

SELENIUM SPECIATION ANALYSIS

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In recent years, there has been increasing interest in the trace determination of selenium. This element has been recognised as an essential nutrient for humans based on its presence in the enzyme glutathione peroxidase, which affords cells protection against oxidative damage. However, selenium reactivity and bioavailability depend not only on its total amount. Additionally knowledge of the chemical forms and oxidation states in which this element exists is needed.

In environmental and biological samples, selenium can exist in inorganic (as elemental selenium, metal selenides, selenite and selenate ions) and as organic species with direct Se-C bonds (methylated compounds, selenoaminoacids, selenoproteins and their derivatives). Selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}) appear to be predominant species in natural waters and soils. The ratio of these two forms depends on the presence of complexing agents, dissolved gases (especially oxygen), suspended matter and pH. Inorganic selenium species can be transformed into volatile compounds such as dimethylselenide (DMSe) and dimethyldiselenide (DMDS₂) through microbial action of fungi and plants. The trimethylselenonium ion (TMSe^+), the major product of selenium metabolism, leaves the body of humans in urine. The biomethylation processes are considered to be detoxification steps, because DMSe and TMSe^+ are less toxic than inorganic Se forms.

Many problems in selenium speciation analysis are associated with low concentration of each species to be determined. Moreover, various factors could affect the losses of Se or interconversion of one species into another during sampling and sample storage could occur.

In natural water samples selenium species in three oxidation states (-II, IV and VI) have been determined mainly by analysing three separate sample aliquots: (1) with no further chemical treatment - determination of Se(IV) using fluorimetry, HG-AAS, HG-ICP-AES or HG-ICP-MS and electrochemical methods; (2) after oxidation by UV irradiation or wet acid digestion - the sum of Se(IV) and Se(-II); and (3) after reduction to selenite with hot hydrochloric or hydrobromic acid - all selenium species. The

difference between total selenium and the sum of Se(IV) and Se(VI) is attributed to organic selenium compounds. Usually, a preconcentration step (solvent or solid-phase extraction and coprecipitation) is necessary to achieve a sufficient concentration level for detection.

Compared with the extensive investigations on total selenium or selenite and selenate determination, very little work has been carried out on organic selenium compounds. The simultaneous speciation of both inorganic and organic selenium species in a single run is still a great challenge. The direct coupling of HPLC or capillary electrophoresis to selenium-specific detection such as GFAAS or ICP-MS is the most promising approach for the determination of selenium species in biological and environmental samples.

This lecture has neither the intention of covering all published methods for selenium speciation, nor of criticizing specific scheme. It would rather discuss some general ideas and highlight some important procedures.