Trace metal analysis using ion chromatography in water partitioned from crude-oil spills

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Abstract

All crude oil contains trace metals with nickel (Ni) and vanadium (V) generally being the predominant elements. In the past, these trace metals were only a concern from the perspective of the fuel cracking process. However, in recent years, Ni/V ratios have been used as biomarkers for determining the origin of crude oil in spills of unknown origin. Boscan crude from Venezuela, for example, has Ni levels on the order of 100 ppm and V of 1,000 ppm. Spills as large as those seen in Kuwait create some concern for the partitioning of these trace metals to the environment. To assess the environmental impact of such spills, one first needs to determine if porphyrins keep these metals from partitioning, and if not, how to detect them at the expected low concentrations and in a speciated form. A cost-effective analysis for looking at these potential trace metals in their various speciations may be the use of ion chromatography with non-metallic pumps and plumbing. Utilization of concentration techniques and the injection of 4-ml samples allow consistent and reproducible detection of most metals at 0.5 ppb or lower. The lower limit is mainly a function of trace metals found naturally in deionized waters, contaminants in chemicals used, or from complication of having several oxidation states in metals such as vanadium. A perfecting of this detection method is discussed as a prelude to answering the question on partitioning and speciation.

Introduction

The introduction of trace metals to the environment via crude oil spills, either intentionally (e.g., Kuwait spills of 1990[1]), or unintentionally (e.g.,

pipeline breaks in Bemidji, MN, USA,[2] or the Valdez oil tanker accident, etc.), has the potential to impact surface and groundwater supplies with toxic levels of metals. The most abundant trace metals in crude oil are nickel and vanadium. The concern for vanadium and nickel has generally been from the standpoint of "poisoning" zeolite-containing cracking catalysts, e.g., Lysenko.[3] More recently, Abu-Elgheit, et al.,[4] Barakat, et al.,[5] and others have shown that the ratio of vanadium to nickel can be utilized as a biomarker with environmental measurement potential. Very little study has been given to potential leaching to the environment, which may create toxic levels in groundwater Our present research indicates that while the partitioning may be expected to be insignificant, it is indeed taking place and may be of concern for larger spills of specific types of crude oil. In addition, low-level detection methods, i.e., ppt, have only been element specific and not species specific. Our research is addressing some of the main questions of trace metal concerns for large oil spills: namely, potential contamination of the environment and detection methods.

One family of pigments is responsible for our green world and our red blood. Milgrom[6] points out that these pigments are based on a macroscyclic ring of carbon and nitrogen atoms, which are called porphyrins. It is generally thought that most trace metals are complexed by porphyrins in crude oil. What is not clear is if water as a polar solvent has the ability to partition any appreciable amounts of these trace metals from the oil, if aging of the crude has an effect, or if the species liberated will affect the transport properties through a porous media. These questions are concerned with partitioning capabilities of the trace metals and their speciation and how to provide low-cost, high-sensitivity detection of these species.

All crude oil has some trace metals, which create concerns for contamination of groundwater. While metals provide known beneficial health effects at low levels, they become toxic at slightly higher levels. Valkovic[7] indicates that generally the ratio of toxic to requirement levels of trace elements is on the order of 50. This indicates a potential for concern for trace metals going into the environment, primarily potable groundwater, for some of the larger crude oil spills.

Patty's *Industrial Hygiene and Toxicology*,[8] for example, indicates that both vanadium and nickel can have a toxic effect on the human body. Vanadium does not have a mean contamination limit (MCL) in accordance with either the U.S. Environmental Protection Agency (USEPA) safe drinking water regulations or World Health Organization (WHO) standards. Indications are that the USEPA plans to assign a level

in the future, but it has not happened yet. The state of Michigan in the U.S.A. has, however, set drinking water standards for both nickel (100 ppb) and vanadium (64 ppb). And Kuwait researchers, for example, are quite interested in drinking water standards and whether or not WHO will set a limit for these two metals [Viswanathan[9]].

Detection Methods

If you want to detect metals at very low concentrations, there are a number of analytical procedures now available, which will detect trace metals at the part-per-trillion (ppt) range. These include, but are not limited to, inductively coupled plasmas (ICP), flame atomic absorption (AA), graphite furnace AA, ICP with mass spectrophotometry (ICP-MS), etc. But if you want to speciate and see complexes, in addition to the particular element, you have to use separation techniques like capillary electrophoresis (CE), high-performance-liquid chromatography (HPLC), ion chromatography (IC), or some combination. To address the problem posed and to do it in a cost-effective manner, we have been looking at IC. In particular, we have been using a DIONEX DX500 IC, which allows detection of the transition metals at very low levels because of its use of non-metallic plumbing and pumps.

Nickel in its ionic form can be quantified with a detection limit of 100 ppt using the IC setup shown in Figure 1. With a 4-ml injection onto a cation concentrator column (CC) and a standard mobile phase eluent of 0.035 mM pyridin-2,6-dicarboxylic acid (PDCA), 0.37 M formic acid, 0.33 M potassium hydroxide, and 0.028 M potassium sulfate, we can detect ionic nickel at <0.5 ppb. This is accomplished with a visible detector set at 520 nm, and using a post-column reagent of 7.4 M ammonium hydroxide, 1.7 M acetic acid, and 0.4 mM 4-(2-pryidylazo) resorcinol, commonly called simply PAR.

Vanadium proved to be much more difficult. Vanadium can exist in a number of oxidation states, which changes with pH. Smith[10] reported that a recipe for seeing vanadium at "5 to 10 ppb" is possible with an eluent mobile phase of 6 mM PDCA and 8.6 mM LiOH. The preferred post-column reagent is 0.5 M Na_2HPO_4 with 2 x 10^{-4} M PAR. Using these recipes we obtained desired sensitivities, but found that the peak elution times changed with concentrations below approximately 200 ppb. These phenomena will be reported on elsewhere. Takaya and Swatari[11] defined an HPLC procedure where vanadium IV and V could be speciated using a combination of 1 mM and 100 mM HNO_3. By using 90% of the standard eluent (PDCA/LiOH) and 10% 100 mM nitric acid, the vanadium peak

was stabilized at low concentrations (ppb). However, the procedure must be shifted back to 100% of the original eluent after the vanadium peak detection to elute any other metals commonly seen by this procedure; for example, Cu, Co, Cr, and Zn, which may be sticking to the separator column.

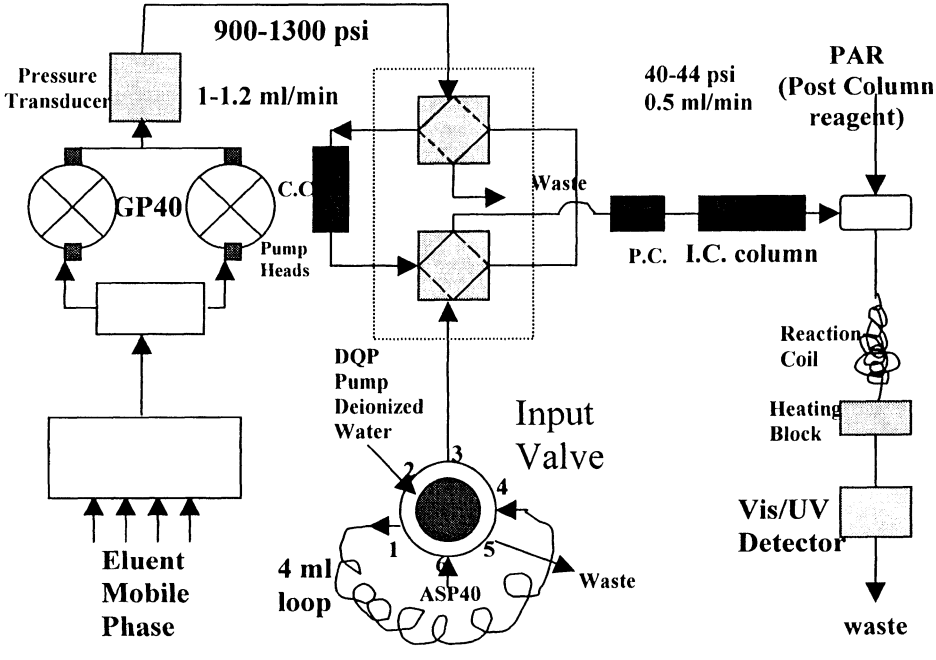


Figure 1: Schematic of Dionex DX500 Ion Chromatography Unit.

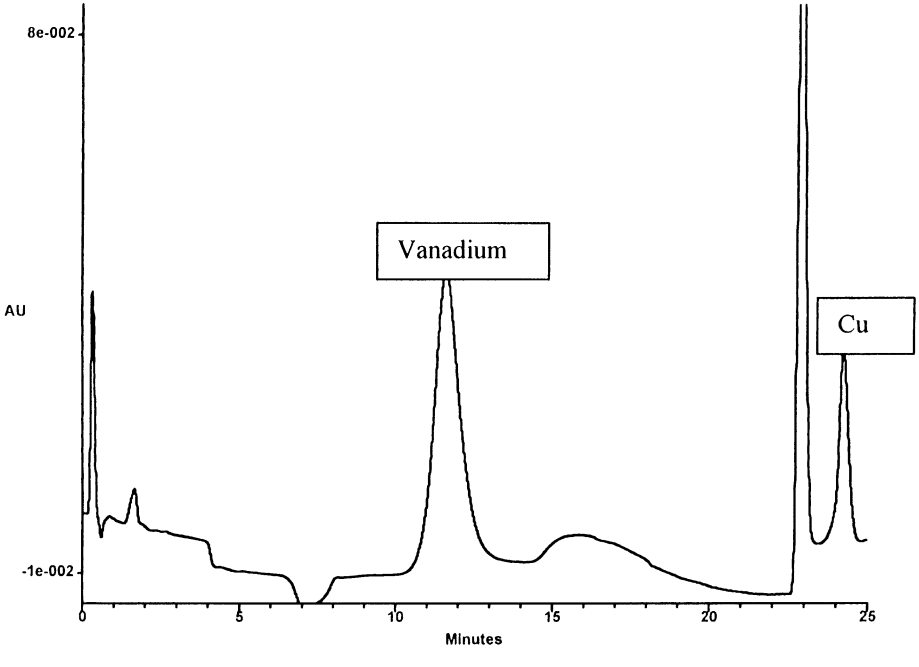
Protoporphyrin IX (3,7,12,17-tetramethyl-8,13-divinyl-2,18-porphine-dipropionic acid as a disodium salt) was added to a nickel standard. While a decrease in nickel was detected at a 40:1 ratio (protoporphyrin IX to nickel), no easy method has been found at this time to detect porphyrin-related peaks with simple IC methods. A higher complexing ratio was not necessarily expected for this procedure since the actual complexing process, as done in nature or in the laboratory, can be quite involved. High-performance liquid-chromatography methods have been used at higher detection methods to analyze for porphyrins.[12,13]

Analysis

A few grams of Boscan crude oil with a nickel content of 95 ppm and vanadium content of 1023 ppm [documented in Material Data Safety

Sheets (MSDS) for this oil and confirmed by an inductively coupled plasma procedure], with 50 ml of deionized water added, was tumbled in a batch reactor for six months. Detailed sequential elutions have not been done yet. Nickel analysis indicated ionic nickel partitioning from the crude at approximately 1-1.5 ppb. Vanadium in the ionic form was undetectable, indicating a value of less than 0.5 ppb. Water that was oxidized (flashed burned at 900 °C and eluted with 100 mM nitric acid) had vanadium detected at levels on the order of 1.1 ppm. This is a partitioning on the order 0.1% of the vanadium in the crude oil. Complexed nickel was on the order of 2.5 ppm, or a partitioning up to approximately 2.6% of the nickel in the crude oil. In addition, there was copper, zinc, and other trace metals. While further analysis needs to be done, it is clear the nickel, vanadium, and other trace metals do partition from the crude oil to water, and most likely in a complexed form.

In addition, sample analysis using a combination of HPLC and Raman spectroscopy with the University of Houston is now being defined to determine the nature of the complexation.



Elution Time

Figure 2: Chromatogram of vanadium elution after 900 °C burn of vanadium partitioned to water from Boscan crude oil.

Discussion and Conclusions

While more in-depth research needs to be completed, initial analysis would indicate that vanadium, nickel, and other trace metals in crude oil seems to be tightly bound in the sense that they are not easily eluted by water-oil partitioning as free ions. However, initial indications are that partitioning is taking place, perhaps in the form of vandyl and nickel porphyrins. Whether or not there should be any environmental concerns from these metals in a major oil spill is not clear at this time, but our initial analysis would indicate that the concern is probably minimal, unless the content of the trace metals is very high. In the direct vicinity of an oil spill toxicity will most likely be driven by the presence of organic compounds (benzene, PAH's). These organics are biodegradable, and the current trend in the U.S.A. is to allow natural biodegradation to proceed while monitoring a site closely and restricting access to contaminated water. This "hands off" approach is called "natural attenuation." Metals will be attenuated only by sorption and will not be destroyed, which calls for a reexamination of this policy if metals and organics co-exist in a site. If the partitioning is indeed primarily in a complexed form, perhaps porphyrins, as indicated by our initial studies, it implies a form that is much more mobile in a porous media. This mobility also implies that it will be diluted more easily in the groundwater system.

The use of low-cost ion chromatography as a detection method is reproducible and has adequate sensitivities for most of the trace metals of concern in crude oil. Further development on a vanadium procedure, at low concentrations (ppb), needs further refinements.

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