A METHOD OF MEASURING AIRBORNE ACIDITY: ITS APPLICATION FOR THE DETERMINATION OF ACID CONTENT ON LONG-DISTANCE TRANSPORTED PARTICLES AND IN DRAINAGE WATER FROM SPRUCES

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ABSTRACT

The acid properties of particles have been investigated by means of measuring the content of mainly strong acid in leaching solutions of particle samples and in drain water from trees. The measurements are based on Gran's plot and on a study of its curvature.

INTRODUCTION

Great attention is now focused on the acidification of lakes and land which seems to be the immediate result of i.a. increasing emissions of SO_2. The lack of quantitative data on the supply of air-borne acid to receptors of different kinds makes it difficult to handle these problems. Below a method is described that provides such data. Some results of its application in the research of the acid properties of air-borne particles are reported.

DEFINITION

To be able to develop a method of measuring a quantity it is necessary to have a definition of the quantity in question. In the present case the relevant quantity is acid for which, as is well known, there is a number of more or less general definitions. If the problem is limited to water-soluble systems only, which seems to be possible in this case, the respective definition will be simple, namely:

An acid is an electrically neutral or charged group which is able to donate protons to a water system. If the donation is made quantitatively even at high concentrations, the acid is referred to as strong, otherwise as weak.

SCOPE OF THE INVESTIGATION

The problem of measuring air-borne acidity can of course be limited to the determination of the amount of protons being transferred to a receptor with defined properties by a certain deposition e.g. as particles or precipitation. In many cases it is, however, interesting to determine the acid properties of a potential deposition without taking the nature of the receptor into account. The latter case actually implies the determination of the nature and concentration of all acids present in the relevant sample. This in turn is a very exacting task which, however, can be limited in many cases. As a guidance for such a limitation a compilation of the most important anthropogenic acids (and their respective pk_a values) occuring in air-borne systems have been made in Table I. Organic acids have not been

Table I

Antropogenic Acids and their approximate Strength

Acid	Strength (pk_a)	Acid	Strength (pk_a)	Acid	Strength (pk_a)
HCl	strong	HF	3.2	$B(OH)_3$	9.0
HNO_3	strong	$Fe(H_2O)_6^{3+}$	∿3	NH_4^+	9.3
H_2SO_4	strong	$Fe(H_2O)_5OH^{2+}$	∿3	HCN	9.4
H_2SO_3	1.9	$Al(H_2O)_6^{3+}$	∿5		
HSO_4^-	2.0	H_2S	6.9		
H_3PO_4	2.1	HSO_3^-	7.2		
		$H_2PO_4^-$	7.2		

considered here, since information about their occurrence in precipitation and particles so far has been very sparse. However, at "The First International Symposium on Acid Precipitation and the Forest Ecosystem" in Columbus, Ohio in May 1975, a paper was presented, dealing with i.a. identification of organic acids in precipitation. The only acid that has been identified until now is the triprotonic isocitric acid (Galloway et al. 1975). If aluminium ions and the isocitric acid with

$$pk_{a_1} = 3.4, \quad pk_{a_2} = 4.75 \quad \text{and} \quad pk_{a_3} = 5.4$$

(Galloway, 1975) are disregarded, the acids in Table I can be divided in two groups: A stronger group which includes acids with $pk_a < \sim 3$ and a weak group including acids with $pk_a > \sim 7$.

The following comments can be made regarding the stronger group of acids in Table I. H_2SO_3 has a limited life in air-borne systems. It oxidizes to H_2SO_4. The acid H_3PO_4 has never been observed in measurable concentrations in the samples (some hundred) which up to now have been analysed in Sweden under the direction of the author. Occurrence of high concentrations of the acid HF is generally connected to certain premises. Trivalent iron ions do occur in almost all samples but as a rule in very low concentrations compared to other acids.

This means that if it is possible to determine free hydrogen ions and hydrogen ions bound in acids belonging to the stronger group ($pk_a < 3$), the sum of the concentration of strong acids and the acid HSO_4^- will be obtained with usually sufficiently good accuracy. As this concentration sum often is of major interest a procedure has been developed which makes it possible to decide to what extent also other weak acids have been titrated when merely determining strong acid and the acid HSO_4^-. This procedure has been used for determining i.a. the acid properties of air-borne particles.

METHODOLOGY

On a proposal from Christer Askne (Askne and Brosset, 1972) investigations were made to establish whether it was possible to determine the concentration of strong acid in particles and precipitation by means of Gran's titration method (Gran, 1952). This has resulted in the development of the following routine method.

The titration is as usual carried out potentiometrically, however, in such a way that the volume of the sample will remain unchanged. As a rule this is achieved by inserting microlitre quantities of a 0.01 N solution of NaOH to 5 ml of the sample which has been released from CO_2 by means of conditioning with N_2 (if necessary a known amount of $HClO_4$ is added to the sample). Now, the remaining amount of hydrogen ions (H^+) calculated from the measured potential is plotted against the

amount of added hydroxyl ions (OH^-). If the acid being titrated is strong, a straight line with a slope of -1 will, as is well known, be obtained. The intersection by the line of the x-axis ($H^+ = 0$) will give the point of equivalence. If weak acids are present in the sample the slope will be >-1 and the curve can bend markedly. The slope of the curve thus gives a certain information about the occurrence of acids of different strengths in the sample. For this reason it seemed to be of interest to deduce the slope of Gran's plot.

Assume that an acid solution is being titrated with sodium hydroxide in steps, and that the remaining amount of hydrogen ions (H^+) is determined after each addition. Then

$$\begin{aligned}\Delta OH^- = {} & H_1^+ - H_2^+ + [(HA')_1 - (HA')_2] + [(HA")_1 - (HA")_2] + \ldots \\ & + 2[(H_2A')_1 - (H_2A')_2] + 2[(H_2A")_1 - (H_2A")_2] + \ldots \\ & + 3[(H_3A')_1 - (H_3A')_2] + 3[(H_3A")_1 - (H_3A")_2] + \ldots \\ & \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\end{aligned} \qquad (1)$$

and so on will be obtained where H_1^+ is the amount of free hydrogen ions before addition of ΔOH and H_2^+ the amount of free hydrogen ions after this addition. The terms in brackets express the decrease of hydrogen ions bound to the different groups originating from the n-protonic acids H_nA', $H_nA"$, and so on.

From the total concentration C_t of the respective acids and their equilibrium equations, the concentrations of the different groups can be expressed in terms of the total concentration (C_t), the hydrogen ion concentration c_H^+ and the equilibrium constants ($k_1 \ldots k_n$). If these terms are inserted in equation (1) and if $H_2^+ \to H_1^+$ the following formula will be obtained

$$\frac{dH^+}{dOH^-} = -\frac{1}{1 + (C_t)_1\alpha_1 + (C_t)_2\alpha_2 + (C_t)_3\alpha_3 + \ldots}$$

where, as already mentioned, C_t is the total concentration of the weak acid and α a function of the hydrogen ion concentration and the dissociation constants of the acid according to the following

$$\alpha = \frac{\beta_1 + \beta_2 + \beta_3 + \ldots + \beta_n}{\left[1 + \frac{c_H^+}{k_n} + \frac{c_H^{+2}}{k_{n-1}\cdot k_n} + \ldots + \frac{c_H^{+n}}{k_1\cdot k_2 \cdots k_n}\right]^2}$$

The quantity β stands for the following expression

$$\beta_1 = \frac{1}{k_n}$$

$$\beta_2 = \frac{4c_{H^+}}{k_{n-1} \cdot k_n} + \frac{c_{H^+2}}{k_{n-1} \cdot k_n^2}$$

$$\beta_3 = \frac{9c_{H^+}{}^2}{k_{n-2} \cdot k_{n-1} \cdot k_n} + \frac{4c_{H^+}{}^3}{k_{n-2} \cdot k_{n-1} \cdot k_n^2} + \frac{c_{H^+}{}^4}{k_{n-2} \cdot k_{n-1}^2 \cdot k_n^2}$$

and so on. In the expression for α the numerator for monoprotonic acid is β_1, for diprotonic acid $\beta_1 + \beta_2$ and so on.

As can be seen every weak acid affects the slope of the curve by the term $C_t \cdot \alpha$ in the denominator, where α is varying with c_H^+. The implication of this can easily be explained if the expression for the slope of a monoprotonic acid is regarded. In this case the following formula is valid

$$\frac{dH^+}{dOH^-} = - \frac{1}{1 + C_t \cdot \frac{1/k}{[1 + \frac{c_{H^+}}{k}]^2}}$$

As can be seen dH^+/dOH^- is constant for low as well as high values of c_H^+ in relation to k.

In the first mentioned case

$$\frac{dH^+}{dOH^-} \rightarrow - \frac{1}{1 + \frac{C_t}{k}} \qquad (c_{H^+} << k)$$

is obtained. In the second case the following is valid

$$\frac{dH^+}{dOH^-} \rightarrow - 1 \qquad (c_{H^+} >> k)$$

Table II is a compilation of α-values for monoprotonic acids with acid constants and c_{H^+} values in the relevant ranges. α-values for phosphoric and isocitric acids are given in Table III. Table IV and V contain dH^+/dOH^- calculated from the respective values.

Table II

Calculated α-values

Monoprotonic Acids

k_a	c_{H^+} mole/l					
	10^{-3}	$3\ 10^{-4}$	10^{-4}	$3\ 10^{-5}$	10^{-5}	10^{-6}
10^{-2}	83	94	98	99	100	100
10^{-3}	250	592	826	943	980	1000
10^{-4}	83	625	2500	5920	8260	9800
10^{-5}	10	104	826	6250	25000	82600
10^{-6}	1	11	98	1040	8260	250000

Table III

Calculated α-values

	c_{H^+} mole/l					
	10^{-3}	$3\cdot10^{-4}$	10^{-4}	$3\cdot10^{-5}$	10^{-5}	10^{-6}
Phosphoric Acid $k_{a_1} = 10^{-2.15}$ $k_{a_2} = 10^{-7.21}$ $k_{a_3} = 10^{-12.36}$	111	140	194	865	6350	846000
Isocitric Acid *) $k_{a_1} = 10^{-3.4}$ $k_{a_2} = 10^{-4.75}$ $k_{a_3} = 10^{-5.4}$	220	800	3180	10200	50400	196000

*) Acidity constants according to Galloway (private communication)

Table IV

Monoprotonic Acids

Values of $-\frac{dH^+}{dOH^-}$

k_a	c_t	c_{H^+} mole/l					
		10^{-3}	$3\cdot10^{-4}$	10^{-4}	$3\cdot10^{-5}$	10^{-5}	10^{-6}
10^{-2}	mole/l						
	10^{-6}	1.00	1.00	1.00	1.00	1.00	1.00
	10^{-5}	1.00	1.00	1.00	1.00	1.00	1.00
	10^{-4}	0.99	0.99	0.99	0.99	0.99	0.99
	10^{-3}	0.92	0.91	0.91	0.91	0.91	0.91
	10^{-2}	+0.55	0.52	0.51	0.50	0.50	0.50
10^{-3}							
	10^{-6}	1.00	1.00	1.00	1.00	1.00	1.00
	10^{-5}	1.00	0.99	0.99	0.99	0.99	0.99
	10^{-4}	0.98	0.94	0.92	0.91	0.91	0.91
	10^{-3}	0.80	0.63	0.55	0.51	0.51	0.50
10^{-4}							
	10^{-6}	1.00	1.00	1.00	0.99	0.99	0.99
	10^{-5}	1.00	0.99	0.98	0.94	0.92	0.91
	10^{-4}	0.99	0.94	0.80	0.63	0.55	0.51
10^{-5}							
	10^{-6}	1.00	1.00	1.00	0.99	0.98	0.92
	10^{-5}	1.00	1.00	0.99	0.94	0.80	0.55
	10^{-4}	1.00	0.99	0.92	0.62	0.29	0.11
10^{-6}							
	10^{-6}	1.00	1.00	1.00	1.00	0.99	0.80
	10^{-5}	1.00	1.00	1.00	0.99	0.92	0.29
	10^{-4}	1.00	1.00	0.99	0.91	0.55	0.04

Table V

Phosphoric and Isocitric Acids

Values of $-\frac{dH^+}{dOH}$

	c_t	c_{H^+} mole/l: 10^{-3}	$3\cdot10^{-4}$	10^{-4}	$3\cdot10^{-5}$	10^{-5}	10^{-6}
Phosphoric Acid	mole/l						
	10^{-6}	1.00	1.00	1.00	1.00	0.99	0.54
	10^{-5}	1.00	1.00	1.00	0.99	0.94	0.11
	10^{-4}	0.99	0.99	0.98	0.92	0.61	0.01
Isocitric Acid							
	10^{-6}	1.00	1.00	1.00	0.99	0.95	0.84
	10^{-5}	1.00	0.99	0.97	0.91	0.66	0.34
	10^{-4}	0.98	0.93	0.76	0.50	0.17	0.05

Now, assume that Gran's plot during titration is linear within the c_{H^+} range $3\cdot10^{-4}$ - $3\cdot10^{-5}$ mole/l. This is generally the case when titrating leaching solutions of particle samples. The tables IV and V will now give the following information about the possible content in the solution part from strong acid.

1) Sulphate can be present in concentrations up to above 10^{-3} mole/l. If the slope of the curve is markedly above -1 the sulphate concentration is probably above 10^{-4}.

2) The concentration of monoprotonic acid with $pk_a \sim 3$ is below 10^{-4} and with $pk_a \sim 4$-6 below $\sim 10^{-5}$.

3) The concentration of phosphoric acid is below $\sim 10^{-4}$ and of isocitric acid below $\sim 10^{-5}$.

4) Most of the acids with $pk_a <\sim 3$ have been titrated in the actual c_{H^+} range, whereas the major part of those with $pk_a > 6$ have not. Higher concentrations of acids with $pk_a \sim 4$-5 would here give non-linearity which would preclude a meaningful evaluation of the titration.

In this connection, finally, something ought to be mentioned regarding the ions $Al(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$ which show a somewhat

specific picture. The dissociation of the aquo-aluminium ion is complicated and not completely understood. The acidity constant for the first step

$$Al(H_2O)_6^{3+} \rightarrow Al(H_2O)_5OH^{2+} + H^+$$

is $\sim 10^{-5}$ and this reaction is slow (Brosset, 1952). If only the first step is being considered an aluminium ion concentration of 10^{-5} mole/l will give a linear titration curve down to $c_{H^+} \sim 10^{-4}$ (Table IV). The fact that the reaction is slow will manifest itself by slowly reaching the equilibrium concentrations and the corresponding EMF-value. A creeping of the EMF is thus usually a good indication of the presence of aluminium ions of interfering concentrations. In Figure 1 a

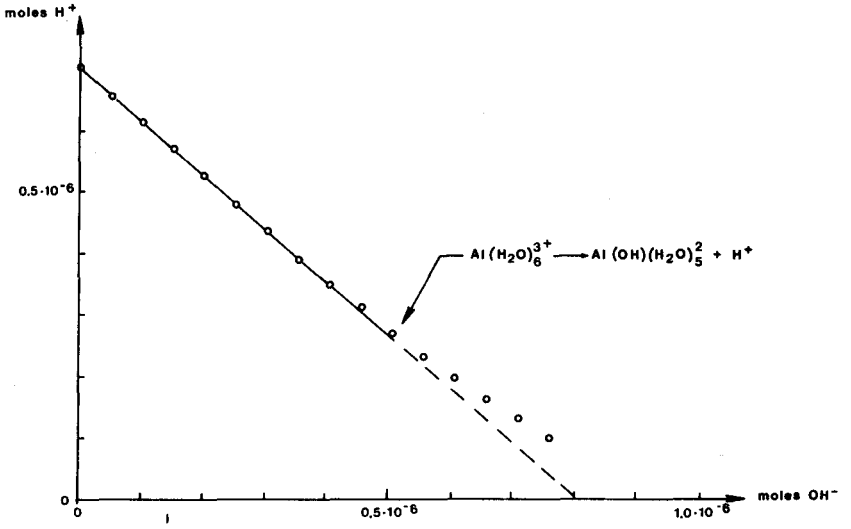

Figure 1. 5 ml sample solution containing 3.75×10^{-7} moles H_2SO_4 ($= 0.7 \times 10^{-6}$ moles H^+) and 1.5×10^{-7} moles Al^{3+}. The titration gives 0.8×10^{-6} moles H^+.

titration diagram is given which was obtained when titrating a 5 ml sample containing $7 \cdot 10^{-5}$ mole/l of H_2SO_4 and $3 \cdot 10^{-5}$ mole/l Al^{3+}. As can be seen from this diagram the linear extrapolation made has resulted in somewhat high a value.

The acid dissociation constants of trivalent iron ions have been determined by many authors (Sillén, 1971). The results differ to a great extent. However, in general it can be said that the first constant is around 10^{-3} and the second just below this value. The subsequent dissociation results in precipitation of iron hydroxide (solubility product at 20° around $3.2 \cdot 10^{-36}$) (Evans and Pryor, 1949).

Figure 2 illustrates the result of titration in the presence of rather

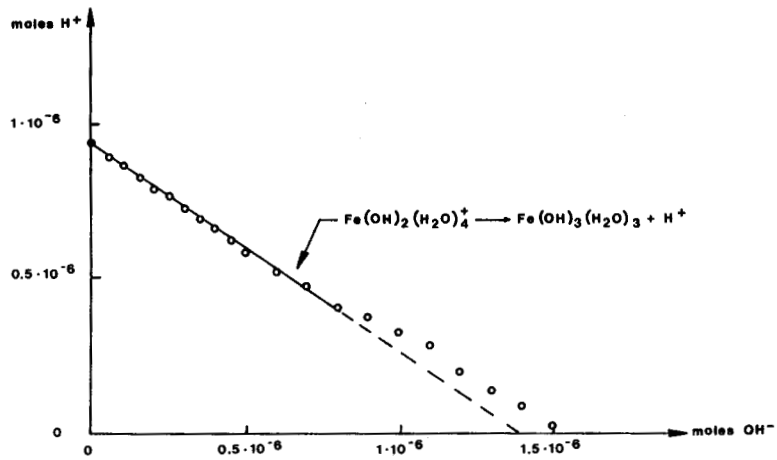

Figure 2. 5 ml sample solution containing 5×10^{-7} moles H_2SO_4 (= 1.0×10^{-6} moles H^+) and 2×10^{-7} moles Fe^{3+}. The titration give 1.39×10^{-6} moles H^+ corresponding to sulphuric acid and trivalent iron as diprotonic acid ($1.0 \times 10^{-6} + 2.2 \times 10^{-7} = 1.4 \times 10^{-6}$ moles).

high a concentration of iron. The sample contained $1.0 \cdot 10^{-4}$ mole/l of H_2SO_4 and $4 \cdot 10^{-5}$ mole/l of an iron salt. Thus the 5 ml being titrated contained $1.0 \cdot 10^{-6}$ moles of H^+ and $2 \cdot 10^{-7}$ moles of Fe^{3+}. Titration and extrapolation of the linear part of the curve (c_{H^+} range $2 \cdot 10^{-4} - 1 \cdot 10^{-4}$ mole/l) give $1.39 \cdot 10^{-6}$ moles corresponding to two H^+ per H_2SO_4 and two H^+ per Fe^{3+}. The trivalent iron has thus been titrated as a diprotonic acid. The third dissociation step and the subsequent precipitation manifest themselves by the parallel displacement of the curve at H^+ $\sim 0.3 \cdot 10^{-6}$ moles (c_{H^+} $\sim 6 \cdot 10^{-5}$ mole/l).

This titration procedure has been used at our laboratory for more than two years. We have found that it is always possible to titrate precipitation samples in this way, which as a rule is pertinent to leaching solutions of particles also. High concentrations of aluminium, which prevent the exact titration, have been observed a few times.

RESULTS OF DETERMINATION OF THE ACID PROPERTIES OF PARTICLES

Since the autumn 1972 air-borne particles have been studied by our institute mainly at a remote station on the Swedish west coast, 40 km south of Gothenburg. In this connection 24 hour samples have been taken partly of total suspended matter and partly of particle fractions with a diameter of $<\sim$ 15 µm. The particles have been leached with water and the concentrations of SO_4^{2-}, NH_4^+ and H^+ in the leaching solution have been determined. In the last mentioned case the above methodology was used. The material obtained this way, part of which has been reported (Brosset et al. 1975) (Brosset, 1975), indicates to some extent what role particles may play in acidification. These indications are reported below.

BLACK AND WHITE EPISODES

A vast material shows that during the winter half of the year and under special meteorological conditions high concentrations of black particles can be built up in Scandinavia as a result of long-distance transport (Brosset and Åkerström, 1972) (Rodhe et al. 1972). Around 50% of the mass of these particles can be water-soluble and consist of mainly $(NH_4)_2SO_4$, sometimes combined with some acid (Brosset, 1973). There are strong reasons to believe that ammonium sulphates have been formed by oxidation of SO_2 to H_2SO_4 under the influence of catalysing substances present in the particles in combination with high humidity and a subsequent neutralization by NH_3 of the sulphuric acid formed (Brosset, 1975). Lack of NH_3 results in somewhat acid particles. However, it should be noted that a high concentration of acid cannot occur here as the solubility of the sulphur dioxide decreases with increasing acidity in the liquid phase covering the particles (Junge, 1958). It is uncertain whether these rather neutral particles play a part in acidification. However, this would certainly be the case if NH_4^+ ions were oxidized resulting in the formation of acid.

During the summer half of the year there is a higher concentration of acid in the particles than during the winter. Our measurements have shown that small white particles ($\varnothing < 0.3\mu m$) consisting of the phase $(NH_4)_3H(SO_4)_2$ or even NH_4HSO_4 can be transported to the Swedish west coast chiefly from south-west. It seems likely that these acid ammonium sulphates have been formed by photochemical oxidation of SO_2 to SO_3 (several types of reactions are possible here) and that the latter is hydrated and partly neutralized by NH_3. If the last mentioned processes occur in a NH_3-poor atmosphere, e.g. over the North Sea the neutralization will, as observed, be very incomplete (Brosset, 1975).

The contribution to the acidification of land and lakes by these

white particles is probably limited due to the fact that the white episodes occur rather seldom. However, when these episodes are present a human being can breathe around 100 µg of sulphuric acid for 24 hours (Brosset, 1975).

During the last week in May, 1973, an episode occured during which it was possible to make studies of the water-soluble phase of the particles analytically as well as by means of X-ray diffraction. The results are given in Table VI. As can be seen all three of the above-mentioned

Table VI

Comparison between Results of Chemical Analysis and Phase Identification by Means of X-ray Diffraction.

Sampling Date	$NH_4^+/_{H^+}$ by Analysis	Phases Identified	Phases not Identified
23 May 12.25-14.00 hours	15.1	$(NH_4)_2SO_4$	traces
24 May 09.15- 25 May 14.00 hours	3.0	$(NH_4)_3H(SO_4)_2$	traces
29 May 06.00-12.00 hours	1.0	NH_4HSO_4	traces

ammonium sulphate phases have been identified. The analytical result is further in good agreement with the stoichiometrical compositions of the phases identified by means of X-ray diffraction.

THE NEUTRALIZATION OF ACID PARTICLES

During August 1974, 24 hour samples of suspended matter were taken at the remote station Råö, mentioned previously, as well as at four sampling sites located as indicated on the map in Figure 3. The samples were analysed in the usual manner for H^+, NH_4^+ and SO_4^{2-}. The intention was to get an idea how the composition of the water-soluble part of the particles varied with different places in South Sweden. The measuring results obtained from an episode which occured during

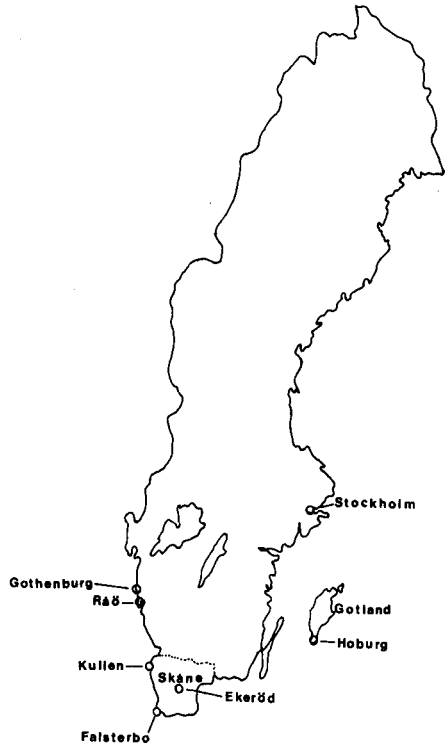

Figure 3. Sampling stations.

7-14 August are illustrated in Figure 4. As can be seen the equivalent concentration of sulphate on this occasion has almost been equal to the sum of the equivalent concentrations of H^+ and NH_4^+. This means that the water-soluble part of the particle fraction sampled, for the most part consisted of more or less acid ammonium sulphates. On this occasion the wind direction was south-west, through which Råö will be subjected to the air masses that had drifted over the North Sea and Skagerack and which evidently contained rather acid particles.

At the above-mentioned wind direction the station at Kullen about 300 km south of Råö is situated to the leeward of Denmark. This is even more the case as regards the station at Falsterbo. As can be seen from Figure 4 there is a decrease in acidity of the particles sampled at these stations as compared to Råö. This may indicate that the particle-borne acid has been neutralized by NH_3 during transportation of the particles over Denmark. It is further very interesting to note that all acid has become neutralized as the particles reach the station at Ekeröd situated in the middle of the province of Skåne, which is a large agricultural district.

The station at Hoburg lighthouse on the south point on the island of Gotland shows a very moderate maximum of acid on 11 August. By this it seems that the acid particles have proceeded this far two days after

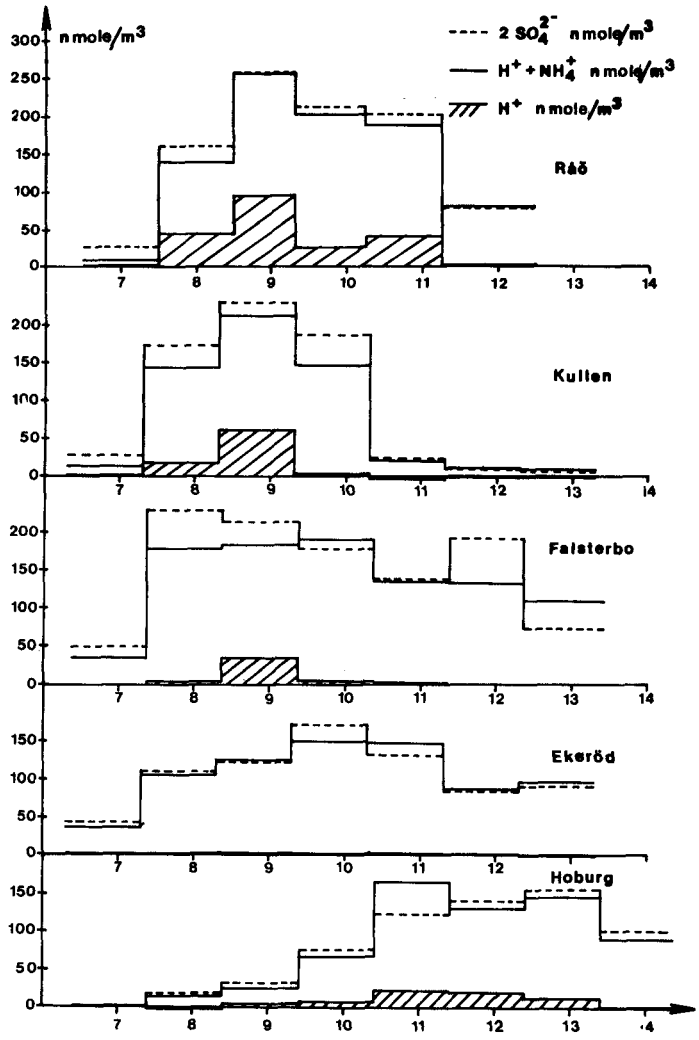

Figure 4. Episode 7-14/8 1974. Concentrations at stations on the Swedish west coast, in Skåne and on Gotlan.

passing the western coast-line. During transport they drifted over land to rather a great extent and somewhat over the sea.

The above observations indicate that certain districts of land may act as ammonia sources and that acid particles passing these districts may be more or less neutralized. It is likely that the neutralization may alter the properties of the particles from the viewpoint of effects. However, the possible oxidation of NH_4^+ resulting in acid has to be taken into account in some cases.

PRELIMINARY MEASUREMENTS OF THE PARTICLE DEPOSITION ON SPRUCES

It has earlier been pointed out that particles containing neutral or acid ammonium sulphate due to their small size (Ø < 1 µm) can cause undesirable effects by deposition in e.g. the respiratory tracts. For the same reason it is, however, likely that they would play a secondary part in the acidification of land and lakes caused by wet deposition since such small particles, unless they would increase in size will be washed out to a small extent only by precipitation during transport. On the other hand marked effects can be expected due to dry deposition if the receptor has a large surface as for example a forest.

Many measurements have previously been carried out with the objective of determining the extent of the dry deposition on trees by analysis of the precipitation filtered by the needles and the respective leaves of trees (Nihlgård, 1970). However, a quantitative determination of acid has not yet been made in this connection. Therefore it seemed of interest to investigate whether the application of the titration procedure described above could give any further information.

In two forest areas north and south of Gothenburg (see map Figure 5) a number of spruces were chosen as subjects of the experiment.

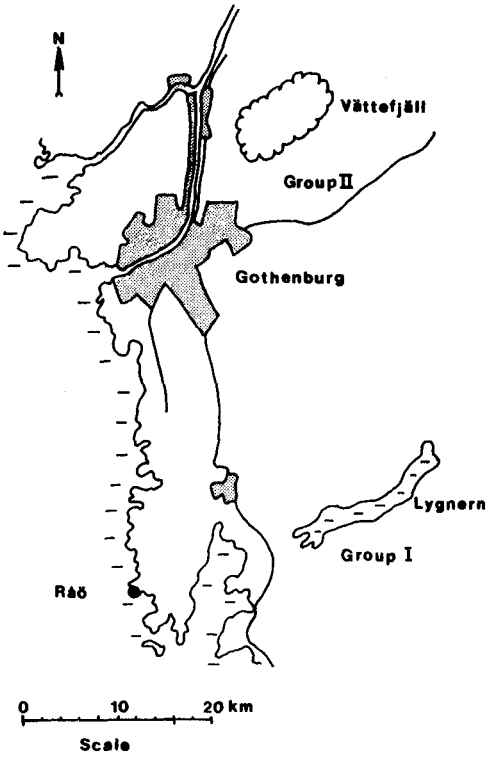

Figure 5. Map showing the location of the different groups of trees.

8 vessels (Ø 0.3 m) were placed beneath the spruces to collect the drain water from the respective tree. The vessels were numbered and placed in numerical order in the respective point of the compass according to Figure 6. The test series included three spruces in group I (the

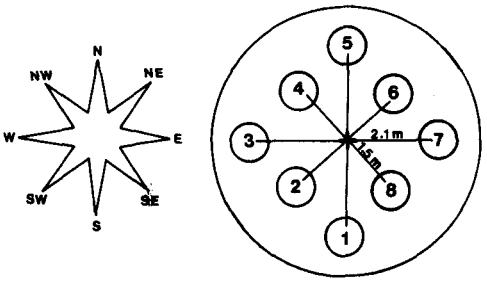

Figure 6. Location of the sample collectors beneath the respective tree.

southern sampling site) and three spruces in group II (the northern sampling site). In this very case the vessels were placed after a rainfall on 28 August, 1974, and brought back on 9 September, 1974. During this period it had been raining mainly for the last few days. It was most likely that the rainwater collected in the vessels had washed out at least part of the particles deposited on the respective spruces during the period 28 August - 9 September. Further a similar vessel was placed outside each tree group to collect rainwater which had not been in contact with the trees. The results given in Figure 7 indicate the amounts of H^+, NH_4^+, and SO_4^{2-} in the respective precipitation samples.

Table VII is a compilation of the amounts of H^+, $NH_4^+ + H^+$ and $2SO_4^{2-}$ contained in the drain water from every tree in the southern (I) as well as northern (II) group, expressed in m moles. This table also includes the sum of the amounts of the respective groups. Correction has been made for the amounts observed in pure rain water. If the values obtained are representative for the deposition on trees at those from each other rather remotely situated test areas the conclusion must be drawn that for trees of the type chosen (spruces as symmetrical as possible about 8-10 m high with a ground level Ø of ∿ 5-6 m) the deposition of the different kinds of ions investigated was almost the same for trees within the respective group as for trees belonging to different groups. This concerns above all the trees numbered 1, 2, 4, and 5. The material is obviously too small for drawing any certain positive conclusions. However, if the observations made should prove not to be occasional it means that the dry deposition in the two areas must be associated with long-distance transport of pollutants and that the city

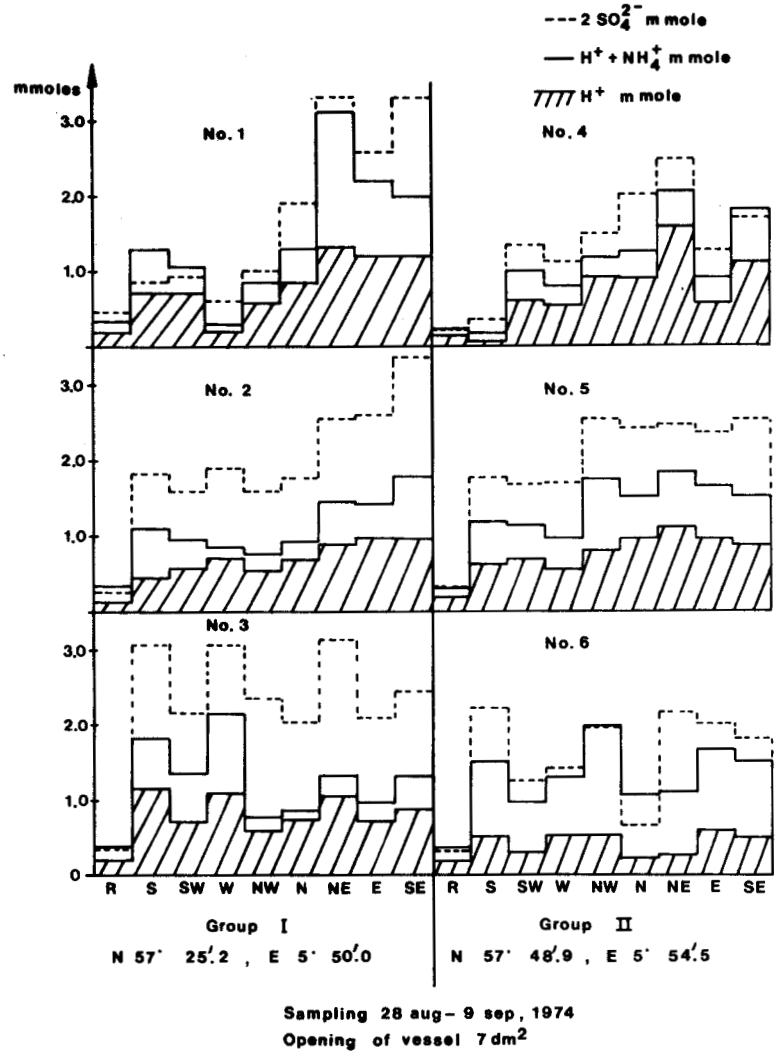

Figure 7. H^+, $NH_4 + H^+$ and SO_4^{2-} in precipitation samples (R) and samples of drain water (S-SE).

Table VII

Content of Some Ions in Drain Water from Trees.

Tree No	mmole			
	H^+	$NH_4^+ + H^+$	$2SO_4^{2-}$	
1	5.5	9.8	11.4	
2	5.0	7.0	14.6	Group I
3	6.4	9.5	19.3	
Σ	16.9	26.3	45.3	
4	5.2	7.4	9.9	
5	5.7	10.0	16.1	Group II
6	2.7	9.6	12.2	
Σ	13.6	27.0	38.2	

of Gothenburg (500,000 inhabitants) is a source of secondary importance in this respect.

Another interesting observation is the high acid to ammonium ratio in the drain water compared to that observed on particles simultaneously sampled at Råö which is situated close to the sampling site of the southern group (see map Figure 5). Data concerning the particles are illustrated in Table VIII. In Table IX comparison is made between the ratio of $H^+ : (NH_4^+ + H^+) : 2SO_4^{2-}$ contained in drain water from the trees and in leaching solutions of the particles.

As appears from Table IX the ratio of $H^+ : (NH_4^+ + H^+)$ in the drain water is ten times higher than the corresponding ratio for the particles. On the other hand the ratio $2SO_4^{2-} : (NH_4 + H^+)$ is on an average 16% higher. This indicates that in spite of the fact that the sulphate concentrations observed are sufficient for explaining the H^+ amounts found as deposited sulphuric acid, other mechanisms may be the reason for the observations made. To get a clear picture of these problems, which seem to be important from the viewpoint of acidification, a much more

Table VIII

H^+, $NH_4^+ + H^+$ and $2SO_4^{2-}$ in Particle Samples from Råö.

(n mole/m^3)

Date	H^+	NH_4^+	$NH_4^+ + H^+$	$2SO_4^{2-}$
Aug 28	1	16	17	26
Aug 29	- 2	9	7	10
Aug 30	11	68	79	98
Sep 3	3	57	60	90
Sep 4	0	66	66	88
Sep 6-9	1	24	25	58

Table IX

The Ratio of H^+ : ($NH_4^+ + H^+$) : $2SO_4^{2-}$ in Drain Water from Trees and Particles.

	H^+	:	$NH_4^+ + H^+$	:	$2SO_4^{2-}$
Group I	0.64	:	1	:	1.72
Group II	0.50	:	1	:	1.42
Particles	0.05	:	1	:	1.35

extensive sampling must be carried out and the samples be subjected to a more detailed programme of analysis. Such investigations are now in progress.

SUMMARY

A titration procedure based on Gran's plot has been developed. The method which enables the determination of stronger acids ($pk_a \lesssim 3$) has been applied for investigations of different depositions. The water-soluble part of particles ($\varnothing \lesssim 1\ \mu$) has been found mainly to consist of more or less acid ammonium sulphates. The phases $(NH_4)_2SO_4$, $(NH_4)_3H(SO_4)_2$ and NH_4HSO_4 have been identified. It also appears that acid particles are successively becoming neutralized during transport over land by uptake of ammonia. Finally one preliminary experiment has been carried out regarding the concentrations of H^+, NH_4^+ and SO_4^{2-} in drain water from spruces. The equivalent ratios have been compared with those observed in the leaching solution of particles sampled during the same time interval. The results indicate the following possible effects.

It is likely that particles containing more or less acid ammonium sulphate can cause undesirable effects e.g. when being inhaled. They may be of secondary importance as regards the acidification of land and lakes caused by wet deposition. On the other hand it seems as if dry deposition of particles on coniferous trees with subsequent secondary reactions and wash out can result in large depositions of acid on the ground level beneath the trees.

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