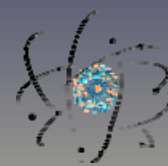


HOW EFFECTS ON NANO LEVEL CAN ENHANCE ANALYSIS OF METAL IONS TRACES IN WATER BY MEANS OF LOW TEMPERATURE SECONDARY ION MASS SPECTROMETRY



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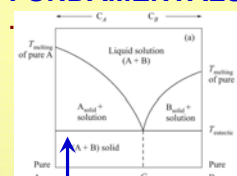
Mass Spectrometry, being both an experimental technique and a branch of natural science, has a reciprocal relation with NanoScience: while nanotechnologies contribute to the enhancement of equipment, the mass spectrometric methods permit studying of various phenomena at the nano-level. In desorption/ionization mass spectrometric techniques ionizing agents, whose aim is to produce molecular ions, in fact affects an area of nano-size dimensions. We utilize this property, together with data accumulated by us in Low Temperature (LT) mass spectrometry investigations of water, to propose a simplified method of identification of metal ions in water. The urgency of the environmental task of analysis of water pollutions, including metal contaminants in natural water, does not need any additional justification.

Precondition: the existence of reliable methods of metal ions analysis does not ban the search for new more perfect solutions. In particular, the **bottleneck** of all methods of pollutants analysis in natural waters is the **necessity of concentrating of large volumes of liquid** and application of auxiliary substances.

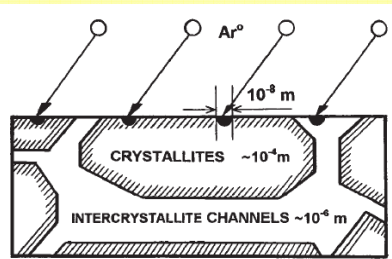
AIM: to propose a method of water sample handling for analysis by Secondary Ion Mass Spectrometry (SIMS) based on dilute water solutions behavior at micro- and nano- levels under cryogenic conditions.

IDEA: to utilize natural phenomenon of phase separation of water solutions on freezing for concentrating the solutes.

FUNDAMENTALS:



Ice crystals and solutes expelled to intercrystalline channels are formed



Estimates show that heterogeneous frozen solids are composed of pure ice crystallites of average size of 10^{-4} m separated by intercrystalline (eutectic) channels of 10^{-6} m width filled by the solutes. (the left wing of the phase diagram) Given that an impact of a single bombarding primary ion under SIMS conditions excites a zone of about 10 nm in diameter, the efficiency of sputtering of the concentrated solutes from the eutectic channels is practically the same as from the macroscopic solute samples [1, 2].

SAMPLE HANDLING: a drop of water of about $5 \mu\text{L}$ is frozen on the sample holder in the vapours of liquid nitrogen for SIMS analysis.

ADVANTAGES: micro liters of sample liquids are required (in contrast to liters); no additional chemicals and time-consuming procedures are required.

[1] Kosevich M. V. Low temperature secondary emission mass spectrometry. Cryobiological applications // Europ Mass Spectrom.-1998.-4.-P. 252-264.

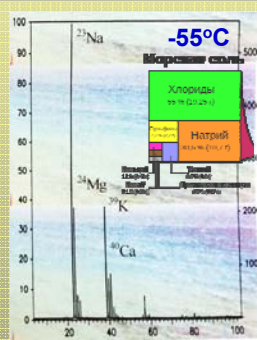
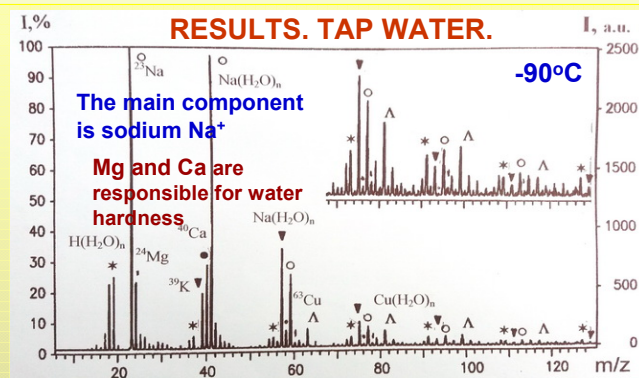
[2] Kosevich M.V., Boryak O.A., Shelkovsky V.S. Low-temperature secondary emission mass spectrometric investigations of a condensed-phase environment of biologically significant compounds // Low Temperature Physics.-2021-47.-P. 335-346.

METHODS. The original data are obtained by Secondary Ion Mass Spectrometry (SIMS) and Fast Atom Bombardment (FAB) realized at MI1201E magnetic sector instrument.

It is proposed to implement the developed method at modern SIMS-TOF (time-of-flight) instruments with rapid spectra recording.

SIMS/FAB is extremely sensitive to METAL IONS, since they are present in the sample as "preformed" ions, i.e. do not need ionization step.

LT SIMS mass spectra of frozen water (with low content of solutes) are composed of a set of water clusters sputtered from ice crystals and ions of solutes concentrated in the intercrystalline channels.



RESULTS. SEA WATER.

The recorded composition of metal ions agrees with the known data.

Experimental Details. The LT SIMS mass spectra can be obtained in the mode of spontaneous thawing of the frozen water sample. The temperature range for reliable recording of the informative mass spectra is -110°C to -50°C . (Ice samples sublime rapidly as the temperature reaches -50°C).

CONCLUSIONS. The results obtained demonstrate the efficiency of the proposed LT SIMS method for analysis of traces of metal ions in natural waters.