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Background

Antimony is increasingly being used in the semiconductor industry in the production of diodes, infrared detectors, and Hall-effect devices. As an alloy, this semi-metal greatly increases lead's hardness and mechanical strength.

The most important use of antimony metal is as a hardener in lead for storage batteries. Antimony compounds in the form of oxides, sulfides, sodium antimonate, and antimony trichloride are used in the making of flame-proofing compounds, ceramic enamels, glass, paints, and pottery. Antimony trioxide is the most important of the antimony compounds and is primarily used in flame-retardant formulations. These flame-retardant applications include such markets as children's clothing, toys, aircraft and automobile seat covers.

Antimony and many of its compounds are toxic. Clinically, antimony poisoning is very similar to arsenic poisoning. In small doses, antimony causes headache, dizziness and depression. In larger doses cause violent and frequent vomiting, and will lead to death in fewer days.

Sample preparation

The freeze dried samples (approx. 200 mg) are digested with a high pressure microwave system (MLS ultraCLAVE II) with nitric acid (5 ml) and filled up to 20 ml. For the **antimony** and **arsenic** measurements 2.5 ml of that digestion solution are mixed with 5 ml of pre-reduction solution. The pre-reduction solution contains one part KJ / ascorbic acid and one part HCl (30%) (1:1 - v:v; daily fresh). The KJ / ascorbic acid mixture is prepared from 5 g KJ and 5 g ascorbic acid which is solved in 100 ml H₂O (UHQ). The chemicals always have the highest degree of purity. After a reaction time (2 h) 2.5 ml H₂O (UHQ) are added to the sample. Quantifications are made via an external calibration, the calibration standards are prepared for each element by the same way.

ICP-MS System

Agilent ICP-MS 7500i with Hydride-System

RF-Power 700 W (Shield Torch); Carrier Gas 1,0 L/min
Make-Up Gas 0,1 L/min; Isotopes ¹²¹Sb, ⁷⁵As
Reduction solution 0,5 % NaBH₄ / 0,1 % NaOH

Spruce Needles

Sampling area	Year	Concentration	
		Sb ng/g	As ng/g
Warndt	2002	111	69
	2003	66	74
	2004	70	82
Scheuern	2000	32	25
	2002	59	29
	2004	81	46
Obereres Steinbachtal	2002	99	71
	2003	134	79
	2004	94	60
Bayerischer Wald	2003	72	58
	2004	71	57
	2004	61	67
Hochharz	2004	40	58
	2004	16	22
Solling	2003	80	52

Selected Results (As data as comparison)

Poplar Leaves

Sampling area	Year	Concentration	
		Sb ng/g	As ng/g
Halle	2002	23	95
	2003	56	186
Saartal	2002	42	175
	2003	107	344
Leipzig	1995	129	310
	1999	132	176
	2000	164	137
	2003	107	373

All analyses
n = 6

All analyses
LOQ Sb 1 ng/g
LOQ As 3 ng/g

Beech Leaves

Sampling area	Year	Concentration	
		Sb ng/g	As ng/g
Pfälzer Wald	2001	57	32
	2003	29	32
Bayerischer Wald	2001	38	18
	2002	22	13
	2003	39	40
Hochharz	2001	42	23
	2002	17	9
	2003	35	38
Solling	1999	87	32
	2001	50	27
	2003	64	43
Bornhöved	2001	43	30
	2003	38	54

Discussion

The present investigation shows that the element Sb also can be quantified as a routine ESB element as As by the same routine chemical conditions. The hydride / ICP-MS method has a large detection sensitivity and is interference free. The concentrations of Sb & As in spruce needles and beech leaves are always in the same range.

In poplar leaves, the concentration of As is higher than the concentration of Sb. Poplar leaves from Leipzig (Düben Heath) contain more Sb than As, compared with poplar leaves from Halle (also Düben Heath) or Saartal (Saarland conurbation). The time series shows no trend. Differences between individual sampling areas are evidently. In industrially influenced regions higher concentrations are obvious than in rural ecosystems. In the marine species bladder wrack, there is a hundredfold higher As concentration than in trees. The concentration of Sb in bladder wrack reaches the same scale as the trees. During the last years, the concentrations decreased.

Latest Result

Sb in bladder wrack (*Fucus vesiculosus*)

Sampling area	Year	Concentration	
		Sb ng/g	As ng/g
North Sea Eckwarderhörne	1999	240	4000
	2000	65	3108
	2001	52	3313
North Sea Königshafen	1999	210	5430
	2000	78	5743
Baltic Sea Varnkevitz	1999	460	2260
	2000	80	2878

Research Program

The German Environmental Specimen Bank (ESB) is an important tool for the long-term monitoring of pollutants in representative ecosystems. Within this program for example in terrestrial ecosystems spruce needles (*Picea abies*), beech leaves (*Fagus sylvatica*) and Lombardy poplar (*Populus nigra* 'Italica') are sampled at different locations in Germany. The specimens are archived and analyzed for environmental relevant substances. The German ESB is coordinated by the German Federal Environmental Agency and financed by the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety.

More information is provided at www.umweltprobenbank.de (English language pages available).

Spruce (*Picea abies*)

The spruce is widespread in Central Europe. Its suitability as a specimen type for the ESB is founded on its economic and ecological significance and the considerable understanding of its patterns of accumulation in relation to many hazardous substances. The target organ is the one-year-old shoot which, when sampled in spring (February to late May before sprouting begins), presents a comprehensive picture of winter pollution in the environment.

Beech (*Fagus sylvatica*)

The common, or European, beech plays a dominant role in most nearly natural and also anthropogenically influenced forest ecosystems in Central Europe. Unlike the coniferous spruce, it prefers lower altitudes. The leaves are the target organ. Sampling takes place in the late summer before the leaves begin to change colour (August to mid-September).

Lombardy Poplar (*Populus nigra* 'Italica')

The Lombardy poplar was chosen as a deciduous tree typical of ecosystems close to dense urban settlements. The leaves are the target organ. Sampling takes place in the late summer before the leaves begin to change colour (August to mid-September).

The sampling of biota within the ESB program is performed by the Institute of Biogeography of the University of Trier.