SURFACE CONCENTRATION OF SULPHUR ON PINE 19.1. 人名西西利斯 11. 医内侧 19. 医克斯氏病 19. 医克斯斯氏病 19. 医克斯特氏病 19. 医克斯特氏病 19. 医二氏病 19. 医克斯特氏病 19. NEEDLES

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A method to determine sulphur as sulphate has been applied to search for surface concentration of sulphate sulphur on needle samples. The method is based on reducing sulphates as volatile hydrogen sulphide gas by using hydriodic acid. The hydrogen sulphide gas is swept with nitrogen into an absorption solution. Sulphide ion concentration in solution is then measured using ion selective electrodes.

The method was applied on samples collected at 0.9 to 15.9 km distances from a 1064 MW coal-fired power plant in Southern Finland.

Surface sulphate values found in the samples closer than 4 km to the power plant were 50 to 100 percent higher than a nearly constant background level. No significant variation of values with needle age was found.

INTRODUCTION

Needles of pine and spruce have naturally quite a high sulphur concentration. If the sulphur deposited on the surface of needles and originating in air pollution is characterized by the total sulphur concentration, the natural sulphur contributes a considerable, high background to the determination. In this work the extraneous sulphur, as deposited on the needles from the air, has been determined directly, i.e. separated from the natural sulphur, by using direct reduction to sulphides of the sulphates deposited on the

needle surface. After collecting the evolved hydrogen sulphide into an absorption solution the measurement of sulphide concentration is carried out with the aid of ion selective electrodes.

The sample objects of this study had been collected at different distances from the 1064 MW coal-fired power plant in Inkoo in southernmost Finland. Needles of one to approximately four years old from 60 to 80 years old pines were investigated.

THE PRINCIPLE OF THE METHOD

the fact that the sulphur on the surface of the needles is in the form of sulphates. Reduction of these sulphates by a method (JOHNSON and NISHITA 1952, ARCHER 1956) as modified for this analysis gives then a possibility to evaluate the sulphur concen-

The determination of sulphur makes use of tration. The method uses a reducing mixture of 900 ml hydriodic acid (57 %), 250 ml hypophosphorous acid (50 %) and 125 ml formic acid (90 %). The reducing solution is prepared by boiling the acid mixture in a nitrogen atmosphere for two hours. The prepared solution remains stable for several of time, thus decreasing (wet) chemical operations and diminishing variations in the reduction process.

The hydrogen sulphide which is evolved during the reduction process, must be collected in a suitable absorption solution. sulphide anti-oxidant buffer (SAOB II), contains 80 g NaOH, 35 g ascorbic acid, and

weeks when stored in an amber bottle, which 67 g disodium EDTA in 1 dm³ of solution makes possible analyses with the same (Instruction . . . 1977). This solution serves reducing mixture over a considerable period also as buffer solution in the ion selective determination of the sulphide concentration; it prevents the oxidation of the sulphide ion and interference due to complexation of possible heavy metals in the studied samples is kept low. The ionic strength and alkalinity for ion specific measurement are also The solution for absorption, which is called adjusted. When the SAOB II buffer solution turns dark brown, it has become oxidized and must be discarded.

PROCEDURE

Figure 1 shows the distillation apparatus opened and the reducing solution forced into used in this work. About 0.2 g of the needle the distillation flask by the pressure of a sample is put into the distillation flask, 5 ml of the reducting solution is then pipetted into the dropping funnel and 10 ml of SAOB II solution into the absorption vessel. The stop-cock in the dropping funnel is thereafter

carrier gas (nitrogen or argon). The sample is boiled in the solution for 20 min and the evolved hydrogen sulphide is swept with the carrier gas into the SAOB II solution. In the experiments performed, boiling times of more than 15 min duration produced no significant change in measured sulphide concentration, thus 20 min was taken to be the optimum time for boiling. The sulphide ion concentration in the absorption solution is measured by using a

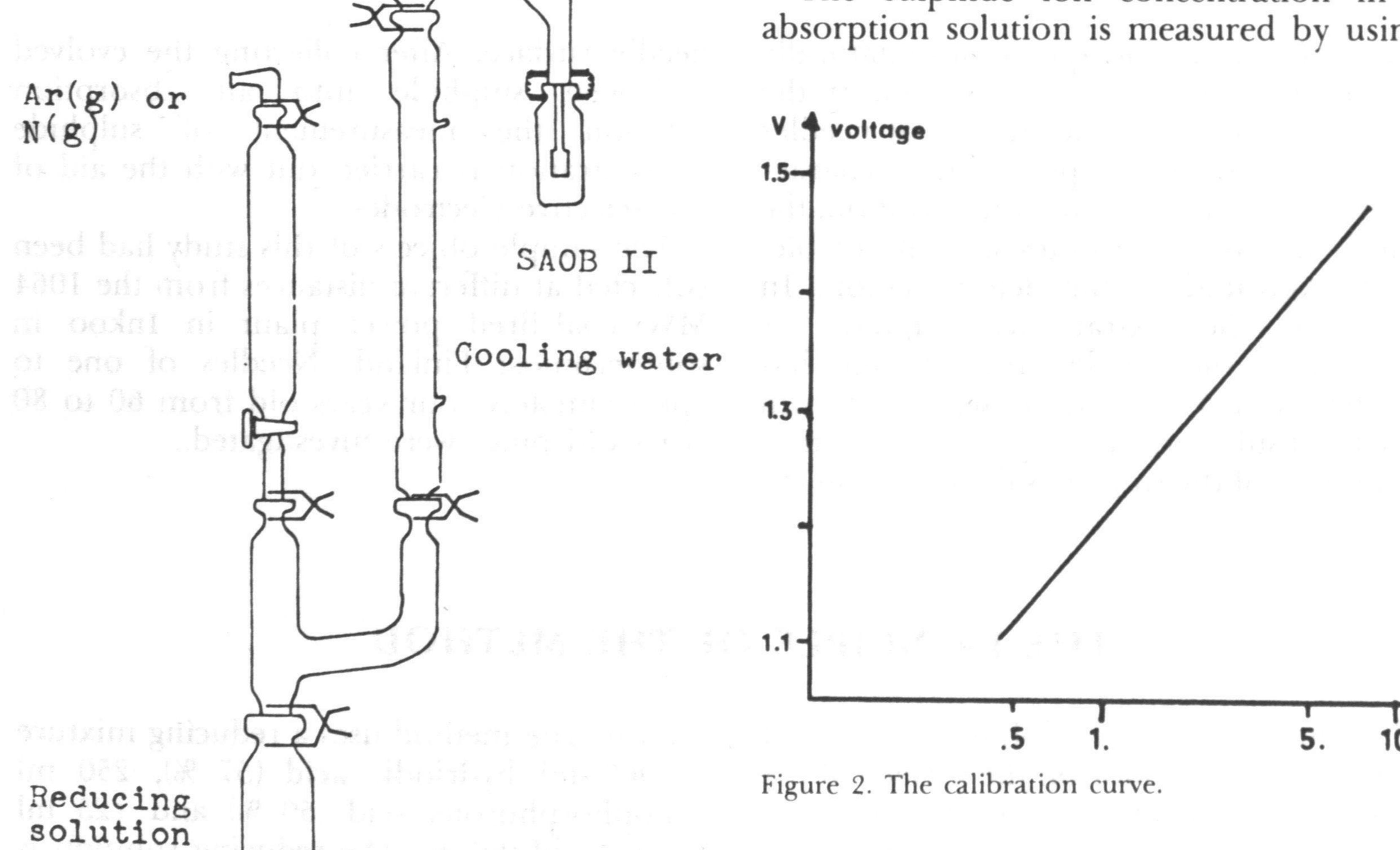


Figure 1. The distillation apparatus.

silver/sulphide1) and a doublejunction reference electrode2) with the outer chamber (see Fig. 1.) filled with 4 M potassium chloride solution. Potential differences of tens to hundreds of mV are measured by a digital voltmeter.

Calibration of the concentration determination is carried out by distilling standardized sodium sulphate solutions in the same way as the samples and by measuring $5\mu g$, i.e. a concentration of 0.5 ppm in 10 g of the respective potentials.

Suitable amounts of sulphur for the

calibration were found to vary from 5 to 1000 µg of sulphur which gave final concentrations of 0.5 to 100 ppm in the absorption solution.

The semilogarithmic plot of the calibration curve is linear up to at least ~ 1000 ppm of sulphur; in this work the practical range for surface determinations was only to ~ 100 ppm of sulphur in the final solution (see Fig. 2.). The detection limit of the method is about sample.

DETERMINATION OF SURFACE SULPHUR IN THE NEIGHBOUR-HOOD OF A COAL-FIRED POWER PLANT

Pine needle samples at distances varying from 0.9 to 15.9 km from a coal-fired (1064 MW) power plant in Inkoo, in Southern Finland, were collected during 1979 and 1980. All needle samples were taken from the sides of the trees facing the power plant and at a height of ~ 10 m. The sample trees were chosen in such a way that the gross depositional conditions should be similar. The trees were of about the same age, 60-80 years old pines or 50 years old spruces and age classes of one year to more than three years old needles were collected. The sampling sites were situated on a line from the power plant, in the north-east direction, which is the most prevailing wind direction in this region of Finland.

Each sample to be processed in the reducing solution contained 0.2 to 0.3 g Table 1. (dried mass) of needles, i.e. an average of 30 pine needles. The needles were dried in 105°C for one day in a drying oven.

For each distance the amount of surface sulphur was derermined by two or more parallel determinations. The results for pine needles are presented in Table I.

The measured average values with estimated ~ 20 percent error bars, including systematic errors, are shown in Fig. 3 as a function of distance from the power plant. The method of moving average was used to smooth the stochastic variations. The moving average ray was calculated by summing three points using formula (1) and by setting the average value in the weighted average distance s_{av} given by equation (2).

$$R_{av} = \sum_{j=i-1}^{i+1} r_j$$

$$(1)$$

$$s_{av} = \frac{\sum_{j=i-1}^{i+1} s_j r_j}{\sum_{j=i-1}^{i+1} r_j}$$
(2)

Distance	Surface concentration	Movint	sav
S _j km	r _j ppm	r _{av} ppm	km
0.9	$72 \pm 14^{(a)}$		
1.2	100 ± 30		
		83	1.6
		73	2.4
2.9	76 ± 15		
4.1	44 ± 9		
		58	5.2
9.2	55 ± 11		
		49	9.9
15.9	50 ± 10		

a) Based on only one determination

¹⁾ Orion Research No 94-16 2) Orion Research No 90-02

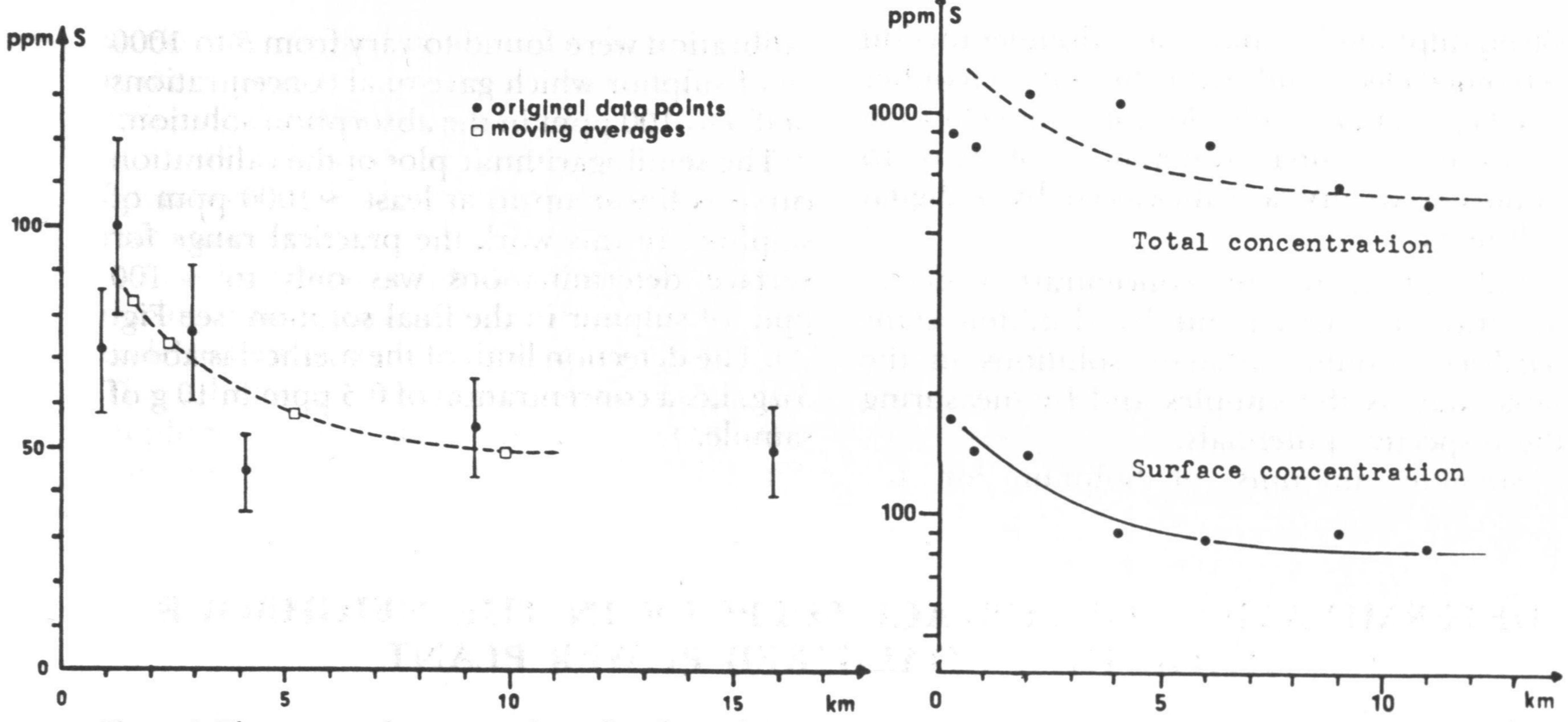


Figure 3. The measured average values of surface sulphur with estimated 20 percent error bars, including systematic errors as a function of distance from the power plant.

Figure 4. Comparison between the total and surface concentrations of sulphur as a function of distance from the power plant.

A nearly constant value is reached at a distance of about 4 km from the power plant. Values closer to the power plant are found to be 50 to 100 percent higher than this background level.

The total concentration of sulphur has been measured also by means of oxidizing the sample in an RF-excited oxygen plasma. Comparison between the total and surface concentrations of sulphur as a function of

distance from the power plant is presented in Fig. 4 for the case where two years old pine needles were analyzed. Similar behaviour as a function of distance for the total and surface values is obtained, the total values being an order of magnitude larger.

In studies on the effect of needle age on the surface concentration of sulphur no significant variation exceeding 10–15 percent was found.

DISCUSSION

The sulphate to sulphide method followed by an ion selective measurement has several advantages as compared to other methods for sulphur determinations. These are the speed, reasonable sensitivity and low detection limit of the method. Also the use of non-toxic reagents and the need for only two solutions for precise analytical work are among the advantages of this method.

Because the specimens being measured

must go through the gaseous phase, most of the possible interferences are eliminated and the method is thus nearly interference free.

Finally, it may be mentioned that this method has also been used extensively in the determination of atmospheric sulphur dioxide, to measure the amount of sulphates in airborne dust and to control sodium sulphite as a food additive (AHONEN, private communication).

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