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I. ABSTRACT OF THE REPORT

This Technical Performance Report summarizes work which was carried out in our research laboratory over a period of several years focusing on metal speciation studies. The aim was to study the solution chemistry of selected heavy metals, using the knowledge gained to develop analytical methods and protocols for the identification and quantification of various forms of these metals in different sample matrices. Speciation protocols were developed for several heavy metals employing the capabilities of chromatographic and spectroscopic techniques augmented by post-column derivatization and solid phase extraction procedures. Twelve refereed publications and over twenty oral and poster presentations have resulted from this work, see bibliographic list included in this report. The involvement of graduate and undergraduate students has produced eleven master of science theses and a number of research reports.

II. RESEACH SCOPE AND OBJECTIVES

The chemistry of heavy metals in natural waters, industrial waste streams, and the environment is influenced by a number of factors including the prevailing matrix, their relative concentrations, and biologically or chemically induced transformations. Speciation, which entails the identification and quantification of all the forms of a metal or any other chemical entity present in a sample, is a necessary step in assessing the toxic and pollution effects and the overall impact of these entities on environmental systems. Analytical methods and protocols that can provide analytical data in the parts per billion concentration range and below are needed for these kinds of measurements.

While the ideal speciation method is one that can provide analytical information in *situ,* no method exists today that can provide reliable information especially on the heavy metals of interest. Instead, metal speciation has relied on the combination of electrochemical, chromatographic, and spectroscopic techniques.

The thrust of our research was to develop metal speciation methods and techniques using direct current plasma (DCPAES) in combination with ion chromatography (IC), whereby the DCPAES serves as an element selective detector (ESD) for the metal species separated in the chromatographic column. The primary requirement in this approach is that the metal species in the sample are separated by the chromatographic column. The (IC-EDS) approach has another potential advantage in that any transformation that the analyte may undergo as conditions change will be detected and monitored.

While the metal speciation work carried out in this program has utilized the IC-DCPAES as the primary analytical measurement tool, other sample processing and preparation approaches have also been developed to enhance the effectiveness and capability of the chromatographic-element selective method of metal speciation. Post-column derivatization and solid phase extraction are two protocols which were incorporated with IC-ESD with significant improvements in the capability of the method.

III. SUMMARY OF THE ACCOMPLISHMENTS OF THE RESEARCH

Solution Chemistry and Speciation of Heavy Metals

The Element Selective –Chromatographic approach was successfully used to study the solution chemistry of and develop speciation methods for arsenic, chromium, iron, manganese, nickel, phosphorus, platinum, selenium, and vanadium. We have demonstrated that species such as As(III), As(V), Se(IV), and Se(VI) are easily separated on an ion chromatographic column and detected via atomic emission. The superiority of the element selective detection over other methods of detection, such as conductivity measurements which are based on universal detectors, was demonstrated in the speciation of As (III) and As(V) which cannot be achieved in the presence of common anions. Furthermore, all species of the same element are measured with equal efficiency and sensitivity since detection is based on the atomic concentration of the element of interest.

A fundamental requirement of metal speciation is that the analyte remains unchanged between sampling and measurement time. For environmental samples, this may not be possible because one of the common practices is to acidify such samples to preserve them and to digest particulate matter. While this is accepted practice, the expectation is that those changes can be predicted and monitored as they occur. The effectiveness of the ESD approach in this regard was demonstrated by speciation of iron and vanadium in hydrochloric acid medium. The chemistry of both of these metals is highly influenced by acidification, especially if hydrochloric acid is used. When V(IV) is placed in different HCl concentrations, different V moieties with different chromatographic properties are formed. The transformation from one moiety to another was easily and effectively monitored as they eluted from the ion chromatographic column by measuring vanadium emission at 437.9nm.

In HCl, Fe forms chlorocomplexes whose chromatographic properties are quite different from those of hydrated Fe(II) but can be measured with the same efficiency using ESD. Fe(III) on the other hand does not appear to undergo a similar transformation in HCl. This makes it possible to determine the Fe(II) and Fe(III) content in a sample even after acidification. Similar transformations were successfully studied and monitored for other metals including platinum as hexachloroplatinum(IV); oxidation/reduction reactions of Mn(II)/Mn(VII); oxidation of Fe(II) to Fe(III); and the hydrolysis of Fe(II) and Fe(III).

The ESD approach using DCPAES as the method of detection has an added advantage in that particulate forms of the analyte metal can be detected and quantified. This was demonstrated by speciating chromium in industrial process stream samples. The analysis was done in three modes. In the first mode, the sample was aspirated directly into the d.c.plasma, providing information on the total chromium present including ionic (Cr(III) and Cr(VI), particulate, and other unfiltered forms. In the second analysis mode, the sample was first filtered with a 0.2 micron filter prior to aspirating into the d.c. plasma. The information obtained here was on the filterable fraction. In the third mode, the filtrate was injected onto the chromatographic column, measuring the effluent via the DCPAES.

This provided data on the Cr(III) and Cr(VII) fractions. In this way, a true material balance for the chromium species was achieved.

Measurement sensitivity is an important parameter in speciation work given that some of the species may be present in very small concentrations. Ordinarily, detection capabilities must be in the ppb range. While the IC-DCPAES approach does not have this inherent capability for some metals, several attempts were made to improve on measurement sensitivity. Two approaches have proved to have the capability to provide data in the desired concentration range. These are the use of large sample introduction loops and sample pre-concentration. Large sample loops ensure the placement of a large sample on the column to begin with. As large as 1000uL loops were successfully employed while good linearity was maintained. In the case of sample pre-concentration, both on-column and off-column procedures were used. In both cases, detection limits were improved to below 50ppb.

Metal Speciation by Post-column Derivatization

One drawback of doing metal speciation using the element selective detector approach described above is that the approach is sequential. Thus, while several species of a given metal can be identified and quantified, only one element can be studied at a time. Attempts were made to overcome this drawback by employing a universal bulk sensitive detector, such as colorimetry. This required a post-column derivatization of the chromatographic effluents followed by colorimetric measurements at a fixed wavelength, in this work at 520nm. Post-column derivatization was accomplished with 4-(2-pyridylazo)resorcinol (PAR) which reacts with most transition metals to form a complex that absorbs at 520nm.

While post-column derivatization provides a capability for multi-species and multi-element measurement, it has two drawbacks: (1) different metals react differently with the ligand used. This, coupled with the fact that the complexes formed are measured at a fixed wavelength means that measurement sensitivities can vary widely among the metals and metal species of interest. The second drawback of the approach is that the metal species which are in the sample as organic compounds may not react with the PAR if the thermodynamics requirements are not met. Thus, the post column approach is rather limited as a speciation method.

Solid Phase Extraction for Metal Speciation

Metal speciation by chromatographic separation as described above are suitable for those species which are separable on the ion exchange columns only. However, metals species in the environment can also exist as organic and inorganic compounds that may not be separable by the ion exchange mechanism involved in ion chromatography. Therefore, solid phase extraction (SPE) was employed in the speciation work as an attempt to use materials that can recognize metal species in various forms including simple inorganic ions, charged complex ions, and neutral metal complexes.

There are several other factors that make SPE suitable for metal speciation. First, relatively small sample sizes are required. Second, the analyte of interest is momentarily immobilized on a sold support, isolating it from the sample matrix. Third, sample pre-concentration is facilitated. Fourth, by controlling the functionality of the sorbent, desired metals or species of a given metal can be selectively extracted from the sample matrix.

Two categories of solid phase extraction materials were employed: those with polar functionality, and those with non-polar surfaces. In both cases, synthetic and naturally occurring materials were employed. The fundamental hypothesis was that by using SPE, metal species in the form of organic compounds can be isolated by adsorption on the surface of a solid matrix. Conversely, inorganic forms of the metal can first be converted into complexes with appropriate ligands followed by extraction on the solid surface.

To demonstrate the efficacy of employing SPE in metal speciation, neutral and charged complexes were extracted on C-18 and LC-NH2 extraction columns, respectively. Chitosan was used as an example of naturally occurring solid phases. Attempts were also made to chemically modify the surface of the LC-NH2 sorbent, altering the functionality.

Immobilization of the analyte on a solid sorbent not only isolates it from the sample matrix but also stabilizes it by apparently protecting it from atmospheric degradation. By careful adjustment of system conditions, practically 100% of the sorbed analyte can be eluted.

Use of Mixed Sorbents for the Extraction of Metal Species

The effects of using mixed sorbents was investigated by mixing LC-NH2 and C-18 separately with a polymeric ion exchange resin obtained from a collaborating researcher. The styrene divinylbenzene (diphonix) which is a sulfonated ion exchange resin has gemdiphosphonic acid groups which account for its chelation properties. The retention characteristics of both LC-NH2 and C-18 for metal ions were significantly enhanced when they were "doped" with relatively tiny amounts of the resin. An investigation of the mechanisms involved in the observed retention capacities led to the conclusion that the sorbents do not appear to undergo any chemical alterations, rather, the retention is solely due to the resin and that the sorbents only acted as support for the resin.

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