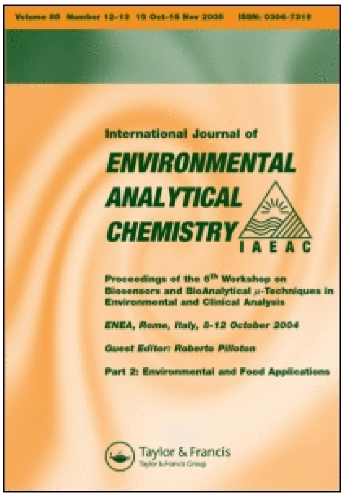

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Characterization of Individual Estuarine and Marine Particles by LAMMA and EPXMA

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Laser microprobe mass analysis (LAMMA) was applied to particulate matter from the Atlantic Ocean. Inferring information about the surface layer by LAMMA was not probe X-ray microanalysis (EPXMA). Geochemically relevant groups of particles had been identified by EPXMA and cluster analysis. For both locations, the most abundant ones appeared to be those rich in silicon and the alumino-silicates. Afterwards LAMMA was applied to obtain more information about the trace element composition and surface characteristics. The iron-rich phase appeared to contain significant amounts of heavy metals and of phosphate. Lead appeared to be associated in detectable amounts with alumino-silicates in the Scheldt but not with those in the Atlantic Ocean. Inferring information about the surface layer by LAMMA was not always unambiguous.

KEY WORDS: LAMMA, EPXMA, water, suspension, marine, estuarine.

INTRODUCTION

Hitherto, most research on the chemical and mineralogical composition of suspended particulate matter in the aquatic environment was done on bulk samples or on separate size fractions. However, in order to understand more about the way these particulates participate in certain physical and chemical reactions, it could be interesting to know more about the properties of individual particles.

Using energy-dispersive electron probe X-ray microanalysis (EPXMA) and laser microprobe mass analysis (LAMMA), suspension particles from the Scheldt estuary (Belgium) and from the North

Atlantic Ocean were analysed on a particle by particle basis. In comparison to the Scheldt, which receives high amounts of municipal and industrial waste waters, the Atlantic Ocean can be considered as unpolluted.

With the aid of EPXMA and an automated image analysis system, suspension particles from both areas were sized and analysed. Multivariate analysis techniques provided for the Scheldt and for the Atlantic Ocean 13 and 8 geochemically relevant particle types, respectively. The power of this procedure has already been proven unambiguously.[1] In the case of the Scheldt, the relative abundances of these types were followed from low to high tide.

LAMMA was applied to a number of representative particles from the different particle types in order to elaborate trace element contents and surface layer composition.

The major purpose of this work was to evaluate the potential and usefulness of LAMMA in research on particles from the aquatic environment, in combination with, and as a complement of EXPMA.

EXPERIMENTAL

Instrumentation

EPXMA measurements were performed with a JEOL JXA-733 Superprobe. The instrument consists of an electron microscope, equipped with energy-dispersive and wavelength-dispersive X-ray spectrometers. It was used at an electron energy of 25 keV and a beam current of 1 nA. The microprobe is automated with the Tracor Northern TN 2000 system, and is controlled by a LSI 11/23 microcomputer. In the automatic image analysis (AIA) system, the electron beam is moved across the area to be analysed. A particle is detected when the backscattered electron signal exceeds a preset threshold value. The particle is then sized, and an X-ray spectrum is accumulated. After this, the beam moves on until it locates another particle, etc. In this way, 300 particles were measured for every sample. The large data set thus obtained, needs to be interpreted using numerical multivariate analysis methods. The followed procedure consists of hierarchical cluster analysis on all measured particles of each individual sample, and then of nearest centroid sorting over all samples for which abundance variations of particle types have to be known. Detailed information about this classification scheme and about the AIA system can be found in the literature.[1]

In the LAMMA-500 instrument, a selected sample is vaporized and ionized by a single high-power pulse ($\tau = 15\,\text{ns}$) of a Q-switched frequency quadrupled Nd:YAG laser ($\lambda = 265\,\text{nm}$; power density of 10^7–10^{11} W/cm^2 for a laser spot of about 1 μm diameter). The laser intensity can be attenuated to 1% of its initial value by means of a 25-step UV-absorbing filter system. The laser-generated ions are accelerated and collimated into the drift tube of a TOF mass spectrometer. Output signals are stored in a 100 MHz transient recorder with 2K memory (Biomation 8100). The instrument is interfaced to a Digital MINC computer, which is part of a laboratory automation network, based on a VAX-VMS computer. Since ions are extracted at 180° relative to the incident laser beam, the sample usually consists of thin specimens (e.g. particles on a thin supporting film). A detailed description of the LAMMA-500 instrument (Leybold-Heraeus, Köln, West Germany) is given in the literature.[2]

Sampling sites

Scheldt suspended matter samples were collected in February 1986 just upstream of the city of Antwerp over a period of 6 hours from low to high tide; with the salinity ranging from 0.24 up to 0.43‰ The Atlantic Ocean sample was taken during a cruise of the Belgian oceanographic vessel "Belgica" in May 1986 at a location south of Cornwall, U.K., 49° 20′ N–5° 40′ W.

Sample preparation

Targets for EPXMA analysis are prepared by filtering an aliquot of water, its size depending on the suspension load, over a 0.4 μm pore-size Nuclepore filter. This filter has to contain a sufficient loading for efficient analysis, while maintaining a low percentage of overlapping particles. It is washed, dried, and finally coated with a carbon layer.

As mentioned earlier, the LAMMA-500 instrument necessitates samples, thin enough to be perforated by the laser; hence, the particles have to be mounted on a TEM grid, coated with a thin

Formvar supporting foil. For this purpose, an aliquot of water is filtered over a 0.4 μm Nuclepore filter. After being rinsed, the filter is transferred to a test tube containing ca. 1 ml twice deionized water, and the particles are resuspended by ultrasonic agitation. Finally, a drop of the eventual suspension is brought onto a Formvar-coated grid. After evaporation of the water, the sample is ready for analysis.

RESULTS AND DISCUSSION

EPXMA-results

The results of the automated EPXMA are given in Tables 1 and 2. Table 1 shows the average composition of the different particle types (in % of the total X-ray signal) in the Atlantic Ocean sample and the Scheldt estuary sample set; Table 2 lists the relative abundance of each particle type in every individual sample of the salinity profile in the Scheldt estuary.

The alumino-silicates and Si-rich groups represent the major fraction of the inorganic particulates. In the Atlantic Ocean, their added relative abundance is 84%; while in the Scheldt estuary more significant contributions of Ca-, Al- and Fe- and S-rich particles are found. Manually performed EPXMA analysis revealed that for the Atlantic Ocean, a large fraction of the suspended particulates is organic in composition. The group no. 13 in Table 1 most probably results from crystallization of dissolved salts on the filter, and, in this way, is not representative for the suspended load of the samples.

Followed from low (Table 2, sample no. 1) to high (Table 2, sample no. 7) tide, the relative abundances of the various particle types do not show very striking variations, but also the sampling station lies about 100 km away from the mouth of the Scheldt.

LAMMA-results

LAMMA was then applied to a number of representative particles from various particle types; it was expected that complementary trace element information and surface characteristics would be obtained. The latter can be achieved using the laser desorption mode, i.e. focusing a laser beam of low intensity onto the particle so that it is not visibly damaged by the laser shot, and only the surface

Table 1 Abundance and composition of the individual particle types for the Atlantic Ocean sample and for the Scheldt estuary sample set

	Particle type number	*% abundance of the group*	*Composition, expressed as percent contribution to the total X-ray signal*										*Average diameter in (μm)*
			Mg	*Al*	*Si*	*P*	*S*	*Cl*	*K*	*Ca*	*Ti*	*Fe*	
A	1	21	0	27	69	0	1	0	9	1	0	0	1
T	2	29	0	25	57	0	0	2	4	0	0	12	2
L	3	8	0	17	44	0	3	0	0	1	0	34	2
A	4	26	0	0	97	0	0	0	0	0	1	2	1
N	5	8	0	0	11	0	0	0	0	0	4	78	0.8
T	6	6	2	1	5	0	0	0	0	91	0	1	2
I	7	1	0	74	0	13	6	14	0	0	0	0	1
C	8	1	0	0	0	0	86	14	0	0	0	0	1
	1	19	0	1	97	0	0	0	0	0	0	1	2
	2	34	0	28	63	0	0	0.1	5	1	0	7	2.5
	3	12	0	10	59	0	0	0	3	1	0	26	2
S	4	12	1	0	2	1	0	0	0	96	0	1	2
C	5	2	0	5	27	4	1	0	1	51	1	9	4
H	6	6	0	99	0	0	0	0	0	0	0	0	1.1
E	7	4	0	0	4	0	1	0	0	7	0.1	88	1.4
L	8	5	0	1	4	0	60	0	0	0	0	35	1
D	9	3	1	5	24	9	1	0	0	8	0	51	2
T	10	1	0	0	4	64	0	0	0	1	2	29	1
	11	1	0	0	1	0	0	0	0	0	98	2	1
	12	0.7	0	2	25	0	4	0	0	2	52	15	0.8
	13	0.2	0	0	1	0	0	79	17	0	0	0	2.5

Table 2 Relative abundance variations for the particle types in the seven Scheldt estuary samples

Particle type number	*Percent abundance of the particle types*						
	no. 1	*no. 2*	*no. 3*	*no. 4*	*no. 5*	*no. 6*	*no. 7*
1	14	19	17	14	21	18	30
2	30	33	27	45	38	24	42
3	11	13	14	14	12	9	9
4	8	13	17	9	13	22	6
5	1.8	4	1.8	2	3	2.0	1.2
6	24	0.7	14	3	0	0.3	0
7	1.4	3	3	4	3	7	1.2
8	3	4	0.7	3	5	11	5
9	3	7	0.7	3	3	4	2
10	1.4	0.4	4	0	0	0	0
11	0.7	1.1	1.1	0.4	1.4	3	3
12	0.7	1.1	0	0.8	1.0	0.7	0.6
13	0.4	0.7	0	0	0	0	0

layer is evaporated for analysis. This was shown by several authors for various model systems, e.g. NaCl particles with a nitrate coating[3,4] and phthalates, coated on asbestos fibres.[5] On the other hand, high laser intensities, resulting in a complete destruction of the target, will yield information on the "bulk composition" of a particle. For each particle type, the identification of most peaks was established by comparison with spectra of pure compounds (e.g. SiO_2, $CaCO_3$, Fe_2O_3, $FePO_4.2H_2O$, $Ca_3(PO_4)_2$). For several elements, the typical isotope pattern provides an unambiguous interpretation of their mass peaks.

For the Scheldt, the following groups were further investigated: the Si-rich group (no. 1), the alumino-silicates (nos. 2, 3, 5 and 9), the Ca-rich group (no. 4), the Fe-rich group (no. 7) and the Fe- and P-rich group (no. 10). For the Atlantic Ocean only the most abundant ones, namely the alumino-silicates (nos. 1, 2, 3) and the Si-rich group (no. 4) were further studied.

Silicon-rich particles

For both the Scheldt and the Atlantic Ocean, the Si-rich group (quartz, opal, diatom skeletons) makes up a significant part of the total inorganic suspended load. When laser shots at high intensities, resulting in a complete evaporation were aimed at these particles, Si^+ and the typical polyatomic $Si_mO_n^+$ clusters,[6] as well as mass peaks of Ca^+, Al^+, Fe^+ and sometimes Mn^+ and Ti^+ appeared in the positive spectra (see e.g. Figure 1a). In the desorption mode, Al^+, Ca^+ and, less frequently, Fe^+ were detected (Figure 1b). This is compatible with the existence of a coating on these particles, but does not provide unambiguous evidence since e.g. preferential vaporization and migration of species within the sample can cause the results to be non-representative for the surface layer. In the negative mode spectra, the phosphate/silicate-ratio decreased as the intensity of the laser shots increased and this might indicate phosphate-adsorption.

Alumino-silicate particles

In the positive mode desorption spectra, we always detected Na^+, Mg^+, Al^+, K^+, Ca^+ and occasionally also Fe^+. The negative ones were dominated by phosphate peaks (PO_2^- and PO_3^-), probably indicative for a phosphate-rich surface layer.

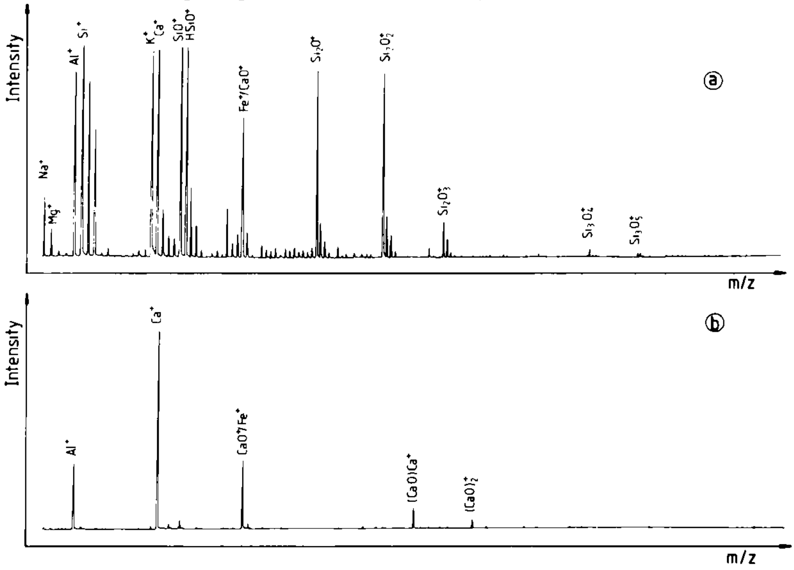

Figure 1 Positive mode LAMMA-spectra of a silicon-rich particle from the Scheldt estuary recorded (a) at high laser intensity, (b) in the desorption mode.

At high laser intensities, the relative intensity of the phosphate mass peaks decreased while Si-O and Si-Al-O clusters appeared. In the positive mode spectra, the Si^+-ion appeared, most of the time accompanied by Mn^+ and Fe^+. Sporadically, some trace elements were also detected, Ba and Pb being the most frequently appearing ones. This does not necessarily imply that Pb and Ba have the greatest bulk concentrations; it can merely be due to the fact that LAMMA is particularly sensititve for these elements.[7] Comparing Scheldt and Atlantic Ocean particles of these groups revealed strikingly that the Atlantic Ocean alumino-silicates do not contain detectable amounts of Pb, while the ones from the Scheldt do. Ba, on the other hand, seems to be associated with both of them (Figure 2a and b).

According to the literature, the adsorption of heavy metals onto clay minerals is relatively insignificant. Their greatest effect on the behaviour of trace metals seems to be in their ability to act as nucleation centres for e.g. hydrous iron oxides and organics. The latter compounds do show strong affinities for trace elements.[8,9]

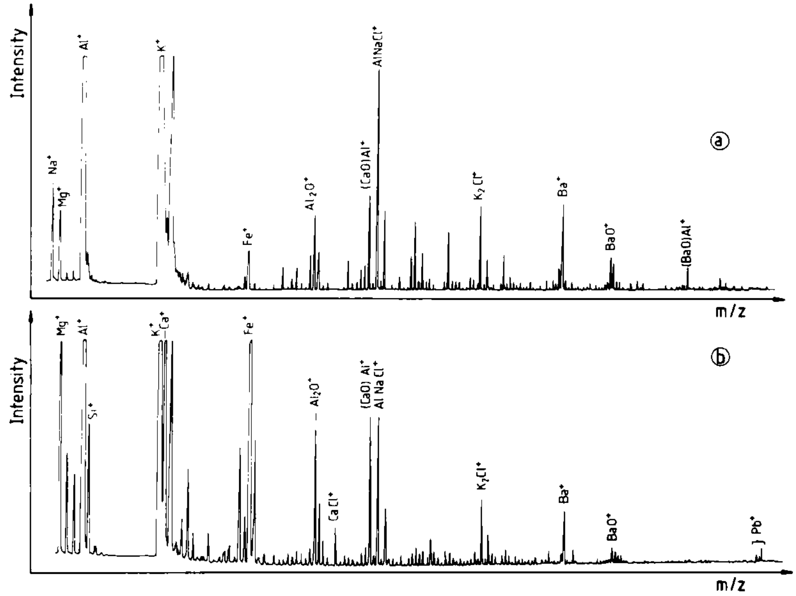

Figure 2 Positive mode LAMMA-spectra of alumino-silicate particles recorded at high laser intensities (a) from the Atlantic Ocean, (b) from the Scheldt estuary.

Calcium-rich particles

The particles of this group contain predominantly Ca as X-ray detectable element; hence they most probably consist of $CaCO_3$. The positive spectra were dominated by the typical $(CaCO)_n{}^+$, $(CaO)_nH^+$ and $(CaO)_nCa^+$ mass peaks[10] but they were always more complex than a pure $CaCO_3$ fingerprint. In most cases these spectra clearly revealed the presence of Mg and Sr (Figure 3a). Sometimes, they even showed Ca-Mg/Sr-O cluster ion peaks. These results were more or less expected since calcite is known to accomodate Mg and Sr in its structure. Moreover, the Sr content of carbonates can be used to trace the origin of the carbonate fraction.[11] A positive ion mass peak at $m/q = 55$ was frequently detected. Compared to the peak of ^{44}Ca, the relative intensity of the one at $m/q = 55$ was always higher in the laser desorption mode (Figure 3b). This could indicate the existence of a Mn-coating around these particles.[12]

In the negative LAMMA-spectra (both desorption and high intensity), mass peaks at $m/q = 63$ and 79 ($PO_2{}^-$ and $PO_3{}^-$) demonstrated an association of phosphate with the $CaCO_3$ particles. This

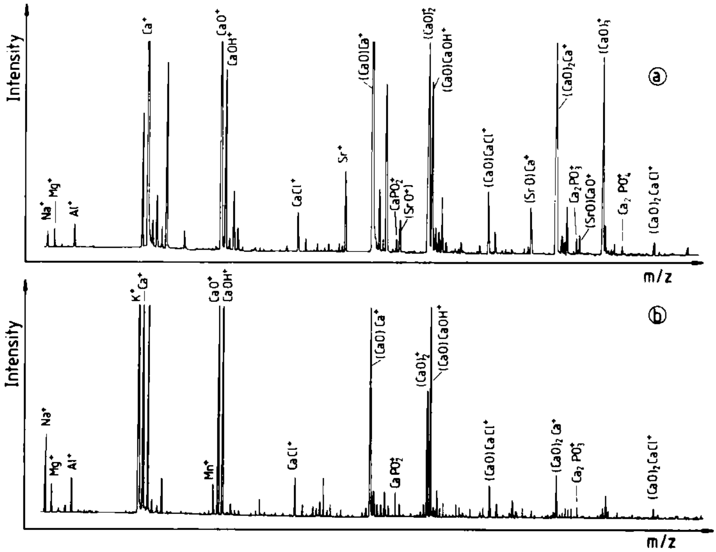

Figure 3 Positive mode LAMMA-spectra of a calcium-rich particle recorded (a) at high laser intensity, (b) in the desorption mode.

association is also proved by the frequent appearance of Ca-P-O cluster ion peaks ($CaPO_2^+$, $Ca_2PO_3^+$, $Ca_2PO_4^+$) in the positive spectra (Figure 3a). In his review article about the surface chemistry of calcium carbonate minerals in natural waters, Morse[13] stated that adsorption of orthophosphate and Mn possibly can lead to new surface phases; respectively apatite and rhodochrosite. The Ca-P-O clusters we found, however, do not provide direct evidence for such a phase; they might just as well have been formed in the laser-induced microplasma. When carbonates occur as a major component, coprecipitation with carbonates is believed to be an important mechanism to limit the concentrations of certain trace elements (e.g. Zn, Cd).[9] Still, no minor or trace elements other than Mn and Sr, appeared clearly in the spectra.

Iron-rich particles

As the EPXMA results in Table 1 show, part of the total particulate iron is associated with the iron-rich alumino-silicates. We also find Fe-rich particles (group no. 7), Fe- and S-rich particles (group no. 8) and, to a lesser extent, Fe- and P-rich particles (group no. 10).

The positive LAMMA-spectra of these Fe- and P-rich particles were somewhat more complex than a pure $FePO_4$-fingerprint. Besides the typical Fe-O and Fe-P-O clusters, they showed a significant Mg and Ca association (Figure 4). These minor elements also appeared in phosphate clusters.

The particles which contain predominantly iron as X-ray detectable element (iron oxyhydroxides and/or carbonates) also showed

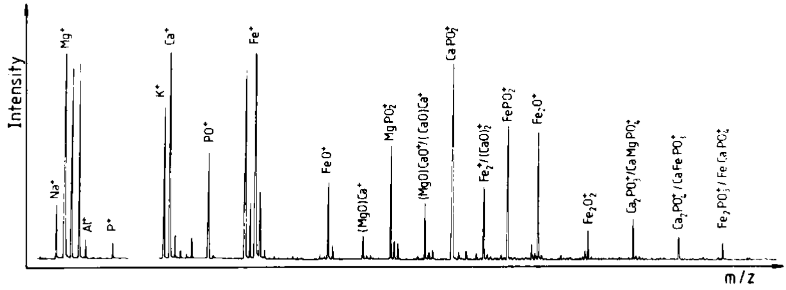

Figure 4 Positive mode LAMMA-spectrum of an iron- and phosphate-rich particle, recorded at high laser intensity.

a considerable phosphate association. This is proved by both the negative and the positive mode spectra (PO_2^-, PO_3^-, PO^+) (Figure 5a and b). In comparison with the other groups, they also seem to contain considerable amounts of trace elements (e.g. Ba, Pb, Cr) (Figure 5b). This property, together with the fact that they participate in the redox cycle, allows them to exercise a significant influence upon the behaviour of trace metals in aquatic systems. The most frequently detected trace elements are Pb and Ba, both very sensitive elements for LAMMA.

CONCLUSION

Automated EPXMA followed by multivariate analysis methods gives, in a relatively short time, information about the major chemical composition of a large number of particles and identifies the geochemically relevant particle types. For the Scheldt estuary, abundance variations of these particle types as a function of time (from low to high tide) could be followed.

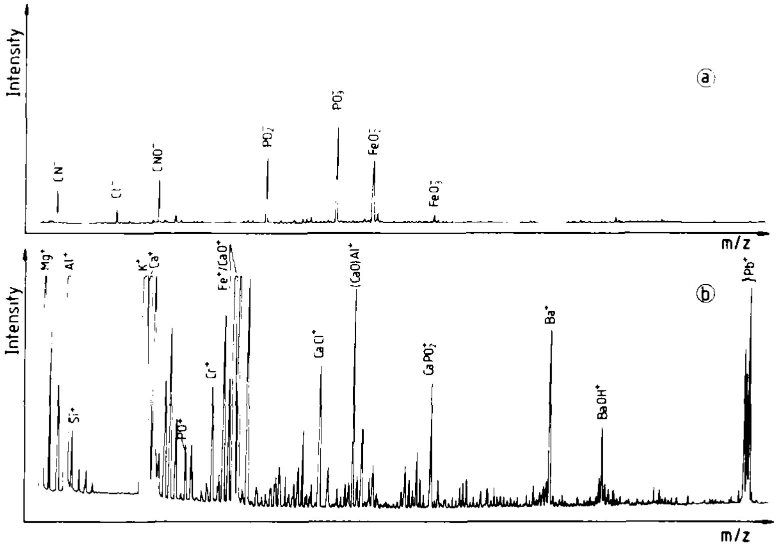

Figure 5 LAMMA-spectra of an iron-rich particle from the Scheldt estuary (a) in the negative mode, (b) in the positive mode, recorded at high laser intensity.

Using LAMMA, we obtained information that largely complemented the EPXMA-results.

In the first place, it was possible to get more knowledge about the trace element distribution over the various particle types. Of all the types investigated, the Fe-rich phase seemed to contain the highest relative amounts of trace elements (Cr, Ba, Pb). However, when interpreting spectra which yield information about trace constituents, one always has to keep in mind that elemental sensitivity varies from one element to another and that it can also be affected by the matrix composition.[14] It was found that the alumino-silicate particles from the Atlantic Ocean do not contain detectable amounts of Pb, while the ones from the Scheldt do. Ba was found to be associated with alumino-silicates of both samples. Inferring from the LAMMA-spectrum the composition of surface layers is not straightforward. The "laser desorption mode" provided spectra which supported, but could not prove, the existence of surface coatings. It is beyond doubt that the latter subject requires the use of model systems.

Acknowledgements

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