

**Speciation in environmental samples:  
a small review**

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Any detailed and realistic study of the environmental, metabolic, toxicological or other properties of chemical elements requires differentiation between its individual compounds. Some work has been done on arsenic speciation at Technological and Nuclear Institute (ITN) on Biomonitoring and Aerosol samples. Apart from arsenosugars (found in some marine organisms and algae), eight compounds are commonly assessed in environmental matrices: inorganic arsenic – arsenite [As(III)], arsenate [As(V)] – and the organoarsenic compounds monomethylarsonic acid (MMAA), dimethylarsinic acid (DMAA), trimethylarsine oxide (TMAO), arsenobetaine (AsB), arsenocholine (AsC) and tetramethylarsonium ion (TETRA). They differ significantly in toxicity, from very toxic (arsenite) to non-toxic (arsenobetaine). While the determination of total concentration in biomonitoring studies is common practice, speciation is still very scarcely used, even in small-scale environmental studies.

This work focuses on the development of analytical methodologies for arsenic speciation in lichen samples from atmospheric-monitoring surveys, since the element can be associated with natural and, especially, anthropogenic sources that usually stand out from multivariate (factor) analyses of lichen-biomonitoring data. The base material for the present study were native thalli of the foliose lichen *Parmelia sulcata* Taylor and *Parmelia caperata* (hammered shield lichen, growing on olive-tree bark), and *Platanus hybrida* either native or exposed in mainland Portugal. Aerosol samples with particles below 10 µm and between 2.5 and 10 µm were arsenic-specified as well. Following suitable field and laboratory procedures, samples were put through instrumental neutron activation analysis (INAA;  $k_0$ -variant) for total-arsenic determination. Separation and determination of arsenic compounds in aqueous extracts were carried out in a HPLC-(UV)-HG-AFS system. The extractability in water ranged from 1.9 to 32 % of the total arsenic. Arsenate was detected in all samples, in many of them as the main arsenic compound. The second most widely found compound was arsenite, followed by an unidentified cationic species. Some samples also contained an unidentified anionic compound. The overall results do not point to a direct relationship between source factors – by Monte-Carlo aided, Target-Transformation Factor Analysis (MCTTFA) – and arsenic species. Still, the potential arsenic biomethylation by lichens and its actual relevance on biomonitoring grounds are discussed by comparing lichen-speciation data with corresponding data from aerosols, collected at the same time and in the same geographical areas.