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STUDY OF INORGANIC AMMONIUM COMPOUNDS IN INDIVIDUAL MARINE AEROSOL PARTICLES BY LASER MICROPROBE MASS SPECTROMETRY

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SUMMARY

Ammonia is important in the atmosphere because it neutralizes acidic species. The relative importance of different inorganic ammonium compounds (chloride, nitrate and sulfate) in marine air chemistry was studied by single-particle characterization with the laser microprobe mass analyser. Standard aerosols were generated as a reference for compound identification, based on the fingerprint spectra obtained, and calculation of the relative sensitivity achieved for different ions in a marine aerosol matrix. The relative sensitivity for ammonium was low. Aerosol samples were collected in the Southern Bight of the North Sea under different meteorological conditions and examined for their ammonium compounds. Samples collected during an inversion period with continental influences showed a much higher content in all particles than samples collected under different meteorological conditions, where ammonium was mostly detected in the submicrometer particle-size range.

Ammonia plays an important role in the nitrogen cycle. Natural emission occurs from biological decomposition of nitrogenous organic matter, both in terrestrial and aquatic environments. Anthropogenic emission of ammonia is generated by activities like coal combustion in urban and industrial areas, and by extensive use of nitrogen-rich fertilisers in agricultural areas. Ammonia is removed from the atmosphere naturally by microbiological nitrogen fixation, by physical processes like wet and dry deposition, and by chemical processes like oxidation to nitrogen oxides and reaction with acidic particles. These reactions are related to the acid rain phenomenon, because ammonia is the major alkaline gas that can neutralize acidic species like sulfuric and nitric acids. In airborne particulate matter, ammonium is closely associated with sulfate in the submicrometer particle-size range.

Reported concentrations of ammonia and ammonium are higher in summer than in winter periods and higher at ground level than in upper levels of the atmosphere. In the marine environment, values are normally lower than in continental areas. In the atmosphere of the Southern Bight of the North Sea, higher levels of ammonia and ammonium must be associated with continental influences. More specifically, the Netherlands and the Flanders region of

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Belgium are responsible for high ammonia emissions due to local agricultural activities.

Laser microprobe mass spectrometry (LMMS), with its speciation capabilities at the single particle level, allows investigations of the relative importance of the different inorganic ammonium compounds in marine air chemistry and their role in the deposition of ammonia.

EXPERIMENTAL

Instrumentation

Single-particle analysis of aerosols was achieved with the LAMMA-500 instrument (Leybold-Heraeus, Cologne, F.R.G.). This instrument uses a pulsed laser for ionization purposes and a time-of-flight mass spectrometer for obtaining information on individual particles. A detailed description of the instrument and its capabilities has been given elsewhere [1].

Aerosols were collected with a single-orifice Battelle-type cascade impactor with five stages (cut-off diameters of 4, 2, 1, 0.5 and 0.25 μm aerodynamic diameter, respectively. Sampling rate was 1 l min^{-1} with a sampling time of 10 min. The impaction surfaces were equipped with Formvar-coated electron-microscope grids that fitted into the LAMMA-500 sample holder.

Standard aerosols

The analysis of ambient aerosols by LMMS was supported by results obtained from analysis of laboratory-generated standard aerosols. These standards were made by pneumatic nebulization of aqueous solutions and subsequent collection of the aerosol with an impactor [2]. For identification purposes, standards were prepared from ammonium chloride, nitrate and sulfate. These compounds are the most likely to be found in the marine environment.

In order to obtain quantitative results with the LAMMA-500 instrument, it is necessary to know the relative sensitivities for different ions in a marine aerosol matrix. Therefore mixed aerosol particles were made containing different $Na^+/K^+/NH_4^+$ ratios in a chloride matrix and in a mixed $Cl^-/NO_3^-/SO_4^{2-}$ matrix. A more general marine aerosol standard was made containing NH_4^+, Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+} and Fe^{3+} in a mixed $Cl^-/NO_3^-/SO_4^{2-}$ matrix.

Collection of marine aerosols, and sampling artifacts

Samples were taken on board the R/V Belgica in the Southern Bight of the North Sea on two separate occasions, from 21/8/1985 to 31/8/1985 and from 10/3/1986 to 14/3/1986. Meteorological maps from those periods show that during the first cruise, southwesterly wind dominated the atmosphere above the North Sea, including some continental influences from Great Britain. During the second cruise, the meteorological situation was quite different: the weak, variable wind came mainly from the eastern direction (Netherlands) and there was an inversion situation unfavourable for the dispersion of pollutants.

Sampling of aerosols with an impactor is subject to a number of different artifacts like incomplete collection of particles by different types of impaction surface, losses of particles by evaporation, and reaction of specific impaction surfaces with gaseous components [3]. Another possible artifact is the reaction between the collected particles and reactive gaseous components. It has been shown [2] that sodium chloride particles may react with gaseous nitric acid when sampled with a cascade impactor. The possibility of reaction between acidic particles and ammonia was further investigated. Such a reaction would amplify the atmospheric reaction between these components and lead to over-estimation of the relative importance of the particulate fraction of a certain component. To overcome these artifacts in routine monitoring, special sampling devices based on collection in a denuder tube have been developed [4].

A sulfuric acid aerosol was generated by pneumatic nebulization and collected with an impactor. In this case, no Formvar-coated grids were used because sulfuric acid destroyed the organic film completely. Instead, Mylar film was used to collect 1 μg of particles with 1-μm aerodynamic diameter. Subsequently, an air stream containing ammonia (0.06 m^3, 16 $\mu g\ m^{-3}$). generated by means of a standard permeation tube, was passed through the impactor. Inspection of the aerosol by visual microscopy clearly indicated the presence of crystalline ammonium sulfate. The same experiment was repeated by using the quartz vacuum seal of the LAMMA-500 sample holder as an impaction surface. The m/z = 18 peak (NH_4^+) was obvious in the mass spectra obtained confirming the reaction of sulfuric acid with gaseous ammonia. This artifact can be avoided by removing the reactive gaseous components during the sampling of aerosols. This is achieved by placing different denuders in front of the cascade impactor. For removing gaseous ammonia, an oxalic acid-coated denuder is used [5]. Impactors for sampling ambient aerosols were also equipped with sodium fluoride coated denuders for the removal of HCl and HNO_3 [4].

RESULTS AND DISCUSSION

General spectral patterns with the LAMMA-500

Spectra of the standard ammonium compounds are shown in Fig. 1. The three ammonium salts are stable in the vacuum conditions of the LAMMA-500 instrument. Cluster-ion formation is quite similar in the cases of ammonium chloride and nitrate. The following clusters were detected (X = Cl or NO_3): NH_4^+, $(NH_3)NH_4^+$ $(NH_3)_2NH_4^+$, $(NH_4X)NH_4^+$ and (NH_4X) $(NH_3)NH_4^+$ in the positive-ion mode and X^-, $(HX)X^-$ and $(HX)_2X^-$ in the negative-ion mode. The m/z = 46 (NO_2^-) to m/z = 62 (NO_3^-) ratio is <1 in the case of ammonium nitrate in contrast with other nitrate salts [6]. Spectra for ammonium sulfate in both modes provide no evidence for clusters with NH_4^+.

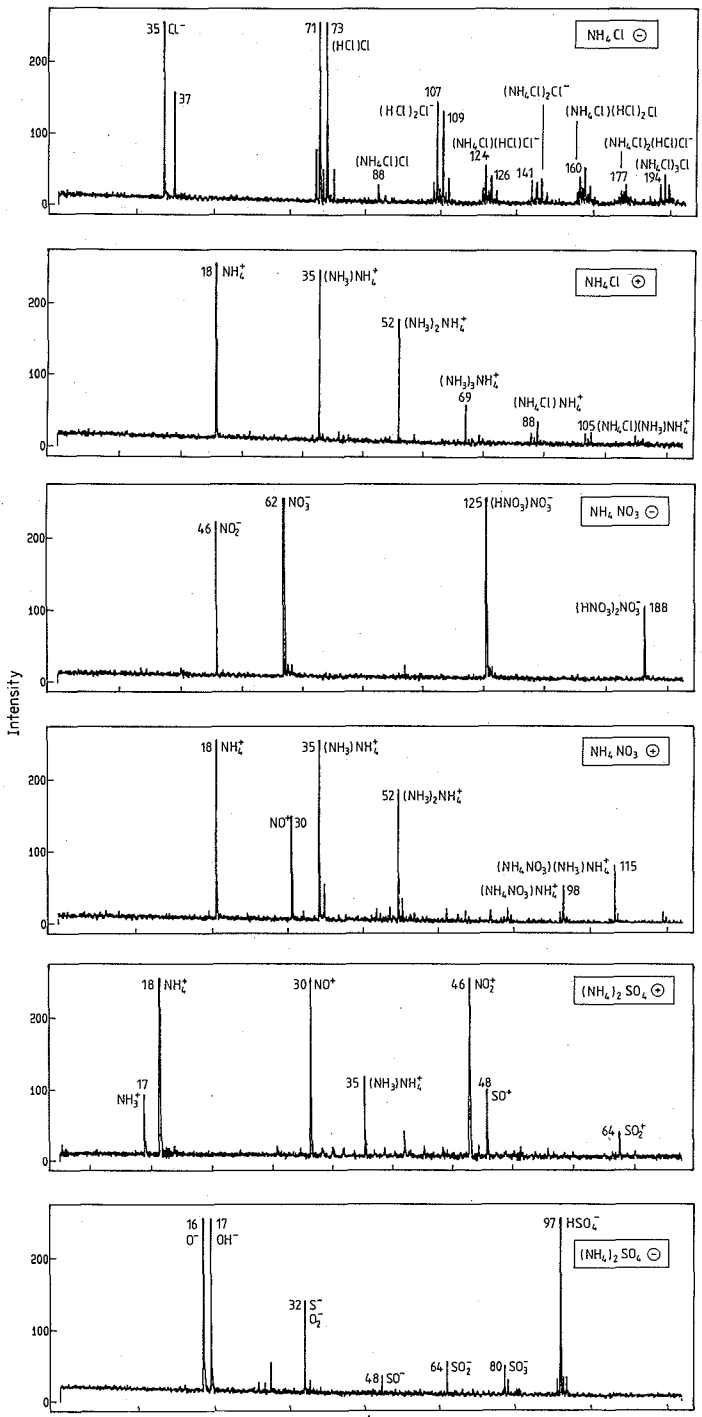

Fig. 1. Laser microprobe mass spectra of standard ammonium chloride, nitrate and sulfate generated by pneumatic nebulization of aqueous solutions. All intensities are given in the same arbitrary units.

Sensitivity for ammonium ion

The results of the measurements of mixed $NH_4^+/Na^+/K^+/Cl^-$ particles are given in Table 1. The Na^+/NH_4^+ ratio measured with the LAMMA-500 instrument, $(Na/NH_4)_L$, divided by the stoichiometric Na^+/NH_4^+ ratio in the aerosol particles, $(Na/NH_4)_P$ is defined as the relative sensitivity coefficient for Na^+ to NH_4^+, (Na/NH_4) L/P (and analogously for K^+).

It is obvious from Table 1 that this LMMS technique is much more sensitive for sodium and potassium than for ammonium in mixed aerosol particles. The sensitivity factors for sodium and potassium relative to ammonium are not constant, but this is merely an artifact of the limited dynamic range of the Biomation transient recorder which was used for signal storage of the secondary electron multiplier output in the LAMMA-500 apparatus. If only the values obtained by using the LMMS intensity ratios that lie between 5 and 0.2 are considered (because the dynamic range at a 100-MHz sampling rate is about 2.3 bits [7]), then the values found are 150 for (Na/NH_4) L/P and 630 for (K/NH_4) L/P. This means that the NH_4/Na ratios in particles that lie between 30 and 750 (97—99.9% of NH_4^+) can be measured accurately.

In marine aerosols, other anions and cations are generally present. To extrapolate the results to a more general marine aerosol matrix, a mixture of NH_4^+, Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+} and Fe^{3+} together with Cl^-, NO_3 and SO_4^{2-} was prepared. The results of these measurements are given in Table 2. Because LMMS is much more sensitive for other cations than for ammonium, it is very suitable for detecting low concentrations of metal ions in single particles made up of ammonium salts. The practical detection limit for lead, an element frequently detected with LMMS in ambient ammonium sulfate aerosols, is 30 mg kg^{-1} [8] in a 1-μm diameter particle. This corresponds to an absolute detection limit of 4×10^{-17} g of Pb. Figure 2 shows a calibration plot for measurement of traces of lead in single sodium ammonium sulfate particles with the LAMMA-500 instrument.

The future use of a new transient recorder (Lecroy model TR-8818) with a higher dynamic range (about 6 bits at a 100-MHz sampling rate) offers good prospects for accurate determinations of ion ratios in single particles.

TABLE 1

Relative sensitivity of the LAMMA-500 instrument for NH_4^+, Na^+ and K^+ in mixed standard $NH_4^+/Na^+/K^+/Cl^-$ aerosols

$(Na/NH_4)_P$	$(Na/NH_4)_L$	L/P	$(K/NH_4)_P$	$(K/NH_4)_L$	L/P
0.001	0.10	100	0.0004	0.15	370
0.002	0.26	130	0.0008	0.48	600
0.004	0.50	130	0.0016	1.0	650
0.01	1.3	130	0.004	2.4	590
0.02	4.0	200	0.008	5.4	680
0.04	63	1800	0.016	47	3000
0.1	130	1300	0.04	150	3800
0.2	—	—	0.08	—	—

TABLE 2

Relative sensitivity of the LAMMA-500 instrument for the seven cations in the mixed standard aerosol matrix

Element (X^+)	$(X/NH_4)_P$	$(X/NH_4)_L$	L/P[a]	Element (X^+)	$(X/NH_4)_P$	$(X/NH_4)_L$	L/P[a]
NH_4^+	1.000	1.000	1.000	K^+	0.00164	1.08	660 (29)
Na^+	0.00514	0.95	185 (6)	Ca^+	0.0384	0.49	12.8 (1.1)
Mg^+	0.0571	0.59	10.3 (0.7)	Fe^+	0.0415	0.50	12.1 (0.6)
Al^+	0.0245	0.41	16.8 (1.4)				

[a]Standard deviation of the mean of 100 spectra is given in parentheses.

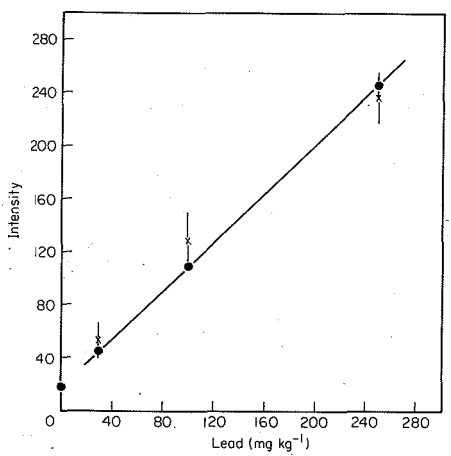

Fig. 2. Calibration plot for measurement of traces of lead in single sodium ammonium sulfate particles. Intensity in arbitrary units.

Analysis of marine aerosols

Marine aerosol particles, collected during the two cruises in the North Sea, were investigated for their ammonium compounds. The results of the Na^+/NH_4^+ intensity measurements are given in Table 3. In the samples taken in August 1985, ammonium was not detected directly, because the m/z = 18 peak (NH_4^+) was mostly absent, except in some particles collected on stages 4 and 5. On these stages, a large m/z = 97 (HSO_4^-) peak was also detected in the negative-ion mode, confirming the presence of an important amount of ammonium sulfate. The ratio of the m/z = 143 $(Na_2SO_4)H^+$ and m/z = 165 $(Na_2SO_4)Na^+$ peaks also indicates the presence of a hydrogen source. These findings are in agreement with numerous other measurements [9]; ammonium and sulfate are highly associated and mostly abundant in the submicrometer particle-size range.

For the samples taken during the second cruise in March 1986, the situation is quite different. The m/z = 18 peak (NH_4^+) is detected in almost all

TABLE 3

Measured Na^+/NH_4^+ ratios in four marine aerosols collected during the second cruise (10—14/3/1986) in the North Sea

Stage[a]	Measured Na/NH_4 intensity				NH_4 (mol-% cations)			
	1	2	3	4	1	2	3	4
1	—	—	5.3	4.1	0	0	77	79
2	48	16	5.4	2.3	47	53	74	89
3	9.6	57	3.4	13	30	79	88	57
4	19	47	4.7	5.3	45	49	75	79
5	11	63	3.5	8.6	39	75	92	85

[a]Diameters of stages 1—5 are 4, 2, 1, 0.5 and 0.25-μm aerodynamic diameter, respectively.

particles on the five stages of the impactor. With the relative sensitivity factors obtained from the standard aerosols, the relative cationic content of the particles can be calculated from the measured intensity ratios. The intensities of the m/z = 18 (NH_4^+), m/z = 23 (Na^+), m/z = 24 (Mg^+), m/z = 27 (Al^+), m/z = 39 (K^+), m/z = 40 (Ca^+) and m/z = 56 (Fe^+) are multiplied by the relative sensitivity factors L/P and normalized to the sum. The peak at m/z = 40 (Ca^+) is corrected for the contribution of MgO^+ and the peak at m/z = 56 (Fe^+) is corrected for the contribution of CaO^+. These contributions were measured by analysis of standard aerosols. Table 3 lists the measured Na^+/NH_4^+ intensity and the calculated mol-% of ammonium in the total cations, taking into account the presence of Na, Mg, Al, K, Ca and Fe.

It is quite clear that particles from all five stages contain very important amounts of ammonium ion, up to 90% of the total cationic content. In the large-size particle range, this ammonium is associated with nitrate and sulfate, but in the submicrometer particle-size range only with sulfate. This distribution of ammonium over the whole range of particles collected is quite unusual. A cause might be the meteorological situation of that period. A weak variable wind, coming mainly from the east, would bring large amounts of ammonia and ammonium from the continent to the sea. Because the wind velocity was low, aerosol production by the sea was negligible. The inversion situation also prohibited the dispersion of pollutants.

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