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ON THE DETERMINATION OF CADMIUM, COPPER, LEAD AND ZINC IN MARINE PARTICULATE MATTER BY ELECTROTHERMAL ATOMIZATION

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Abstract

The effects of mineral and biological components of the particulate matter as well as that of inorganic acids used for digestion of the particulate matter on the ashing and atomization in the graphite furnace have been studied. Interferences from biological material, inorganic acids and material of membrane filters during the determination of trace metals by flameless AAS technique have also been discussed.

1. INTRODUCTION

In the sea, trace metals occur in solution and bound to suspended matter. Their proportion in each phase depends on the inflow from the land, the hydrological conditions, and their biological activity in the marine environment. The determination of trace metals dissolved in sea water is rather difficult, mainly because of the low concentrations of the metals, of the order of 0.001 to 10 $\mu\text{g}\cdot\text{l}^{-1}$. This fact imposes particular requirements as regards the sampling and storage of sea water, the detection limits and the sensitivity of the analytical methods used.

The concentrations of trace metals dissolved in the sea generally alter very little in space and time. Concentration changes depending on the sampling area and the season have been found in marine suspensions from the Baltic. The differences of metal content in suspensions of Southern Baltic and of polar regions (Table 1) show that suspensions could be better indicator of trace metal pollution in the sea than dissolved forms.

The concentrations of trace metals in suspensions are of the order of several to several thousands $\mu\text{g}\cdot\text{g}^{-1}$ of dry matter (Table 1), which means that they can be determined by flameless atomic absorption spectrometry with sufficient sensitivity and precision. There are, however, still many problems with the method, which are due to the complex and variable composition of the particulate matter.

In the current literature more and more papers can be found which recommend the digestion of biological and geological material with a mixture of nitric and sulphuric acids [1, 3, 6-8], and with hydrofluoric acid [5]. In these papers it was assumed that the suspended matter comprises only mineral compounds, and geological reference materials were used as standards.

Table 1. Trace metal concentration ($\mu\text{g}\cdot\text{g}^{-1}$ of dry weight) in marine particulate matter of the Southern Baltic and Admiralty Bay

Particulate matter	Region	Cd	Cu	Pb	Zn	Ref.
- separated from sea water on membrane filters	Southern Baltic	2 - 30	50 - 6700	10 - 600	40 - 4000	[2]
	Admiralty Bay (Atlantic Section) of the Antarctic Sea	1.7 - 10	43 - 193	14 - 105	121 - 1010	[4]
- sampled on sediment collectors	Southern Baltic	2 - 10	52 - 300	48 - 601	36 - 168	[2]

This paper presents the interferences in the determination of cadmium, copper, lead and zinc in marine suspensions by graphite furnace electrothermal atomization. To this end, the effect of mineral and organic compounds on the conditions of ashing and atomization of metals in a graphite furnace was studied. The yields from the digestion of samples with various acids were considered as well as the effects of the membrane filter materials on the determination results.

2. MATERIALS AND METHODS

Marine particulate matter was obtained in two ways. The first method involved passing sea water through membrane filters of pore size $0.4\ \mu\text{m}$ and 45 mm diameter. Nuclepore (Shandon N° 040) filters made of polycarbonate foil and Sartorius 11606 cellulose nitrate filters were used. The mass of suspended matter obtained in this way varied from 0.3 to 6 mg. In the second method, samples of suspended matter were accumulated using sedimentation collectors which were placed on the sea bottom for periods from 30 to 60 days. The object of this was to collect a large sample (several grams) for comparative hydrochemical and analytical investigations.

As a participant in the research programme on sedimentation processes in the Gdańsk Basin, the author had at her disposal data on the mineral composition of the suspended matter and the organic carbon content [2]. The mineral composition of the suspended matter was established using a Philips 410 X-ray diffractometer. The lines for quartz, halite, illite, kaolinite, calcite and chlorite were mostly found. The organic carbon content was determined on a Perkin-Elmer CHN analyzer. This was in the range from 4 to 7.6%, i.e. 12 to 24% of the organic matter content.

Illite, kaolinite, calcium carbonate, sodium chloride and fish meal were used for the preparation of artificial suspensions. The minerals were obtained from Polish Geological Survey. Lyophilized fish meal from the North Sea fish was prepared by the organizers of 5th ICES Intercalibration Exercise and contained low amounts of trace metals. The concentrations of cadmium, copper, lead and zinc in minerals were near the detection limits. Biological reference materials were obtained from the National Bureau of Standards (USA). All reagents and inorganic standards were manufactured by MERCK. The total weight of mixed samples used in the experiments was 100 mg, the content of mineral or biological components varied from 0 to 50%.

The materials were mechanically mixed in a agate mortar. The samples were completely digested in the 10 cm³ mixture of concentrated nitric, sulphuric and hydrofluoric acid (1 : 1 : 1). The digestions were carried out in home-made closed teflon vessels (Polish PTFE) at a temperature of about 120°C and at pressure of approx. 0.2 MPa (2 atm) for 5 hours. After cooling the volume was adjusted up to 25 cm³ by distilled deionized water.

The effects of nitric, sulphuric and hydrofluoric acids, taken in different concentrations and proportions, on mineralizations yields of suspensions from collectors were compared.

All the measurements were done on a Beckman 1272 atomic absorption spectrophotometer equipped with a Massmann cuvette and a deuterium lamp background corrector. Ashing and atomization temperature were measured by a thermocouple placed in the furnace. The volumes of injection were 5 µl for zinc and 20 µl for other trace metal measurements.

3. RESULTS AND DISCUSSION

In order to establish optimal conditions for the determination of cadmium, copper, lead and zinc in a graphite furnace the relationships between the ashing and atomization temperatures of metals and the content of illite, kaolinite, calcium carbonate, sodium chloride and biological material (fish meal) added to the suspended matter from the collector were studied.

3.1. ASHING TEMPERATURE

It was found that the increased mineral content in the suspension involved the increase in the maximum ashing temperature for all studied metal compounds in the digested samples (Figs. 1, 2, 3). Most evident was the effect of illite, kaolinite and calcium carbonate on the ashing temperature of zinc compounds, which rises from 580 to 750°C. Calcium carbonate also increased the ashing temperature of lead compounds from 500 to 650°C, i.e. by more than other minerals. In the remaining cases the increase in the ashing temperature was no greater than 100°C.

Unlike minerals, inorganic acids reduced the ashing temperatures of zinc and lead in digested artificial suspensions. The ashing temperature of zinc decreased with the concentration of nitric acid from 550 to 400°C (Fig. 4). Hydrofluoric acid also lowered the maximum ashing temperature taken for zinc and lead. The reason for this may be the more effective mineralization of zinc and lead compounds, which accelerates the ashing process.

Additions of sodium chloride and biological material such as fish meal, bovine liver and plant material did not brought about any significant change in the maximum ashing temperatures of the metals under study in the digested samples.

When considering the ashing temperatures of trace metal compounds in biological material and in pure minerals (Table 2), it can be seen that they are on average 100 -

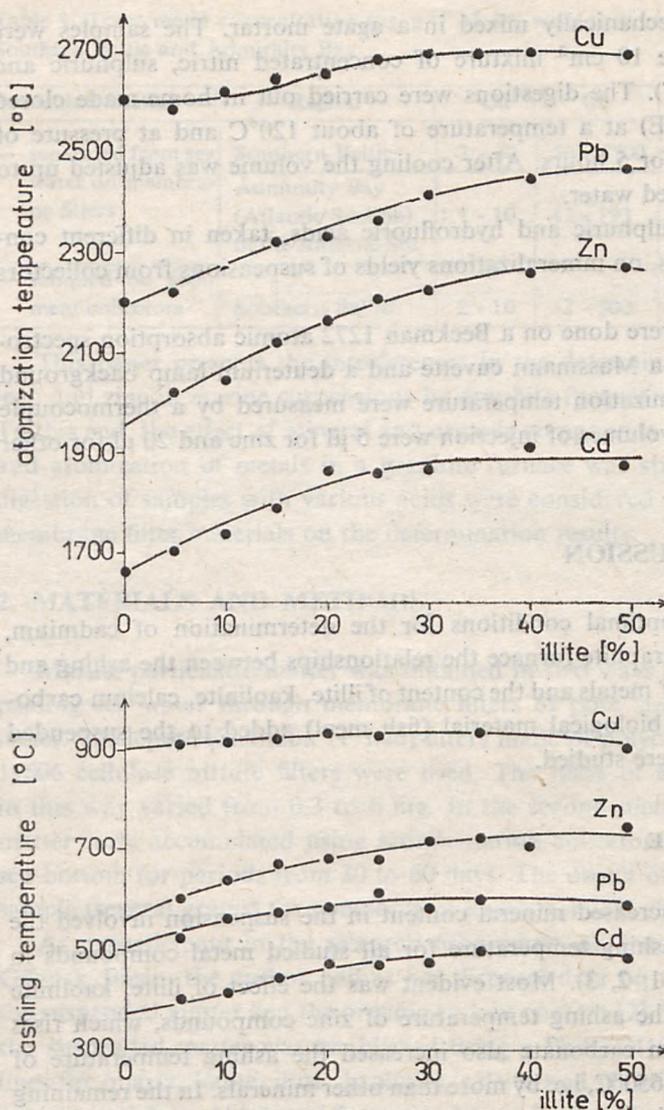


Fig. 1. The effect of illite on the ashing and atomization temperature of trace metals in marine particulate matter from collector.

- 150°C higher in mineral than in organic compounds. In comparison with other biological substances, a slight increase in the ashing temperature of cadmium and zinc was found only for bovine liver.

3.2. ATOMIZATION TEMPERATURE

The influence of mineral compounds in suspended matter on the atomization of trace metals is more obvious than in the case of ashing processes. The presence of mineral compounds causes the minimum atomization temperature of all the metals to rise (Figs. 1, 2, 3). An increase in illite content raised the atomization temperature

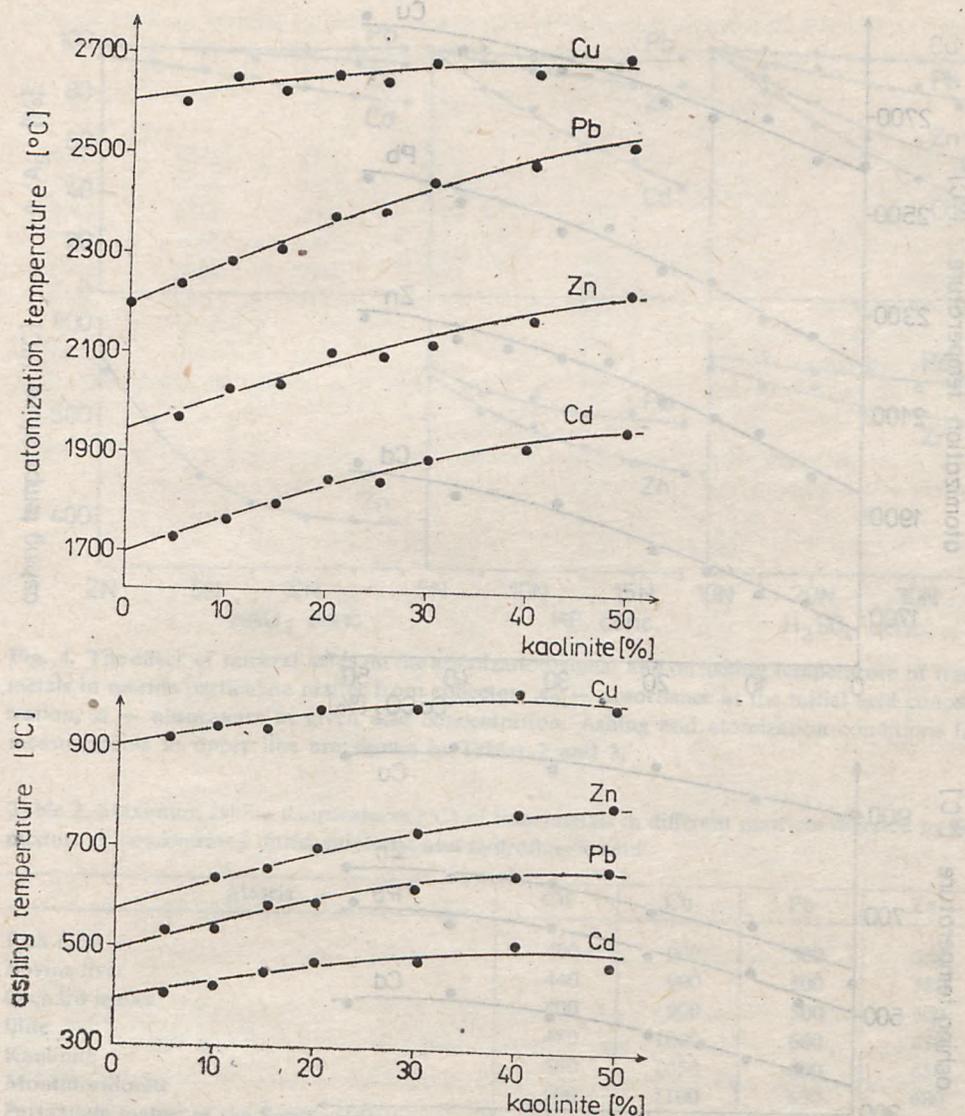


Fig. 2. The effect of kaolinite on ashing and atomization temperature of trace metals in marine particulate matter from collector.

of cadmium from 1700 to 1900°C, of lead from 2200 to 2500°C and of zinc from 1900 to 2350°C (Fig. 1). If the kaolinite content increased, the atomization temperature of cadmium and lead rose only slightly (by about 50°C) in comparison with what happens when illite is present. Kaolinite raised the atomization temperature of zinc somewhat less than illite did (Fig. 2). For calcium carbonate, an increase in the atomization temperature of only lead was found, which was greater here than after the addition of the remaining minerals.

The addition of mineral and biological compounds did not significantly alter the atomization temperature of copper in digested artificial suspensions.

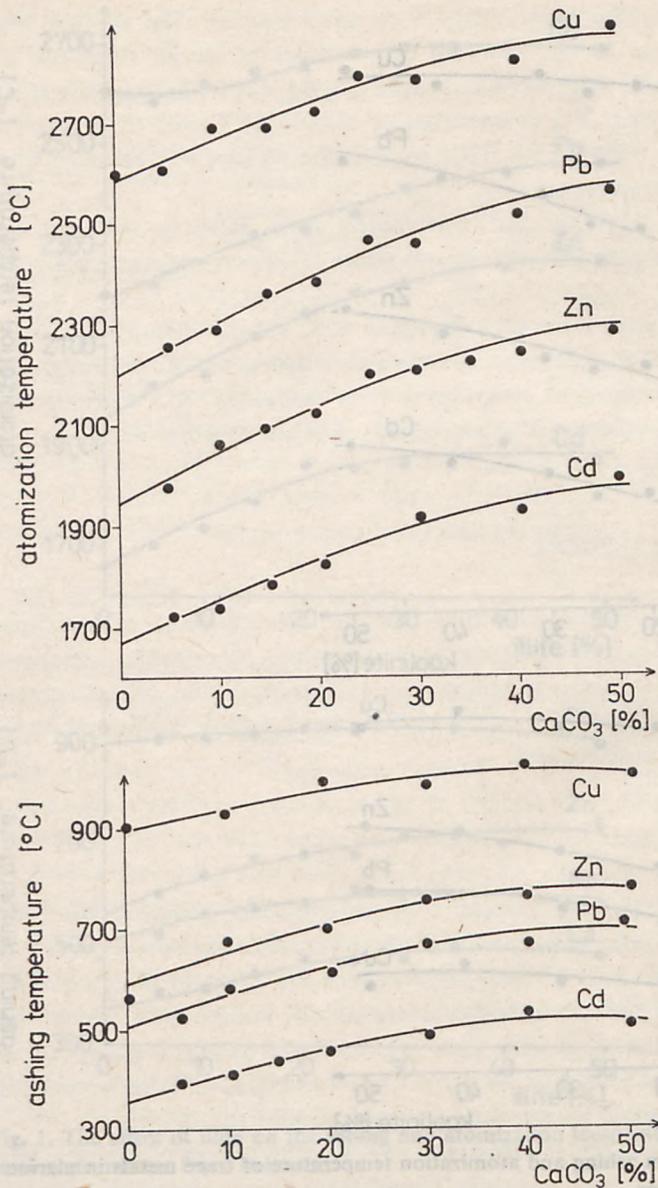


Fig. 3. The effect of calcium carbonate on ashing and atomization temperature of trace metals in marine particulate matter from collector.

When considering the atomization temperatures of metals in mineral and biological compounds, it was found that the atomization temperatures in minerals are on average 100 - 150°C higher than in biological material (Table 3). As was the case for ashing temperatures, atomization temperatures of metals are also slightly higher in bovine liver than in tested fish meal and plant tissues.

Sodium chloride and inorganic acids did not significantly affect the atomization temperatures of any of the metals.

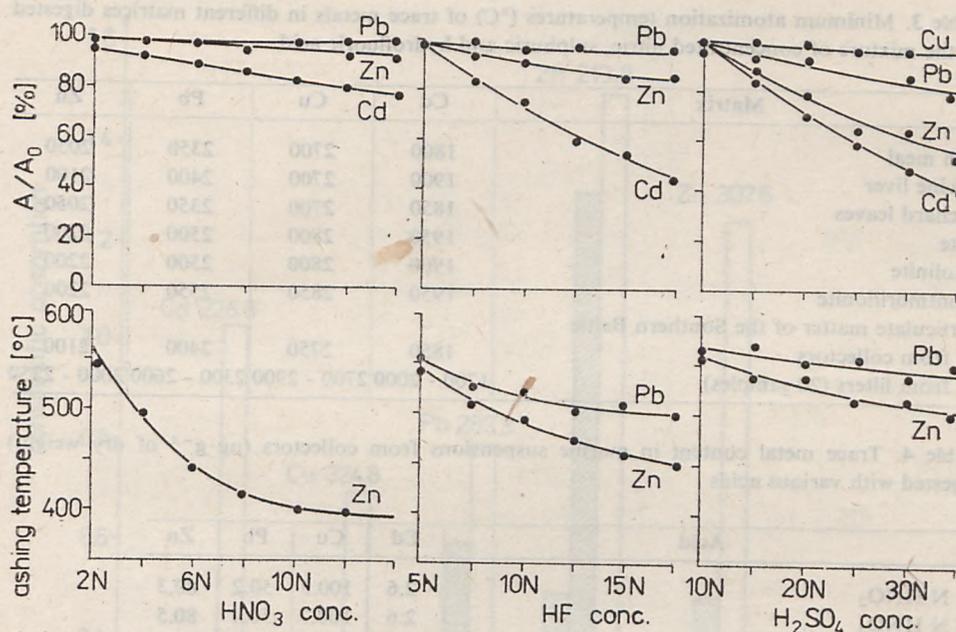


Fig. 4. The effect of mineral acids on the atomization signal and on ashing temperature of trace metals in marine particulate matter from collector: A_0 – absorbance at the initial acid concentration, A – absorbance at given acid concentration. Ashing and atomization conditions for measurements in upper line are shown in Tables 2 and 3.

Table 2. Maximum ashing temperatures (°C) of trace metals in different matrices digested by the mixture of concentrated nitric, sulphuric and hydrofluoric acid

Matrix	Cd	Cu	Pb	Zn
Fish meal	400	900	500	550
Bovine liver	440	900	500	580
Orchard leaves	400	900	500	500
Illite	480	1000	600	650
Kaolinite	480	1050	600	650
Montmorillonite	500	1100	650	680
Particulate matter of the Southern Baltic				
– from collectors	450	1000	600	550
– from filters (20 samples)	350 - 500	900 - 1100	500 - 650	550 - 700

3.3. THE EFFECT OF ACIDS

In this study, 100 mg samples of suspended matter from collectors were mineralized using different concentrations of nitric, hydrofluoric and sulphuric acids, and also mixtures of them (Fig. 5, Table 4). The volumes of acids and their mixtures were kept up to 10 cm³. The samples were digested in closed teflon vessels at a temperature of about 120°C and at pressure of approx. 0.2 MPa (2 atm) for 3 hours. Every analysis was ten times repeated.

Table 3. Minimum atomization temperatures ($^{\circ}\text{C}$) of trace metals in different matrices digested by the mixture of concentrated nitric, sulphuric and hydrofluoric acid

Matrix	Cd	Cu	Pb	Zn
Fish meal	1800	2700	2350	2050
Bovine liver	1900	2700	2400	2100
Orchard leaves	1850	2700	2350	2050
Illite	1950	2800	2500	2200
Kaolinite	1900	2800	2500	2200
Montmorillonite	1950	2850	2550	2200
Particulate matter of the Southern Baltic				
– from collectors	1850	2750	2400	2100
– from filters (20 samples)	1700 - 2000	2700 - 2900	2300 - 2600	2000 - 2250

Table 4. Trace metal content in marine suspensions from collectors ($\mu\text{g}\cdot\text{g}^{-1}$ of dry weight) digested with various acids

Acid	Cd	Cu	Pb	Zn
5 N HNO_3	2.6	100.5	50.2	80.3
10 N HNO_3	2.6	100.7	50.4	80.5
Conc. HNO_3	2.7	110.0	48.2	76.2
5 N HF	1.9	100.2	47.2	75.2
10 N HF	1.8	100.3	47.3	75.3
5 N HNO_3 + 5 N HF	2.4	100.2	48.2	79.8
1 : 1				
5 N HNO_3 + 10 N H_2SO_4	1.7	96.2	45.2	72.4
1 : 1				
5 N HNO_3 + 20 N H_2SO_4	1.6	94.3	44.3	62.2
1 : 1				
5 N HNO_3 + 5 N HF + 10 N H_2SO_4	2.2	99.2	49.2	78.8
1 : 1 : 1				

Concentrated nitric acid and diluted hydrofluoric acid reduced evidently the absorbance of cadmium, and zinc, whereas sulphuric acid reduced the absorbance of cadmium, lead and zinc. A mixture of these acids (Table 4) produced effects comparable to those obtained with 5 N and 10 N nitric acid.

If we consider the non-specific absorption of pure acids (Fig. 5), it can be seen that for sulphuric acid and hydrofluoric acid it is quite large, e.g. for zinc at the wavelength of 213.8 nm it is of the order of one absorbance unit. Such absorbances can not be always compensated by deuterium background corrector.

Using Student's test significant differences were found between the mineralization yields with the mixtures of nitric and sulphuric acid and with concentrated or diluted nitric and hydrofluoric acid. No significant difference was found between the results obtained after complete digestion with the use of hydrofluoric acid and those after partial dissolution of samples by nitric acid. The reason of this may be the lower sensitivity of trace metals in hydrofluoric acid than in oxidizing nitric acid, probably caused by the loss of metal fluorides during ashing process.

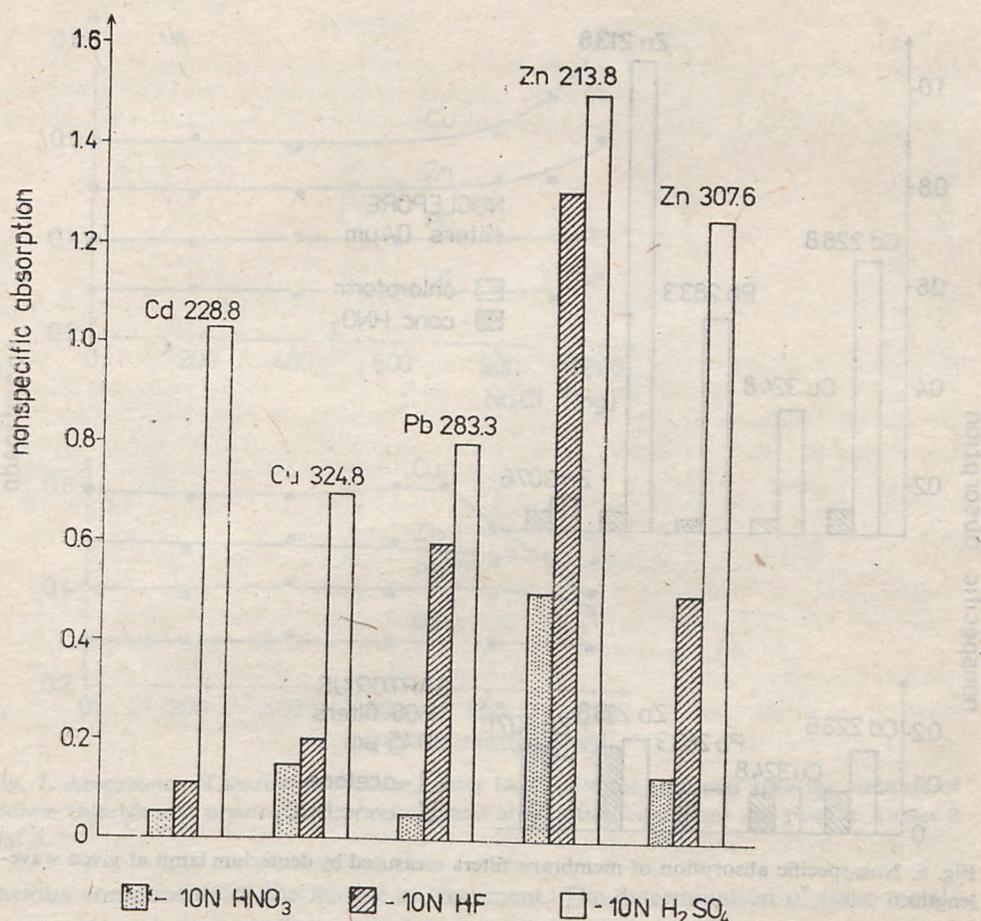


Fig. 5. Non-specific absorption of inorganic acids measured by deuterium lamp at given wavelengths.

3.4. THE EFFECT OF FILTER MATERIAL

At present, the most suitable filters for the determination of trace metals in suspended matter are considered to be polycarbonate filters of the Nuclepore type because of their low metal content and regular pore distribution. Weigel and Kremling [9] suggest dissolving the filters and suspended matter in chloroform and determining the metals against aqueous inorganic standards. These filters dissolved in chloroform do have, however, a very large non-specific absorption (Fig. 6). Treatment of the suspended matter with nitric acid which do not dissolve the filter in this case eliminates the interference effects caused by the filter.

Cellulose nitrate filters have also been found useful in the determination of trace metals in suspended matter. From time to time, however, higher concentrations of metals may be found in them than in Nuclepore filters, so their use for trace metal determinations in suspensions can be limited when dealing with suspended matter poor in metals.

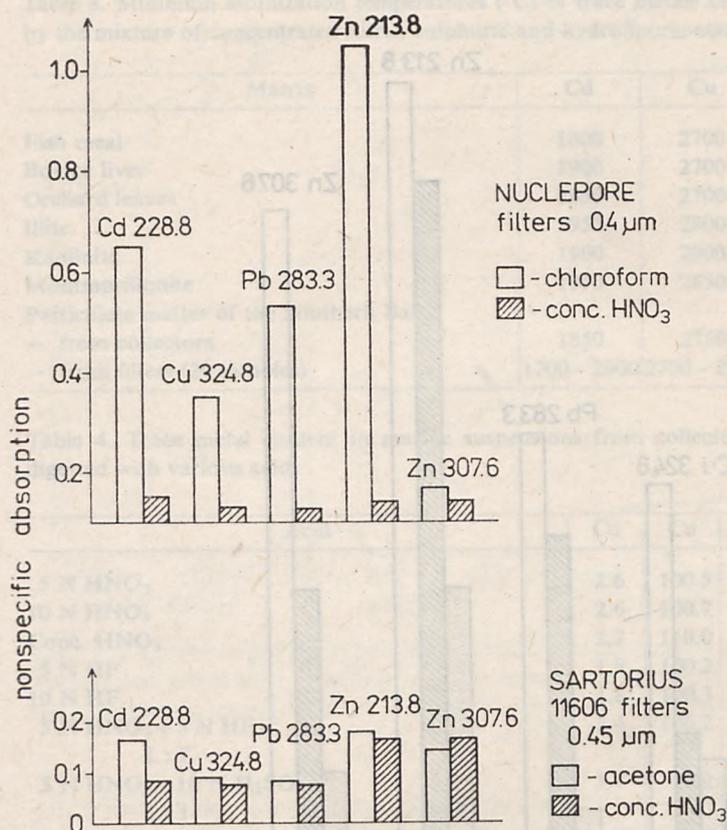


Fig. 6. Non-specific absorption of membrane filters measured by deuterium lamp at given wavelengths.

3.5. THE EFFECT OF SODIUM CHLORIDE AND ORGANIC COMPOUNDS

The addition of sodium chloride has practically no effect on the results of determinations of metals in suspended matter. Its presence in larger quantities may just increase the absorbance of copper (Fig. 7). In order to test the effect of organic compounds, lyophilized North Sea fish containing trace amounts of cadmium, copper, lead and zinc was added to the suspended matter from the collector. Additions of biological organic compounds to suspension samples of mass 100 mg reduced only the absorbance of copper, and that of zinc to a small extent (Fig. 7). This was reflected in the background magnitudes for these metals, shown by samples of fish meal and bovine liver (Fig. 8). These magnitudes several times exceed the specific absorbance measured for the metals.

4. CONCLUSIONS

The ever greater interest in the problem of trace metals in the marine environment and the increasing number of monitoring studies in large areas of water necessitate the use of simple, rapid and precise methods for determining trace metals in

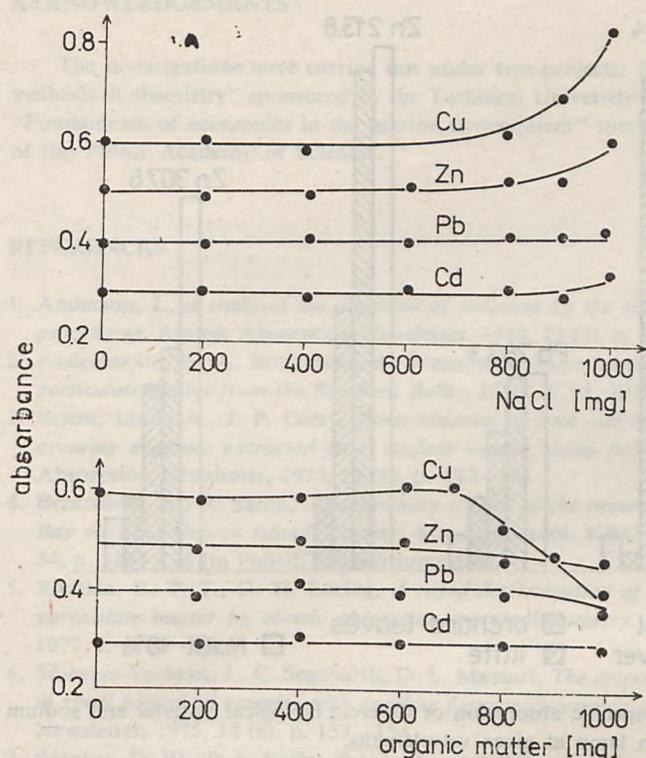


Fig. 7. Absorbance of marine particulate matter from collector (100 mg) after the addition of sodium chloride and organic matter. Ashing and atomization conditions are given in Tables 2 and 3.

various components of the marine environment. The determination of trace metals in sea water, bottom sediments and in organisms has so far been a separate and difficult analytical problem. The analytical chemist undertaking the task of determining trace metals in marine suspended matter must also be well versed in marine chemistry, hydrological conditions and changes in biological activity in the given area of water. This helps to predict approximately the composition of the suspended matter and the range of metal concentrations. For example, it is known that in the warm season in surface waters there occur suspensions made up of almost 100% organic matter containing high concentrations of metals. For such material, bovine liver enriched with metals is a good standard and there is no special need to use the method of standard additions. At other times of the year and in other water layers the composition of the suspended matter may vary. So, before setting out to determine metals in a series of suspensions under test, the organic matter and carbonate content of the suspended matter should be approximately determined. These determinations are very simple, and the results permit us to prepare standards of suspended matter consisting of biological and geological material taken in the proportions occurring in the suspensions.

The variability of the composition of suspended matter requires the use of a widely

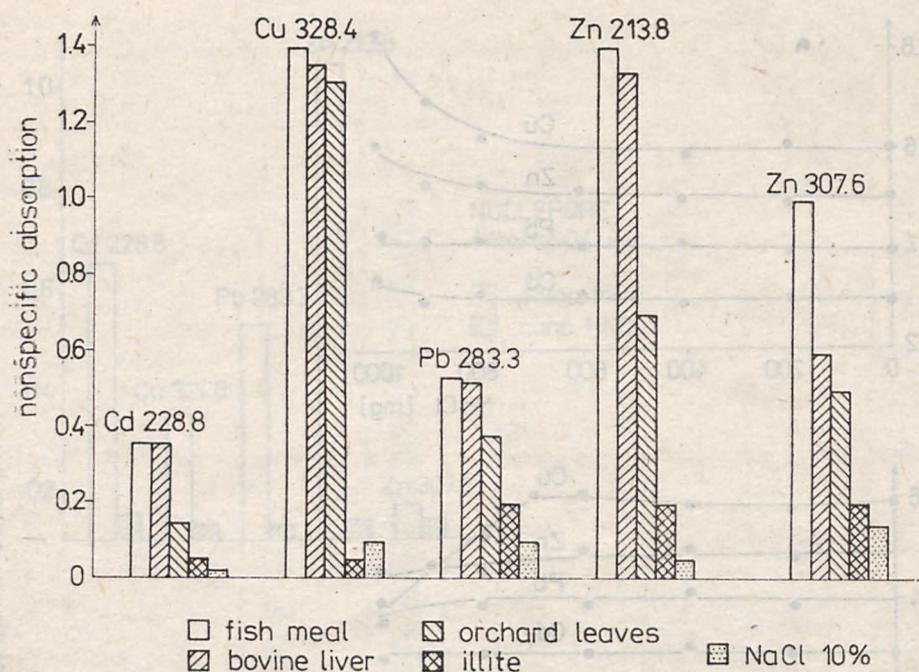


Fig. 8. The comparison of non-specific absorption of different biological material and sodium chloride measured by deuterium lamp at given wavelengths.

applicable method of sample mineralisation. In this study it was found that to estimate the pollution of the sea by particulate cadmium, copper, lead and zinc it was sufficient to extract the suspensions twice with 5 cm³ of 5 N nitric acid in closed teflon vessels at a pressure of 0.2 MPa (2 atm) in a pressure-cooker for 3 hours. The heating time can be shortened by initially decomposing the suspended matter at room temperature for some hours. In fact, only metals accumulated in organisms and carbonates and part of metals build in aluminosilicates are determined by this method. However, the fraction contained in silica and aluminosilicates is of greater importance in geochemical investigations and in many cases can be omitted from the point of view of marine environmental protection. The determination of zinc should be carried out at the 307.6 nm wavelength rather than at the more usual 213.8 nm resonance line. In this way, both interference effects and the need to dilute the samples are avoided.

As far as determinations of metals in suspensions are concerned, polycarbonate and cellulose nitrate filters can be used. Nuclepore filters are recommended for their more quantitative separation of suspended matter from sea water. The filters should not be dissolved in chloroform.

Since the suspended matter in the sea is strongly involved in the trophic web, the problem of the accurate determination of toxic trace metals in this material will continue to be of importance.

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