



PS7.5 — TU

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TRACE ELEMENTS IN FOOD: EFFECTS OF DIGESTIVE ENZYMES ON SOLUBILITY

Treatment of food with digestive enzymes can have a marked effect on the solubility of trace elements such as Cu, Zn, Fe, Pb and Cd. In some cases the change in solubility indicates enzymic release of the trace element from a previously insoluble form but in other cases solubility decreases. This may indicate enzymic breakdown of a soluble complex to release the element in a «free» state which then forms an insoluble species; alternatively it may indicate the enzymic release of a chelating agent which forms an insoluble complex with a trace element which was previously in a soluble form.

A range of foods (bread, crab, beef, liver, green vegetables) have been examined and show these effects in varying degrees which reflect compositional (and processing) differences between the foods. Changes which occur when foods are enzyme-digested together, rather than separately, can be attributed to analogous processes.

The possibility of extending this information through chromatographic separation of the soluble species has been explored in studies of the cadmium species in canned crab; these indicate release of enzymes of a Cd species with an apparent molecular weight around 500 dalton. Further extension of the work through interfacing chromatography with an ICP-MS (VG «plasmaquad») is in progress.



PS7.6 — TH

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ANALYTICAL DETERMINATION OF METALS IN BIOLOGICAL AND ENVIRONMENTAL SAMPLES

For the determination of trace elements in various samples there are a lot of analytical methods which are described in the literature. The application of the optimal method depends on different properties of the sample:

- 1) element to be determined
- 2) concentration range of this element
- 3) composition of the sample (matrix, interference)
- 4) amount of the sample
- 5) phase in which the sample is available.

Instrumental neutron activation analysis and X-ray fluorescence analysis are the preferable methods for solid samples, whereas atomic absorption spectrometry, atomic emission spectrometry with an inductive-coupled plasma and electrochemical methods have to be applied to liquid samples.

Obviously solid samples can be transferred into the liquid phase by dissolution or by digestion and trace elements in liquid samples can be concentrated in a solid phase by evaporation of the solvent or by separation at an ion exchanger or adsorbents.

For an optimal analysis first the right method has to be chosen and examples are summarized in the following part.

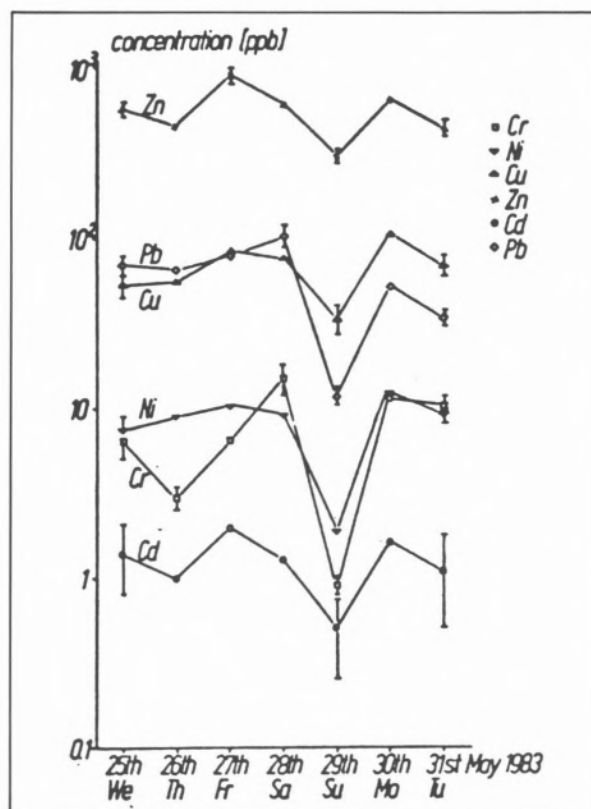
The water of the river Rhine has been analyzed by instrumental neutron activation analysis and by atomic absorption spectrometry because the con-

tent of toxic trace elements is very low. In consideration of the fact that such a natural water is a heterogeneous system the solid suspended matter had to be separated by filtration or centrifugation and the results are given in the Table.

Table

Element	Suspended matter $\mu\text{g/l(ppb)}$	Water without suspended matter $\mu\text{g/l(ppb)}$
Ag	6.3	0.014
As	14.7	0.70
Au	0.20	0.007
Ba	478	38.6
Br	18.4	117
Ca	65380	61030
Ce	55.7	0.33
Co	13.5	0.36
Cr	222	1.94
Cs	26.8	0.40
Eu	1.18	0.001
Fe	31727	295
Hg	0.55	1.36
K	30427	2820
La	28.5	0.26
Na	2820	46158
Rb	165	5.9
Sb	2.6	0.36
Sc	10.3	0.01
Se	1.1	0.19
Ta	0.8	0.001
U	3.7	0.80
Zn	612	22.2

Waste water has a much higher concentration of toxic elements and can therefore be analyzed by atomic emission spectrometry. The course of the elements Cr, Ni, Cu, Zn, Cd and Pb in a mainly industrial waste water in a calendar week is given in the Figure. For this case a digestion procedure had to be performed using HNO_3 and H_2O_2 to get the trace elements in solution.



The solid suspended matter of waste water, soil, dust and sludge samples and plants have been analyzed using the X-ray fluorescence with X-ray tube or radionuclide excitation and energy-dispersive detection. For those cases standard materials had to be built up with matrices which are similar to the samples.

Rain water samples with only a few ppb of Cu, Zn, Se, Cd and Pb were analyzed using electrochemical methods.

The speciation of trace elements in liquid samples has been performed using ion exchangers, adsorbents, polarography and voltammetry, whereas solid samples have been examined by extraction, by powder diffractometry and by electron microscopy with microprobe.



PS7.7 — TH

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AMAVADINE, AN OXOVANADIUM(IV) COMPLEX OF *N*-HYDROXY-IMINO- α,α' - -DIPROPIONIC ACID

Although the presence of vanadium in vegetal ashes has been referred to for the first time more than one century ago, it wasn't until 1931 that TER MEULEN reported a definite determination of the contents of this element in a plant, namely in the toadstool *Amanita muscaria* [1].

Results obtained since then have shown that *Amanita muscaria* is indeed unusual in these respects, concentrating comparatively high amounts of vanadium, up to 120 ppm dry weight.

More recently it has been reported that high vanadium content is not restricted to *Amanita muscaria* and that other *Amanita* species also contain

this metal, e.g. *Amanita regalis* (169 ppm) and, particularly, *Amanita velatipes* (397 ppm), an american variety of *Amanita pantherina* [2]. Still, the ability to concentrate vanadium seems to be a unique property of just a few probably primitive species of the genus *Amanita*.

In 1972, BAYER and KNEIFEL isolated a vanadium containing compound from a german variety of *Amanita muscaria* (Black Forest and Schonbuch) which they named "Amavadine" [3]. About 40 mg of the compound were obtained per kg of the fresh mushrooms by an elaborated procedure which included extraction with methanol of a thawed mixture of frozen mushrooms, followed by isolation through a series of chromatographic processes using cellulose, sephadex and cation exchange resins.

Table 1 summarizes the properties of Amavadine, as reported by Bayer and Kneifel.

Following hydrolysis by 6N HCl, which gives mainly alanine, or by 1N NaOH, which affords sodium pyruvate and acetaldehyde as well as alanine, and after reduction by zinc and acetic acid which yields α,α' -iminodipropionic acid, a first model of amavadine as a 2:1 complex of this last ligand was assumed. Additional information came from EPR spectroscopic detection of a nitroxyl radical on oxidation of amavadine in alkaline media. Finally, a dimethylester $C_8H_{15}NO_5$ was isolated after methanolysis of amavadine in methanol/ H_2SO_4 ; this was identified as dimethyl *N*-hydroxy-imino- α,α' -dipropionate and the corresponding acid was postulated as the natural ligand in the complex [4].

The structure proposed by these authors for amavadine, taking into account the various data obtained, is represented below, as (I):

Table 1
Some properties of Amavadine

Colour	pale blue
Melting point	no melting point; colour disappears at 170°C, turns to yellow at 185°C and to brown at 220°C
UV, vis. spectra	bands at 775 nm ($\epsilon=19.3$), 715 nm ($\epsilon=18.9$), 565 nm ($\epsilon=23.5$), 270 nm (sh., $\epsilon=6800$), 235 nm (sh., $\epsilon=12300$), 218 nm (sh., $\epsilon=12600$)
IR	strong CO band at 1600-1650 cm^{-1} and a V=O band at 985 cm^{-1}
EPR	indicative of VO^{2+}
M.W. (osmometry)	415
Composition (analysis)	$C_{12}H_{22}N_2VO_{12}$ (with two free acid groups)