area normalisation (which assumes equivalent response for both species) enabled estimation that less than 1% of the chromium present was Cr(VI). This result is consistent with expectations as Cr(VI) is readily reduced by organic matter under acidic conditions to Cr(III). Tentative identification of the major peak as Cr(III) was confirmed by spiking experiments (**Figure 5**).

(Figure 6) demonstrates that the potential polyatomic interferences $^{35}Cl\ ^{16}OH^{+}$ on ^{52}Cr and $^{37}Cl\ ^{16}O^{+}$ on ^{53}Cr due to presence of chloride in the sample matrix are chromatographically resolved.

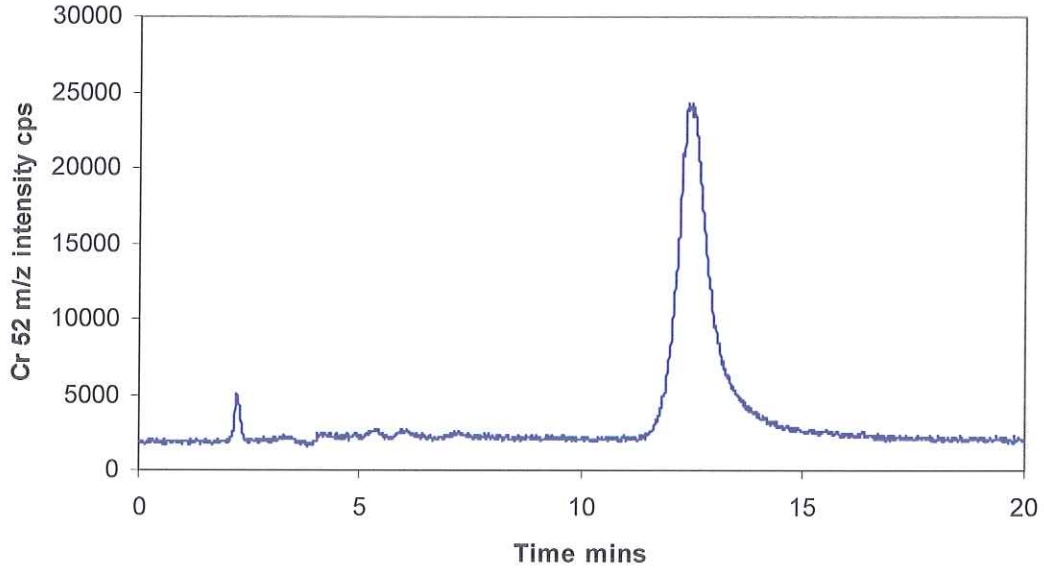

Figure 4: Sample 1133 prepared as per procedure described (diluted 1:6 with *diluent*)

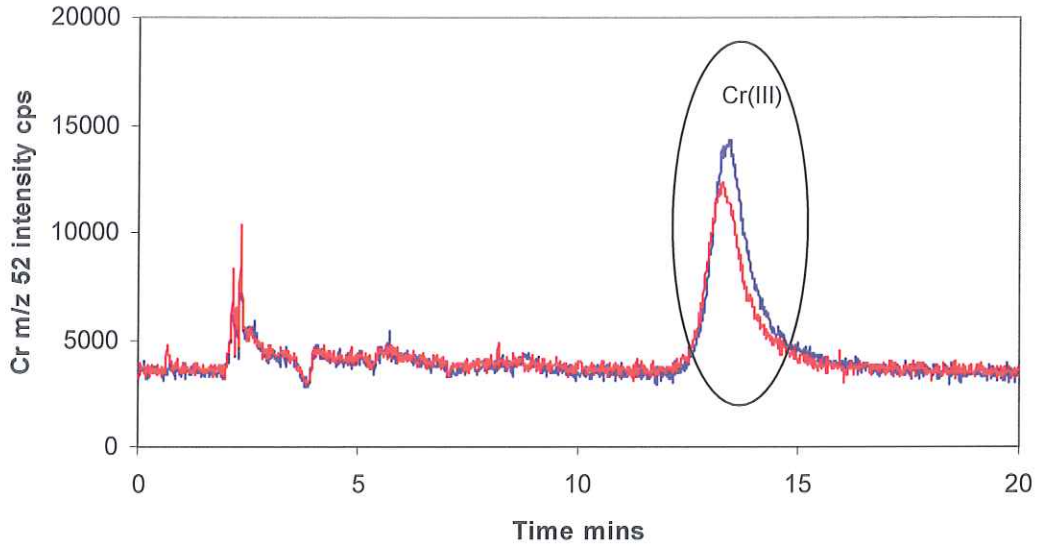

Figure 5: Sample 1152 neutralised and diluted 1:10 with *diluent* and spiked with Cr(III) ≈3 ng g^{-1} (blue trace) or non-spiked (red trace), both heated.

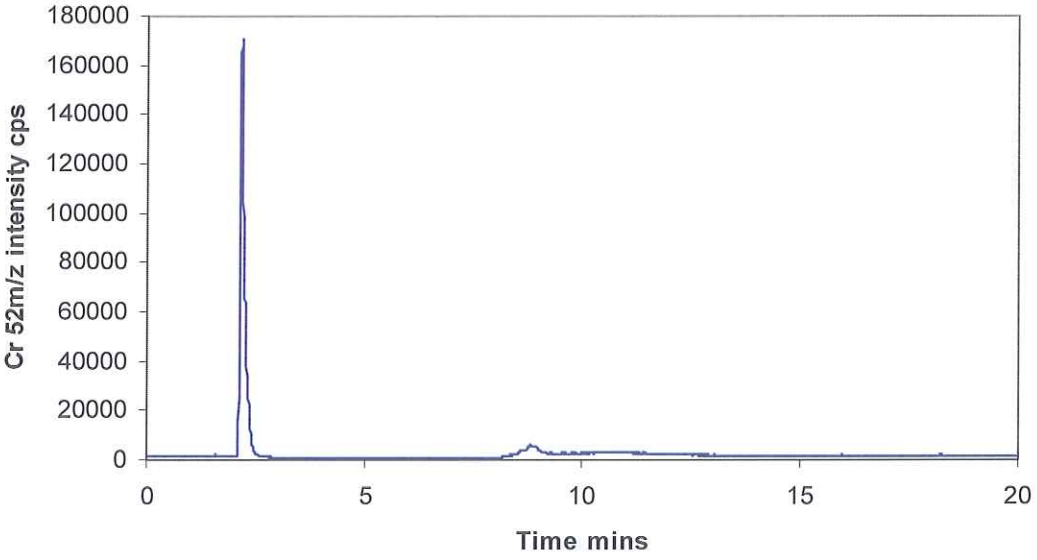

Figure 6: Ammonium chloride ≈1000 µg g^{-1} in *diluent*

Conclusion

A procedure for preparation of dilutions compatible with the chromatographic separation without causing significant species inter-conversion. The procedure employs minimal dilution ensuring the possibility of detecting minor concentrations

of Cr(VI) in the presence of major quantities of Cr(III). The chromatographic system has proved to be robust to a heavy matrix containing significant quantities of other ions and components. Identification of chromium species present in LGC 6177 landfill leachate solutions (bottles 1133, 1152, 1158, 1164 and 1166) was carried out. Chromium speciation analysis by HPLC-ICP-MS and retention time standards identified Cr(III) as the only detectable species.

Suggestions for further work

Quantification of the Cr(III) content is the next logical step but it may be significantly less than the total Cr content due to particulate matter in the leachate sample containing insoluble Cr species. Therefore, it would be advisable to analyse a portion of the particulate matter and the supernatant separately for clarification. As the chromatographic system has proved to be robust to complex matrices it may be applicable to a wider array of sample type. The sample leachate chromatogram could be monitored for other major/minor elements to determine their retention time and therefore the likelihood of interference with the detection of the Cr species.