[PP 1.3]

The Chromatographic Trapping and Separation of Chromium Species Prior to Atomic Absorption Spectrometric Detection

David J Roberts*, Nisakorn Thongkon

School of Chemistry, University of Bristol, Cantocks Close, Bristol, BS8 1TS UK;
Telephone: 44 117 9289118 Fax: 44 9289251295 E-mail: d.j.roberts@bristol.ac.uk
*Author to whom correspondence should be addressed

The form or species the metal is in is very important, because of the effect it may have on the environment, as some forms of the same metal are more toxic than others. For example chromium (VI) is carcinogenic and chromium (III) is found to be involved in some enzyme systems. It is therefore important to be able to separate these two species in a water sample and to determine how much of each is present. Other forms of metals also have toxic properties, the inorganic form of arsenic for example, is more toxic than its organic form. There is always a need to develop new and more sensitive methods of sample preparation and separation without changing the particular species of interest, prior to analysis. The following describes how it is possible to separate and measure both chromium (III) and chromium (VI) sequentially.

A solid phase extraction device (SPE-NH_2) containing NH_2 as the functional group on the sorbent [-Si-CH_2-CH_2-CH_2- NH_2] was used for the separation and preconcentration of chromium (VI) from chromium (III) prior to flame atomic absorption spectrometric detection. In order to trap the chromium (VI) it is important to protonate the NH_2 functional group to NH_3^+ with an acid solution which is then paired with the anion group (CrO_4^{2-}) which is separated from the cationic group Cr (III) passing through SPE (NH_2). A range of acids with varying acid strengths were tried such as different concentrations of hydrochloric acid and acetic acid. Under laboratory conditions 1.0M HCl was found to be the most suitable for conditioning the column.

If it is necessary to determine only chromium (VI) by separation and preconcentration from chromium (III), a single micro-column packed with 3-aminopropyl silica can be used. This is then conditioned prior to use with MeOH and 1.00M HCl. The chromium (VI) can then be eluted with 2.00M HCl directly to the flame AAS. The concentration of chromium (III) is then obtained by difference between the total concentration of chromium and the determined concentration of chromium (VI).

If two micro-columns are used in this system packed with 3 -aminopropyl silica using a different preconditioning stage, the method can be used to preconcentrate and separate both chromium species. The first micro-column was protonated with MeOH and 1.00M HCl to trap chromium (VI) and the second micro-column was conditioned with only MeOH to trap chromium (III). Using this method, chromium (VI) and chromium (III) in a water sample can be preconcentrated and separated. 2.00M HCl was used to elute chromium (VI) and H_2O_2/NaOH was used to elute chromium (III) on-line detected by FAAS.

Different concentrations of H_2O_2/NaOH in the eluting solution were also studied to improve the removal and conversion of chromium (III) to chromium (VI). The function of H_2O_2/NaOH was not only as an eluent for removing chromium (III) from the -NH_2 function group, but also as an oxidizing agent to oxidize chromium (III) to CrO_4^{2-}. The CrO_4^{2-} form cannot be trapped by the -NH_2 function group alone and can easily pass out of the non-protonated aminopropyl micro-column directly through to the flame atomic absorption spectrometer (FAAS). This on-line method using two micro-columns coupled to the FAAS can be used to preconcentrate and separate both chromium (III) and chromium (VI) species with a total chromium concentration of less than 1 ppm in water samples. The method can also be modified to determine inorganic arsenic speciation such as arsenic (III) and arsenic (V) in environmental samples.

An off-line separation method can also be improved to achieve more sensitivity, better separation, preconcentration and determination of the chromium species in water samples by introducing 1 or 2 micro-columns connected to the flow injection device and coupled to a graphite furnace AAS (GFAAS). High sensitivity can be achieved by coupling the flow injection device to a GFAAS.

A design for coupling a flow injection device with 1 or 2 micro-columns with a GFAAS has been studied. The use of an amino column as the weak anion exchange column in an HPLC system coupled to FAAS and GFAAS for the total concentration and speciation of chromium at the ng or pg level in the water samples has also been investigated. The CrO_4^{2-} trapped on the SPE (NH_2) was eluted with 2.0M HCl and then detected by FAAS at the ppm level or GFAAS at the ppb level.

In summary it has been shown that it is possible to separate both Cr (III) and Cr (VI) species from the same water sample using a SPE (NH_2) weak anion exchange column to selectively retain each species prior to analysis by AAS.