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PROBLEMS INVOLVED IN CHOOSING A SUITABLE METHOD OF DETERMINING HAZARDOUS ACIDITY ON PARTICLES.

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PROBLEMS INVOLVED IN CHOOSING A SUITABLE METHOD OF DETERMINING HAZARDOUS ACIDITY ON PARTICLES.

Abstract

In view of the harmful effects that strong acid borne by respirable particles can have on human health the possibility has been discussed within WHO of recommending a method for determination of this particle-borne acid. This report is a brief summary of our current knowledge concerning the nature of different proton donors and their relationship to recipients with different pH-values. It is evident that the question of a suitable method for determination cannot be discussed before it has been established which proton donors that are relevant under the circumstances.

Particle-borne acid can originate from different types of sources and be of varying kinds. Since the acid products formed through oxidation of SO_2 are most relevant here, the following discussion will mainly focus on these.

During combustion of sulphurous fuels, sulphur dioxide is primarily formed. A small part of this SO_2 (2-3%) is oxidized already in the stack to SO_3, which together with water vapour forms drops of rather concentrated sulphuric acid. When these drops are emitted to the ambient air they will gradually be diluted to a degree which corresponds to equilibrium with water vapour at the temperature prevailing at the time. Under normal conditions the drops will contain approx. 5 M H_2SO_4. That part of SO_2 which is not oxidized in the stack will after emission to the ambient air undergo oxidation; the time this takes varies with external conditions. The process is relatively rapid when SO_2 gas comes in contact with a wet surface containing catalyzing substances. A typical example is small particles having aqueous film containing, most commonly, iron ions. The process can be conceived of in two steps. The first step is a solution of SO_2 in water, the solution thereby containing the groups H_2SO_3, HSO_3^- and SO_3^{2-}. The concentration of H_2SO_3 is dependent on the partial pressure of SO_2 (P_{SO_2}) and is constant as long as P_{SO_2} is constant and the temperature unchanged.

The concentration of HSO_3^- and SO_3^{2-} is dependent on the abovementioned partial pressure and on the hydrogen ion concentration of the solution, and will decrease when the latter concentration increases. Since HSO_3^- is a very weak acid, SO_3^{2-} will be present in any appreciable concentration only if the solution is neutral or alkaline.

The acid H_2SO_3 is medium strong. Its acidity constant is approx. 10^{-2}. This means that at pH$\sim$4, the concentration ratio

$$\frac{[HSO_3^-]}{[H_2SO_3]}$$ is approx. 100

whereas at pH$\sim$1, this ratio is approx. 0.1.

The second step comprises the oxidation itself. It has been shown that the groups SO_3^{2-} and HSO_3^- participate in this process (Ref. 1), whereby the acid H_2SO_3 is converted into H_2SO_4, a strong acid in the first step. The pH of the solution drops and consequently also the concentration of HSO_3^- and SO_3^{2-}. Since the rate of oxidation is a function of the latter concentrations, this, too, decreases. According to Junge (Ref. 2), the oxidation is very slow already at a pH value of $\sim$2.

Consequently in accordance with the above, contact between SO_2 and wet particles (which practically always contain some iron) results in drops of diluted sulfuric acid. Through vapourisation of water, some increase in the concentration may occur. The equilibrium concentration becomes dependent on all ions present in the system and the water vapour pressure of the air.

Thus, in view of the foregoing one can consider it likely that there are two populations of acid aerosols, one resulting from dilution of very concentrated sulfuric acid, the other from increase in the concentration of a diluted sulfuric acid. Both types of acid aerosols can undergo changes with the passing of time.

Since the relevant aerosol particles seem to be made up, in most cases, of acid water drops surrounding solid particles, a partial dissolution of the solid particles is likely. Through this dissolution, iron and aluminium - inter alia - can be introduced into the liquid phase. Furthermore, in the event that the particles are transported into an environment with a certain content of NH_3, (which should be a rule in the case of long distance transport) absorption of NH_3 may occur. This would lead to a decrease in the hydrogen ion concentration and formation of NH_4^+ ions.

The picture outlined above of the formation and change of the acid aerosol particles is partly founded on the experiences made in Sweden concerning the composition of the water-soluble part of the particles. It has been found that if aerosol samples are leached with water and the water solution is titrated with respect to acid, the titration curve has in all the cases examined a behavior which is characteristic of a mixture of strong and weak acids. If metal ions are exchanged for hydrogen ions (cation exchange) the solution will entirely take on the characteristics of a strong acid. This means that the weak acids are cations, i.e. most probably $Fe(H_2O)_6^{3+}$, $Al(H_2O)_6^{3+}$ and NH_4^+. Thus, in the aerosols we are dealing with here, we have to expect the presence of different proton donors. These behave differently in recipients with different pH values, as can be seen from the following table.

Acid	k_a	Dissociation Range (pH of recipient)
HCl HNO_3 H_2SO_4 (first step)	high	donates all protons at all relevant pH-values to the recipient
HSO_4^- H_2SO_3 (first step) H_3PO_4 (first step)	10^{-2}	donates ~90 % of its protons to a recipient with a pH-value ~ 3.
$Fe(H_2O)_6^{3+}$ (conc.range: $10^{-2}$to 10^{-5})		donates 3 protons to a recipient with a pH-value >3 - 4 (estimated value)
$Al(H_2O)_6^{3+}$ (conç. range: 10^{-2} to 10^{-5})		donates 3 protons to a recipient with a pH-value of >3.5 - 5.
NH_4^+	10^{-9}	donates ~90 % of its protons to recipient with pH-value ~10.

In practice, these reactions can be assumed to occur in three steps:

1) SO_2 is oxidized on the surface of a wet particle giving sulfuric acid, whereby the solution will contain i.a. H^+ and SO_4^{2-} ions.

2) Hydrogen ions react with certain iron and aluminium compounds in particles, e.g. oxides giving aquo-ions:

$$Fe_2O_3 + 6H^+ + 6\ H_2O \longrightarrow 2\ Fe\ (H_2O)_6^{3+}$$

$$Al_2O_3 + 6H^+ + 6\ H_2O \longrightarrow 2\ Al\ (H_2O)_6^{3+}$$

Depending on the pH of the solution, some of these aquo-ions can be dissociated, e.g. $Fe\ (H_2O)_5\ OH^{2+} + H^+$. (The real reaction is more complex).

3) Alternative I:
If particles referred to under 2) above are taken up in a raindrop, a considerable dilution occurs and the pH increases and colloidal iron and aluminium hydroxides fall out. The result is a weakly acid solution. It is likely that fairly large amounts of SO_2 can be taken up in this solution and be oxidized to sulfuric acid. The rain is acidified.

Alternative II:
The particle is deposited directly in a recipient assumed to have a pH-value > 5. By protolysis the following is thereby donated to the recipient:

a) All H^+ ions originating from strong acids
b) Three H^+ ions per Fe (three valent) according to the reaction $Fe\ (H_2O)_6^{3+} \longrightarrow Fe\ O\ (OH) + 3H^+ + 4\ H_2O$
c) Three H^+ ions per Al according to reaction $Al\ (H_2O)_6^{3+} \longrightarrow Al\ (OH)_3 + 3H^+ + 3H_2O$

If the pH in the recipient is < 5, the hydrogen ion donation decreases, primarily from the aluminium ions. If, on the other hand, the pH is > 10, $Al(OH)_3$ is dissolved forming aluminate ($Al(OH)_4^-$).

Item 3, Alt. I above is of interest mainly in studies of the acidification of lakes and soil. Information about such acidification effects can be obtained by determination of strong acid in precipitation, which can be done with good precision (Ref. 3). In this case, iron and aluminium ions contribute only slightly to the acidification. During 1972 a large number of precipitation samples have been examined, i.a. in Norway and Sweden by the method referred to.

Item 3, Alt. II, on the other hand, is of direct relevance to human health. Three different situations can be distinguished:

1. Polluted town air during dry weather and good atmospheric ventilation.
   A fairly low concentration of very acid particles (the acid having been formed already in the stack) is to be expected. Also alkaline particles can be present at the same time.

2. Polluted town air during humid weather and poor atmospheric ventilation (inversion).
   Here, we can expect accumulation of the acid particles mentioned under 1. In addition, a relatively rapid oxidation of SO_2 occurs on the particles which are not acid. This gives us a new population of acid particles with a lower concentration of acid. The presence of alkaline particles is in this case less likely.

3. Long-distance-transported particles (old aerosols)

If an aerosol formed according to 1. and 2. above is transported over long distances and consequently resides for some time in the atmosphere, the acid can dissolve some metal ions from the solid particles. In addition NH_3 can be taken up from the atmosphere. The water-soluble part of the aerosol will contain i.a. ammonium, iron and aluminium ions, and in many cases large amounts of sulphate ions.

Aerosols described under 1. and 2. above have not, so far, been studied at IVL, but such studies are planned. An aerosol according to 3. however has been subject to thorough investigations, as can be seen from the following:

On December 21-24, 1972 a particle-cloud was transported from the south in over Scandinavia. By means of specially constructed probes, 6-hour samples were taken during this time at a remote station located about 45 km south of Gothenburg. The samples corresponded to 1000 m^3 air per 6 hours. Parallel with the sampling, particle counting was performed within 8 size ranges between >13 and <0.3 µm. The results of these measurements were as follows:

Number of particles in the range 0.3-1 µm: Approx. 60.000/litre air.
Total particle concentration: Approx. 90 µg/m^3

Surprisingly it was found that the concentration of strong acid was too low to be determined ($H^+ < 2 \times 10^{-3}$ µg/m^3 air). The content of other here relevant ions was the following:

NH_4^+ : 6.8 µg/m^3 air

Fe^{3+} : 0.27 µg/m^3 air

Al^{3+} : 0.20 µg/m^3 air

SO_4^{2-} : 19.7 µg/m^3 air

The above is to be interpreted that the water-soluble part of the particles mainly consisted of $(NH_4)_2SO_4$ and that the acid properties were due primarily to the iron and aluminium concentrations.

Conclusions

From the foregoing it is quite clear that respirable particles- and this is also known - can have acid properties. It has been discussed if there were methods available for quantification of these properties. However, it has been found that the acidity in question may be due to the presence of different proton donors which act differently depending on the pH of the recipient. In view hereof, it appears to be necessary to begin with ascertaining which of these proton donors that can be assumed to have adverse effects on human health and to which extent they do so. Not until this is done will it be possible to discuss the choice of suitable measurement techniques.

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