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DETERMINATION OF MASS OF FILTER-COLLECTED AIR-BORNE PARTICLES BY MEASURING ABSORPTION OF BETA RADIATION

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Abstract

The use of B-radiation absorption measurements for determination of the total mass of filter-collected air-borne particles was investigated for small surface densities. The technique was applied to various types of test dust and atmospheric dust. All the dust showed a dependence between the beta absorption and the surface density of the particles on the filters that differed from the exponential curve which was obtained when using thin foils. The absorption did not only depend on the surface density of the filter-collected particles but also of characteristics of the collected particulate matter.

The B-absorption method showed a standard deviation of about 13 $\mu g/cm^2$ and the lowest allowable amount of particles collected on a filter was set to 50 $\mu g/cm^2$. With a filtration area of 1.54 cm^2 and a sampled volume of 8 m^3 the method enables concentrations of particulate matter down to about 10 $\mu g/cm^3$ to be measured.

Introduction

Low volume sampling is widely used in many air pollution monitoring networks (1,2). For the analysis of the most common gaseous pollutants a sampling volume of a few cubic meters will be sufficient even in remote areas. For the analysis of the particle phase methods based on the measurement of physical or chemical properties of the filter-collected particles have been applied. Good results for the qualitative and quantitative determination of a number of elements and constituents of the particle phase have been obtained by for example x-ray fluorescense, x-ray diffraction and neutron activation analysis (3,4). However, the heterogenous character of the particle phase has resulted in low correlations between physical characteristics and the total mass of particulate matter. Therefore in order to quantify the total mass the weight increment of a filter sample is usually determined.

Gravimetric analysis of filter-collected particles of about 100 µg orless is a rather time-consuming procedure since the filters need to be conditioned prior to and during the weighing. The fact that the result will be a very slight difference (less than 1 %) of the total filter weight after and before sampling may also introduce significant errors.

A promising approach to the problem of determining the total mass of particles is the utilisation of β-radiation absorption. Techniques based on β -radiation absorption are used in a number of automatic instruments, which are adapted to ambient air as well as to stack monitoring. In these instruments the analysis are carried out by measuring the β-radiation absorption of the same filter area prior to and after particle sampling. The difference in absorption is then converted to the mass of particulate matter.

For network purposes the use of β-absorption field instruments usually is considered too costly. However, a measurement pro-

cedure consisting of a combination of field sampling and laboratory analysis seems to be a possibility. When β-absorption techniques are to be used the measurements must be made either before and after sampling on the same filter area, or after sampling on a loaded and an unloaded part of the same filter. The first technique requires that a very good reproductibility of the β-radiation measurements can be achieved and that the humidity is controlled. The second technique needs a filter material of a very constant thickness (surface weight).

In this report experiments have been made to evaluate a method based on loading only a part of the filter and measuring the absorption of β-radiation of the loaded and the unloaded part of the same filter.

Theory

General theory

The intensity of low energy beta-radiation transmitted through an absorber decays exponentially with the thickness of the absorber. This relation holds as long as the thickness of the absorber is less than the range of the actual β-radiation.

For the light elements, where the number of electrons are roughly proportional to the atomic weight, the intensity decays exponentially with the surface density (mass/unit area) of the absorber and thus independently of its chemical composition. This can be expressed by the equation:

$$I/I_{oo} = e^{-\mu_m m_s} \qquad (1),$$

where I_{oo} and I are the intensities before and after absorption, μ_m is the absorption coefficient and m_s the surface density. μ_m is characteristic for each kind of β-radiation and is according to Gleason et al. (5) slightly dependent on the actual geometry and source backing. For a general survey see Overman and Clark (6).

Applied theory

The mentioned effects might be used to determine the surface density of a particle-layer on a filter. When the collection area is known the total mass of the particles may be calculated.

It can easily be shown from equation (1) that the change of the transmitted radiation with the surface density is largest for a surface density

$$m_s = 1/\mu_m$$

Precision

Assume that small differences in $\mu_m \cdot m_s$ are studied. Set

$$\mu_m m_s = \mu_m(m_{so} + M_2)$$

where $\mu_m M_s$ is small. m_{so} can as is shown later represent the surface density of a filter and M_s the surface density of thin layers of a homogenous material on the filter. Fquation (1) can be written

$$I = I_{oo} e^{-\mu_m m_{so}} (1-\mu_m M_s) = I_o (1-\mu_m M_s)$$

and

$$M_s = (1/\mu_m)(1-I/I_o) \qquad (2)$$

The decay of a beta-radiation source can be described by Poisson statistics. Thus, the standard deviation σ of a number of pulses N is $\sigma = \sqrt{N}$. The standard deviation of M_s becomes

$$(1/\mu_m) \sqrt{(1 + I/I_o)/I_o T}$$

where T is the counting time. Observe that this is the theoretical standard deviation resulting from the stocastic nature of the process.

It can be shown that measurement errors due to statistical fluctuations have a minimum when $m_s = 2/\mu_m$, and that measurement errors due to instrumental instability have a minimum when $m_s = 1/\mu_m$ according to Shumilovskii and Mel'ttser (7).

Equipment

Nuclepore filters, 80 CPR 03700, with a nominal pore diameter of 0.8 µm, a thickness of 10 µm and a density of 1 g/cm^3 were chosen. This corresponds to a surface density of roughly 1 mg/cm^2. The diameter of the filters was 37 mm.

A disc (diameter 8 mm) electroplated with ^{63}Ni (activity 3 mCi) was used as beta-radiation source. The half-life of ^{63}Ni is 98 years, the maximum betaradiation energy is 0,067 MeV and the absorption coefficient is roughly 1 cm^2/mg. Thus the product of the absorption coefficient and the surface density is approximately equal to 1, the value of which the sensitivity has a maximum.

The detector was a Geiger-Muller tube (Frieseke & Hoepfner FHZ 80) operated at 800 volts.

The beta-radiation source was placed in a holder. Filters could be inserted directly above the source and placed in two positions. In one position the transmission through the central area of a filter could be measured and in the other position the transmission through an area close to the edge. The GM-tube was mounted above the filter to register transmitted radiation. This set up was enclosed in a brass case to protect the operator from radiation. See figure 1.

For collection of particles on filters, the filter holders were constructed so that the flow would only pass through a circular area (area 1.54 cm^2) centered on the filters.

Measurements

Absorption coefficient

In order to determine the absorption coefficient μ_m, absorption in homogenous layers was studied. A filter was placed in the filter holder and aluminium and mylar foils were laid on the filter. The intensity was measured for surface densities up to 2 mg/cm^2.

Homogenity of Nuclopore filters and edge effects of the filter holder

The uniformity of two filters was examined. The absorption was measured at the centre of the filter and at points of the edge. This was done for eight points evenly spread around the edge. The mean square deviation between different points was found to be of the same magnitude as the statistically expected standard deviation, which was 5µg/cm^2. No nonhomogenities were detectable at this level.

The intensity of transmitted β-radiation was measured at the central area of a filter and at the edge. The mean square deviation between the center and the edge was the same as the expected standard deviation (2 µg/cm^2). Thus, at this level no edge effects were noticeable. When the distance between the GM tube and the filter was increased, edge effects were noticed.

The effect of an increased surface density in the central area of a filter, on the absorption at the edge, was studied. The transmitted intensity at the edge was measured with and without foil with a surface density of 1 mg/cm^2 on the center of the filter. A difference within the expected statistical standard deviation, corresponding to 2 µg/cm^2, was noted. The effect was negligible.

Measurements on talc dust

Two types of ground talc with mean Stokes' diameters with respect to weight of 4 and 8 µm and with densities of 2.8 and

2.9 g/cm^3 were used as test dust. The talc was suspended in water to which wetting agents were added. This suspension was drawn through the central area of a number of filters. The mean surface densities of talc layers were determined gravimetrically.

The absorption was measured for the fine and coarse talc for surface densities up to 2 mg/cm^2.

Measurements on air-borne particles

Sampling of air-borne particles was performed in a marine, clean air area. Air was drawn through a 50 mm funnel at a flow rate of 1.5 l/min as recommended in the OECD report, "Methods of Measuring Air Pollution" (1). The particles were collected on Nuclepore filters, masked as for the talc measurements. The sampling period lasted for three or four days.

The filters were weighed before and after sampling. For each sampling period four filters were used, two filters for collecting particles after the funnel probe, and two as weight reference filters.

Prior to all the weighings the filters were dried in 110°C for 1 hour, and kept in an exicator for half an hour. The filters were weighed on a microbalance with controlled humidity. Prior to weighing the filters were neutralized electrostatically by a β-radiation source.

Particles were also sampled in the city of Gothenburg. A cylinder probe with an internal diameter of 99 mm was used. The flow rate was 0.70 l/min, corresponding to a cut-off size of approximately 5 µm. The sampling periods lasted for one to seven days.

Results

Foils and talc particles

The quotient I/I_o between the transmitted intensity at the central area (I), and at the edge of a filter (I_o), at varying surface densities (M_s) for aluminium and mylar foils as well as the talc particles is found in table 1 and figure 2.

Table 1. The quotient I/I_o between the transmitted intensities at the central area and at the edge of a filter. M_s is the mean surface density of talc layers or foils at the central area.

Fine talc		Coarse talc		Al. and mylar foils	
M_S $\mu g/cm^2$	I/I_o	M_S $\mu g/cm^2$	I/I_o	M_S $\mu g/cm^2$	I/I_o
120	0.913	170	0.878	120	0.905
260	0.847	290	0.849	240	0.830
380	0.715	470	0.709	350	0.740
510	0.638	620	0.621	470	0.642
690	0.540	720	0.614	590	0.571
790	0.490	910	0.525	940	0.431
990	0.411	1040	0.462	1060	0.391
1050	0.421	1160	0.397	1290	0.340
1300	0.334	1240	0.584	1530	0.297
1560	0.299	1550	0.332	2000	0.286
1940	0.264	1620	0.319	2120	0.282
1950	0.256	1810	0.302	2350	0.262
		2110	0.273	2590	0.258

The decay was found to be exponential for the foils up to a surface density of 1 mg/cm^2 with an absorption coefficient for the actual geometry and source backing of 0.874 cm^2/mg.

The absorption curves for the particle layers did not follow the exponential absorption curve. The dependence was linear for low surface densities and approached the exponential dependence for higher surface densities. The slopes of the

linear parts of the curves were 0.62 cm^2/mg for the fine talc and 0.53 cm^2/mg for the coarse talc. The slope of the tangent to the exponential curve at the point where $M_s = 0$ is equal to 0.874 cm^2/mg. See figure 1.

Air-borne particles

Twenty samples of air-borne particles were taken at the clean air station. The absorption $1 - I/I_o$ at different surface densities M_s, is found in table 2 and figure 3.

In order to determine the precision of the gravimetric mass analysis and effects due to handling of the filters, 24 reference filters were weighed. The reference filters were handled as the other filters except for the fact that no air was passed through them. The systematic error was negligible; the mean deviation between the second and the first weighing was found to be -0.2µg. The standard deviation was set equal to $\sqrt{\Sigma \Delta m^2/2 N}$, where Δm was the difference of the weight between two weighings of the same filter. A standard deviation of 9.3 µg was found, corresponding to a surface density of 6.0 $\mu g/cm^2$. Observe that the weighing of the foils and the talc particles was not as accurate as this.

Table 2 The absorption $(1 - I/I_o)$ at different surface densities (M_s) for filter-collected particles from a marine clean air area.

M_s µg/cm²	I-I/I$_o$	M_s µg/cm²	I-I/I$_o$
14	0.0202	55	0.0247
18	0.0037	65	0.0428
18	0.0157	67	0.0526
19	0.0094	72	0.0527
21	0.0099	72	0.0659
29	0.0266	75	0.0421
30	0.0392	89	0.0696
48	0.0555	91	0.0624
52	0.0303	95	0.0678
53	0.0284	117	0.1102

Linear regression analysis gives the relation $1 - I/I_o = 0.783 \cdot 10^{-3} M_s + 0.00157$ (M_s in $\mu g/cm^2$). The value of the intercept is equal to 1.5 $\mu g/cm^2$ (approx.), and the slope of the line is $0.783 \cdot 10^{-3}$ $cm^2/\mu g$ with a total standard deviation corresponding to 15 $\mu g/cm^2$.

Analysis

General absorption curve

The discrepancy between the absorption curves for particle layers and for foils can be explained by two effects:

i) For small surface densities the particles do not cover the whole radiated area.

ii) For larger surface densities the particles cover the whole area, but the surface density varies over the area.

Assume that particles with a total mass M are collected on a filter area A. This results in a mean surface density of the particle layer $M_s = M/A$

Effect i) The particles do not cover the whole filter area.

Assume further that the weight distribution of the collected particles is described by the function $g(m_s(f))$, where $m_s(f)$ is the surface density of a certain fraction f of particles. Moreover m_s is a function of the particle density and shape.

The fraction (f; f + df) has the mass $M \cdot g(m_s(f))\, df$ and covers the area

$$\frac{M}{m_s(f)} \cdot g(m_s(f))df$$

This gives an area, covered by particles

$$\int_0^\infty \frac{M}{m_s(f)} \cdot g(m_s(f)df$$

over which the absorption of β-radiation occurs.

From equation (1):

$$I/I_o = \frac{1}{A} \int_0^\infty \frac{M}{m_s(f)} g(m_s(f))e^{-\mu_m m_s} df + 1 - \frac{1}{A} \int_0^\infty \frac{M}{m_s(f)} g(m_s(f))d$$

which may be expressed

$$I/I_o = 1 - \bar{m}_s \int_0^\infty \frac{g(m_s(f))}{m_s(f)} \cdot (1 - e^{-\mu_m m_s(f)}) df \qquad (5)$$

For a constant μm and weight distribution the integral is a constant k and

$$1 - I/I_o = k\,\bar{m}_s$$

The model is derived from the assumption that the weight distribution determines the surface density and that the area is only partly covered.

The latter is true for

$$0 \leq \bar{m}_s \leq \frac{1}{\int_0^\infty \frac{g(m_s(f))}{m_s(f)} df}$$

Observe that

$$\lim_{m_s \to \bar{m}_s} k = 1 - e^{-\mu_m \bar{m}_s}$$

Which gives the exponential expression for the absorption.

Observe also that

$$\lim_{m_s \to 0} k = \mu m$$

which means that the slope of the absorption curve is always smaller than the slope of the tangent to the exponential absorption curve in the point $M_s = 0$.

Effect ii) The particles cover the whole filter area, but the surface density is not constant over the area.

Assume that the surface density over the filter area can be expressed as $m_s(S)\,dS$, and

$$M = \int_A m_s(S)ds$$

From equation (1)

$$I/I_o = \frac{1}{A}\int_A \exp\,(-\mu_m m_s(S))dS$$

This expression together with

$$\bar{m}_s = (1/A) \int_A m_s(S)\,dS$$

determines the absorption as a function of the mean surface density $\bar{m}_s$.

Note that

$$\lim_{m_s(S)\to\bar{m}_s} I/I_o = \exp\,(-\mu_m \bar{m}_s)$$

which is the exponential expression for the absorption.

Small surface densities

Assume small surface densities, where effect i) works, and that the constant

$$k = \int_0^\infty \frac{g(m_s(f))}{m_s(f)}\,(1 - e^{-\mu_m m_s(f)})\,df$$

is determined for one kind of dust. If the constant $k = k'$ is used in calculations with another kind of dust with a constant k'' the result will be an erroneous value M_s' of the real surface density M_s''. From equation (5)

$$M_s' = k''/k' M''_s = M_s'' + \Delta M_s$$

The error is proportional to the actual surface density.

Example: If the shape and density of particles are constant, but the size growing larger, k will decrease. When the uncorrected k is used, this will result in an underestimation of the surface density.

Theoretical calculation of the slope of the absorption curve

Assume that the talc particles are cubical in shape. Using given data on the particle size distributions and the talc densities give k = 0.63 mg/cm^2 for the fine and k = 0.54 cm^2/mg for the coarse talc. These values can be compared with the results from the absorption measurements 0.62 and 0.53 cm^2/mg respectively.

Air-borne particles have previously been studied at the clean air station. The size distribution have been studied with a Royco particle counter, which registers the number of particles in certain size intervals. An uncertain value of the particle density has also been determined. When the particles are assumed to be cubic, the results give k = 0.50 cm^2/mg. The constant was found to be 0.78 cm^2/mg at the absorption measurements. The differences might be due to the uncertain determination of density and non-cubical particles.

There is not enough relevant knowledge of air-borne particles to make a correct calculation of the constant k.

Air-borne particles

Evaluation of the primary results of the particles from the clean air station gave k = 0.783 cm^2/mg. The total standard deviation from this line was found to be 15 µg/cm^2. If the standard deviation of the gravimetric analysis is corrected there will still be a standard deviation of about 13µg/cm^2 due to the characteristics of the particles, counting statistics etc.

Discussion

Absorption of β-radiation in thin particle layers cannot generally be described as an exponential function. For particles, smaller than approximately 10 µm, at surface densities lower than approximately 1 mg/cm^2, the absorption is a linear function of the surface density. The proportional factor depends on the size distribution, density and shape of the studied particles.

For measurements of the concentration of air-borne particulate matter two alternatives exist; measurement of surface densities larger than 2 mg/cm^2 or measurement of surface densities lower than 1 mg/cm^2. The high surface densities result in an exponential absorption. However, this requires large sampling volumes and/or small collection areas on filters. Assume for example that there are a minimum particle mass concentration of 5 µg/cm^3 and a sampling volume of 1 m^3. If the surface density is to exceed 2 mg/cm^2, the particles would have to be collected on a filter area less than 2.5 · 10^{-3} cm^2. Low surface densities result in linear absorption, but reflect variations in particle size distribution, density and shape.

The statistical nature of the radiation process will give a contribution to the standard deviation. It is mainly dependent on the counting period. For counting periods of 1 minute it is in this case 5 µg/cm^2. It composes a small part of the total standard deviation.

The described method for determination of surface-densities by β-absorption measurements resulted in a standard deviation of about 13 µg/cm^2 for surface-densities of 100 µg/cm^2 and less. This standard deviation reflects deviations of the β-absorption technique as well as changes of the particle phase, losses of particles during filter handling, absorption or desorption of water or other volatile compounds and variations in particle collection characteristics of the sampling probe and filters.

In view of the magnitude of the standard deviation a minimum determinable surface-density can be set at about 50 $\mu g/cm^2$ When concentrations of particulate matter around 10 $\mu g/cm^3$ are to be analyzed quantitatively, it is necessary to sample an air volume of 8 m^3, using the filters described in this report (sampling area 1.54 cm^2). It is moreover necessary to know the characteristics (the constant k) of the particulate matter to be sampled.

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Figure 1 Schematic of the measuring set up. In position 1 the ß radiation is measured after passing the filter and the particle layer, in position 2 after passing only the filter. Distances in mm.

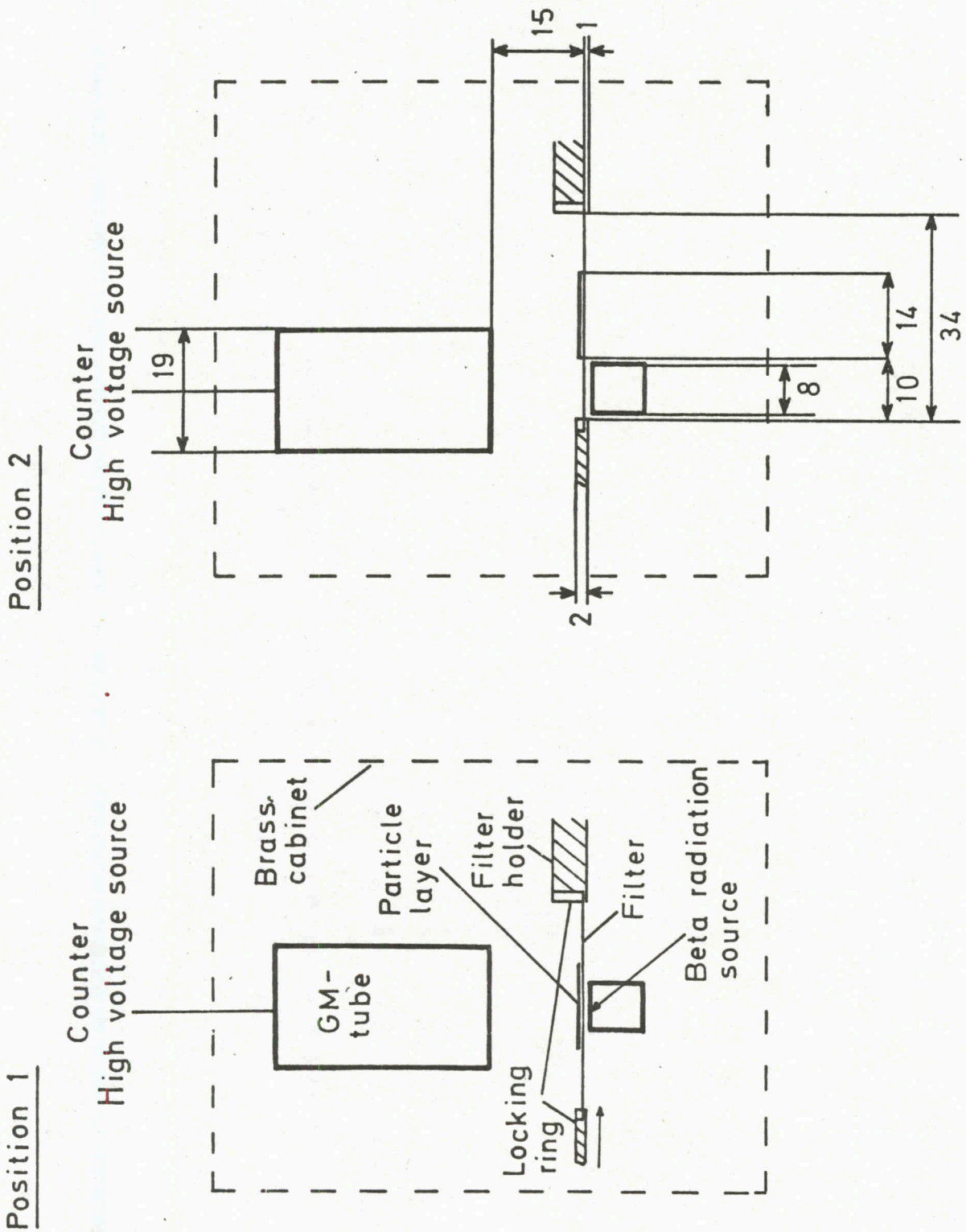

Figure 2 $1 - I/I_0$ as a function of mean surface density (M_S) for talc particles and foils.

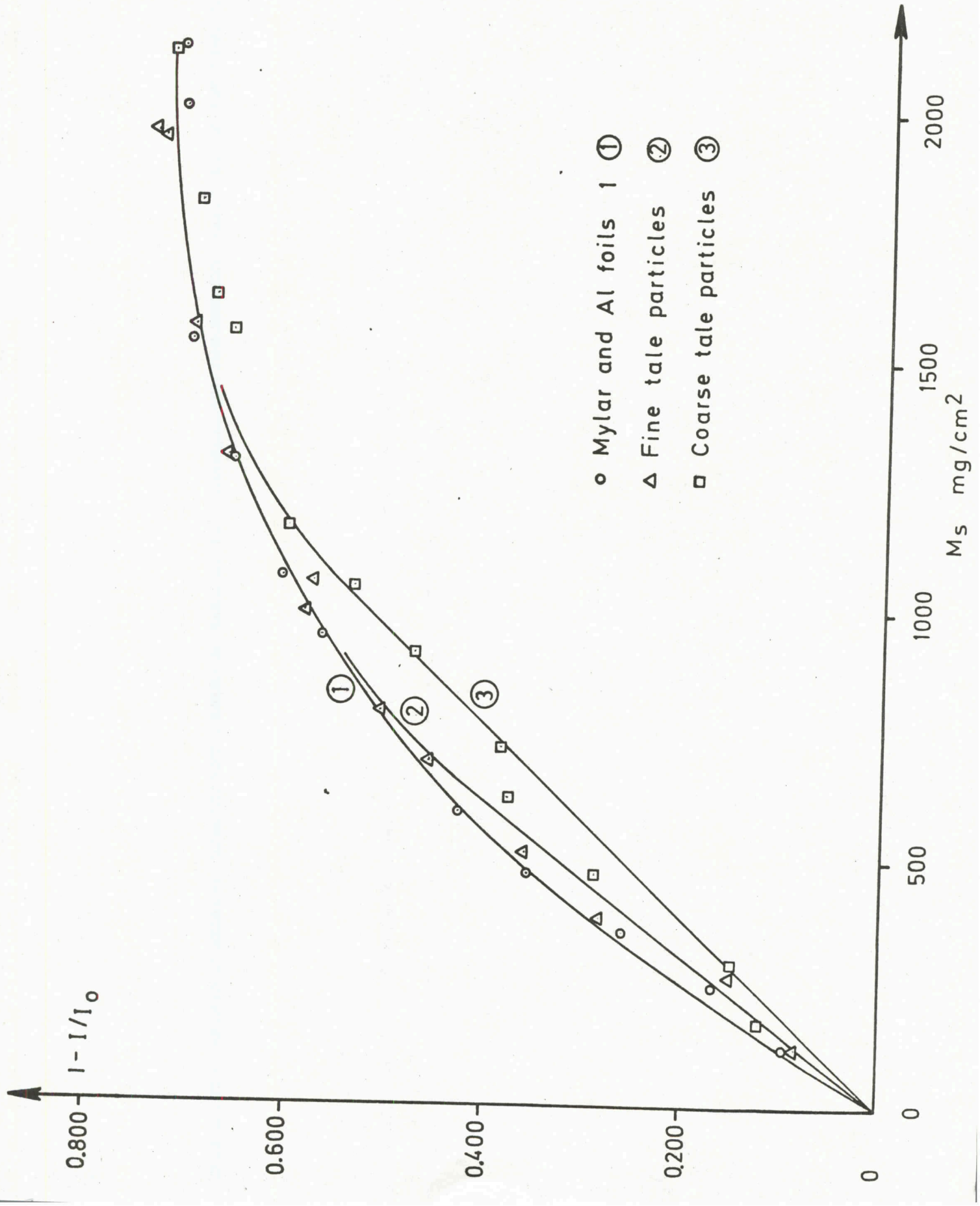

Figure 3 The β absorption $(1 - I/I_0)$ as a function of the mean surface density (M_S) of particles collected at a remote station 40 km south of Gothenburg.