

**Note on intercalibration
of trace metals in a marine
suspension carried out
by the Co-ordination Centre
of the COMECON Countries
at the Institute of Oceanology
of the Soviet Academy of Sciences**

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Improvement and unification of analytical methods have recently become one of the most crucial problems in marine chemistry. Therefore, numerous international organizations co-ordinate and inspire this type of research in their research projects.

In 1986, the Co-ordination Centre of the COMECON Countries at the P. P. Shirshov Institute of Oceanology of the Soviet Academy of Sciences initiated, within the project 3.1 *Development, unification and intercalibration of methods of sampling and chemical analysis of marine and interstitial waters, deposits and suspensions*, a research connected with intercalibration of trace metals in oceanic suspension. Dr. V. V. Gordeev from the Institute of Oceanology of the Soviet Academy of Sciences was in charge of sampling and sending the samples. Water for investigations was drawn on 19th of November, 1986, from the surface of the Carribean Sea at the point with co-ordinates $\lambda = 69^{\circ}08.4' W$ and $\varphi = 17^{\circ}18.2' N$ during the 12th cruise of r/v "Akademik Mstislav Keldysh". A 160 dm³ sample of water drawn using a special pump was transferred to two clean polyethylene barrels. The water was occasionally stirred. In order to obtain samples of suspension, 5 dm³ of water was filtered through a "Dubna" membrane filter 47 mm in diameter and having a 0.45 μm pore diameter. Thirty two samples of suspension were obtained altogether. Mean concentration of the suspension on 28 filters was equal to 106 $\mu g/dm^3$, the individual values ranging from 52 to 214 $\mu g/dm^3$. Mass of the suspension on two filters was much larger (352 and 707 $\mu g/dm^3$), while on other two filters it was equal to zero.

Filters with suspension, as well as clean ones, were sent to 7 laboratories in the COMECON countries. The results were sent back by four scientific institutes, *viz* Institut für Meereskunde of the Academy of Sciences of GDR, Institute of Oceanology of the Bulgarian AS, Institute of Oceanology of the Soviet AS and Institute of Oceanography of the Gdańsk University. The results sent by the Bulgarians are not considered in the discussion because lack of data on the blank determination and because the results of blank determination were not taken into

account in the results of determination of metal concentrations. The discussion of the results of intercalibration took place in the Institute of Oceanology of the Soviet AS in Moscow between 7th and 9th of June, 1988.

The largest number of analyses were performed in the Institut für Meereskunde. The following elements were determined in the samples: Cu, Cd, Pb, Zn, Fe, Mn, Ni, Al, Ca, and Mg. The Institute of Oceanography of the Gdańsk University sent the results of determination of the first six elements, while the Institute of Oceanology of the Soviet AS—of Cu, Pb, Fe, Mn, Cr, and Al. The German laboratory determined additionally the labile and bound forms of the elements. Each institute performed determinations of copper, lead, iron and manganese. A uniform procedure of mineralization of the filters was not recommended in the investigations. Utilization of various methods of mineralization of filters and of various chemical reagents resulted in a considerable scatter of the blank determination values. It happened that the same laboratory obtained the results of blank determination differing by an order of magnitude. The results of concentration of metals in the samples of suspension were also diverse. Each of the elements mentioned above was determined in 15 samples. Concentration ranges, arithmetic means \pm standard deviations had the following values: **Cu**: 13.1–125 ng/dm³ and 50 ± 43 ng/dm³, **Pb**: 12–623 ng/dm³ and 121 ± 178 ng/dm³, **Fe**: 894–3566 ng/dm³ and 1575 ± 834 ng/dm³, **Mn**: 1.5–114 ng/dm³ and 42 ± 29 ng/dm³. The least satisfactory results were obtained in the case of lead. During recent years, this element has become omnipresent. It is present in large amounts in the air, while only few laboratories determining trace metals are equipped with suitable air filters and air-locks and use high purity reagents.

It should be additionally taken into account that part of the errors results from the differences in mass of suspension on filters, ranging from 260 to 780 μ g (mean: 485 ± 165 μ g). Such differences might be due to poor homogeneity of water, as well as non-uniformity of pore diameters.

It has been confirmed during the meeting that contamination of the samples constitutes a limiting parameter during the analysis of trace metals. The following factors were recorded as major sources of systematic errors inherent to the analysis of trace metals in a marine environment:

- (i) the method of sampling and storage of samples (majority of available hydrographic bottles contaminate samples which causes poor repeatability of the results),
- (ii) separation of suspensions from water (various kinds of filters, contamination during contact with laboratory equipment),
- (iii) contamination through a contact with polluted air, reagents, laboratory glass-ware (sorption and desorption on their surface),
- (iv) matrix effects resulting in an additional signal during the measurement (interference due to background and accompanying components),
- (v) calibration errors resulting from application of imperfect standards.