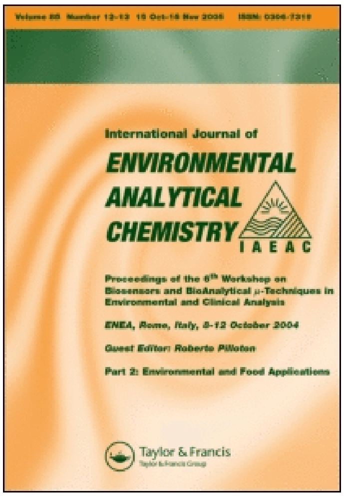

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Development and Laboratory Investigations of a Denuder Sampling System for the Determination of Heavy Metal Species in Flue Gases at Elevated Temperatures

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DEVELOPMENT AND LABORATORY INVESTIGATIONS OF A DENUDER SAMPLING SYSTEM FOR THE DETERMINATION OF HEAVY METAL SPECIES IN FLUE GASES AT ELEVATED TEMPERATURES*

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A denuder sampling system was developed to measure volatile metals at elevated temperatures. By using the denuder technique it is possible to avoid condensation and adsorption losses in the sampling line. To investigate the behavior of heavy metal species under different physical and chemical conditions, a laboratory scale quartz stack was built. Metal aerosol generators based on evaporation, diffusion and condensation are described. The diameter of the generated particles varied between 0.05–0.3 μm. The day to day reproducibility of the generation varied between 0.6–5.0% for chromium and2.8–4.0% for cadmium (95% stat. significance).

Denuders coated by elemental silver seem to be an efficient means for sampling of elemental Cd at 200 °C. The diffusion coefficient of Cd was calculated from experimental data, and the value of $(0.42 \pm 0.04)\,\mathrm{cm^2/s}$ was obtained. A detection limit of $0.2\,\mu\mathrm{g/m^3}$ for Cd determination can be reached by using a Ag-denuder, when a sampling time of 30 min and a flow rate of 60 l/h is employed.

KEY WORDS: Aerosol generation, metal species, emission measurement, cadmium, denuder sampling, incineration, speciation.

INTRODUCTION

Many toxic heavy metals like Cd, Hg and Pb volatilize easily in high-temperature processes like waste incineration, coal combustion and metal smelting.[1] In Figure 1 a schematic diagram of the formation of heavy metal aerosol after combustion is shown. Usually fuel is burned in the form of particles or droplets at temperatures of 800–1400 °C depending on the type of process (800–1100 °C for waste incineration, 1300–1400 °C for coal combustion).

Part of the usually non-volatile material (Fe, Cr, Si) can vaporize under the locally reducing conditions, i.e. in the presence of carbon monoxide[2]:

$$MO_n + CO \rightarrow MO_{n-1} + CO_2 \tag{1}$$

Suboxides formed this way will reoxidize quickly in oxidizing atmosphere

$$MO_{n-1} + \tfrac{1}{2}O_2 \rightarrow MO_n \tag{2}$$

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†On leave from Technical Research Centre, Finland, Laboratory of Heating and Ventilating, Espoo, Finland.

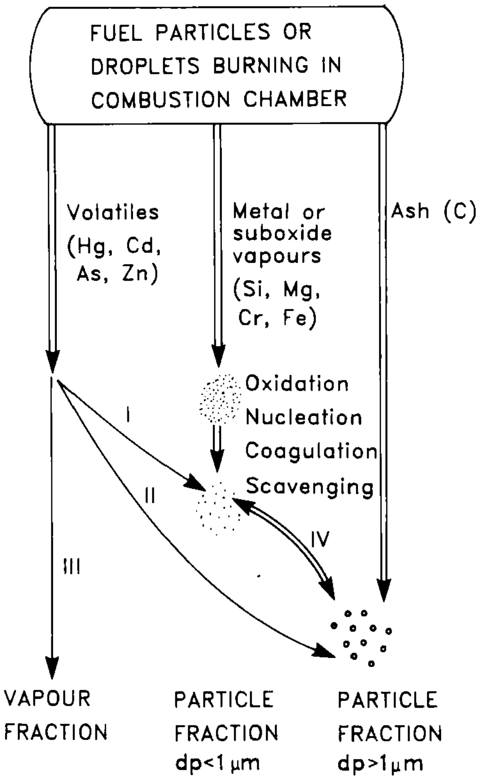

Figure 1 Schematic diagram of the formation of heavy metal aerosol after combustion of fossil fuel or waste.

Because of the high supersaturation state of the volatilized metal species small particles will be formed through homogeneous nucleation.[5] These particles grow by condensation and coagulation but remain still in the submicron range. Volatile metals (Hg, Cd, Zn, As) condensate on small particle surfaces or remain as vapors (pathways I and III, Figure 1).[3,4] Condensation on residual ash particles ($d_p > 1\ \mu m$, pathway II) is insignificant because of the relatively small surface area in this size range—about 1% of that of small particles.[5]

According to thermodynamic calculations[6] volatile metals appear mainly in elemental form or as halogenides at higher temperatures.

In emission measurements it is important to be able to collect metals in gas phase and particle phase separately in order to understand the behavior of trace metals in the combustion process and in the environment after release into the atmosphere. Particles can be collected by filters or in size fractions by cyclones or impactors. Because of many difficulties in sampling of the gaseous fraction, new methods have been developed.[3,4] Instead of using conventional absorption in liquid acids, direct gas phase reaction between metal and acid vapor and subsequent efficient cooling have been employed also.[3,4] This type of sampling is undoubtedly more efficient than liquid absorption, but also more complicated. One problem in these systems is possible adsorption and condensation of metal vapor on the walls of the tube between the probe in the stack and the sampling device itself. In laboratory experiments it could be noticed that for instance 40% of Cd in gas phase was deposited in the PTFE tubes employed (=0.6 m length).

This problem can be avoided by using a denuder sampling technique, which is based on deposition of gas molecules on a reactive wall coating when passing through a diffusion tube. Particulate matter, due to the order of magnitudes lower diffusion coefficients, is penetrating such a tube almost completely. Denuder sampling has been mostly used to collect acids and acidic compounds in the atmosphere.[7–9] In a few cases gaseous metal species such as tetra-alkyl lead have also been determined using denuder tubes.[10] The efficiency of denuders may be expressed by

$$\frac{C}{C_0}=f\left(\frac{DL}{Q}\right) \tag{3}$$

Here D is the diffusion coefficient, L the tube length and Q the flow rate through the tube. The ratio $C/C0$ is a measure for the penetration, and C and $C0$ are the concentrations of the species under study at the outlet and the entrance of the denuder tube, respectively. The ratio (C/C_0) can be calculated by the Gormley–Kennedy equation.[11] When diffusion coefficient and flow rate are known, the tube length necessary to achieve complete deposition of the gaseous metal can be calculated.

Denuders offer the advantage that they can be adapted to the temperature necessary to avoid chemical or physical changes of the matrix from which the trace compounds have to be extracted. In case of emission measurements of flue gases from e.g. combustion processes, a temperature typical in a stack at the sampling point, i.e. 200 °C, should be employed.

The flow in a denuder tube must be laminar and fully developed. Consequently Reynolds number must be smaller than 2000, and this fact restricts the flow rate to an upper limit, which however is never reached in the denuder sampling systems described in the literature so far.

The flow is normally not laminar at the entrance of the tube. The tube length L_t (turbulent length) required for the development of laminar flow can be expressed by equation (4).[12]

$$L_t=0.035\,d\,Re \tag{4}$$

Here Re is Reynolds number and d is the tube diameter.

In order to avoid turbulent deposition of compounds to be determined, the section L_t at the entrance of the tube should not carry a wall coating and should not be used for analysis.

We report here the development and laboratory investigation of a denuder sampling system for the collection of gaseous metal species at elevated temperatures. Also described are aerosol generators and a laboratory "stack" for simulation of flue gas conditions and investigation of denuder performance. The latter is demonstrated using Cd metal aerosol as a first example.

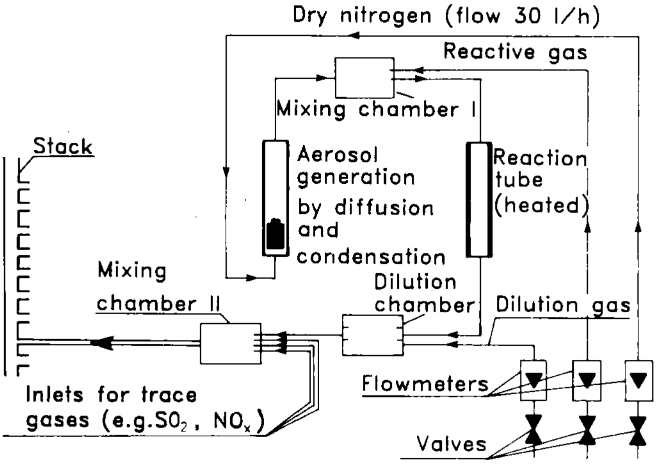

Figure 2 Scheme of the generation system for metal aerosols.

GENERATION OF METAL AEROSOLS

In Figure 2 a scheme of the generation system for metal aerosols is presented. Primary aerosol is generated in a heated diffusion cell (Figures 3 and 4).[13] In mixing chamber I the primary aerosol can be mixed with a reactive (e.g. O_2) or non-reactive gas (e.g. N_2) and be converted by e.g. oxidation (generation of $PbSO_4$ from PbS) or just by thermal decomposition (generation of chromium from Cr $(CO)_6$). The aerosol can be diluted with an inert carrier gas (normally N_2) and additionally be mixed with some trace gases, typical for the composition of exhaust (e.g. SO_2, NO_x, CO), in mixing chamber II.

The diffusion cell (Figure 4) is made from a special ceramic material (Stenan^R) and is installed in a quartz tube, which can be electrically heated (Figure 3). The cell is filled with 5–10 g of the metal or metal compound (analytical grade) to be vaporized. It is closed by a pierced plate (aperture 1–5 mm) and a plug with a bore hole of 5 mm diameter. A stream of dry nitrogen (30 l/h) flows through the quartz tube and carries the vaporized material.

After having passed the diffusion cell the gas is cooled down and small particles are formed through homogeneous nucleation. Part of the material stays in the gas phase and a fraction of it is deposited immediately on the glass walls. The particles remaining in the gas flow grow through coagulation.

The output of the generator—in mass per time unit—was determined by taking filter samples in the generator outlet and analysing them, for instance by XRF.

Some results for aerosols generated in this way are presented in Table 1. The amount of particulate matter released in a certain time was found to be exponentially dependent on the temperature in the diffusion cell, which agrees well with the Clausius–Clapeyron equation.[14]

The influence of the holeplate aperture on aerosol concentration was also investigated. In Figure 5 the results obtained by chromium are given as an example.

Particle size distribution of the generated aerosol was investigated by taking scanning electron micrographs on polycarbonate filters. Particle diameter varied

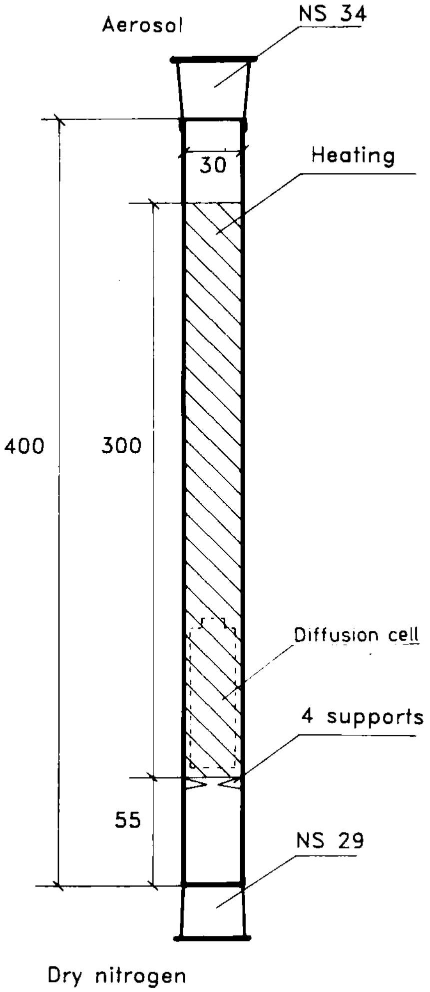

Figure 3 Heated quartz tube for the generation of metal aerosols. (Dimensions in mm).

between 0.05–0.3 μm. The day to day reproducibility of the generation of the metal aerosols varied for instance for chromium between 0.6–5.0% (95% stat. significance) and for cadmium between 2.8–4.0% (95% stat. significance). The stability of the output of the aerosol generators was investigted employing different sampling times. In this case the samples were taken with Whatman 40 filters (behind mixing chamber II), the sampling flow being 140 l/h. The filters were analyzed by XRF (Figure 6).

LABORATORY "STACK" FOR SIMULATION OF FLUE GAS CONDITIONS

To investigate the behavior and measurement of heavy metal species under different chemical (addition of reactive trace gases) and physical (temperature)

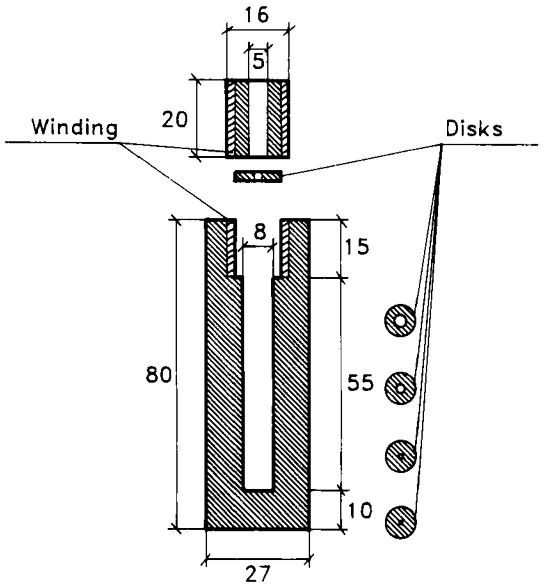

Figure 4 Diffusion cell made from Stenan^R for the generation of metal aerosols. (Dimensions in mm).

Table 1 Aerosols generated by the described technique.

Generated aerosol	*Primary aerosol*	*Generation-temperature (°C)*	*Reaction-gas*	*Temperature reaction tube (°C)*	*Generation-rate (µg/min)*	*Ref.*
Cd	Cd	470	—	—	11	—
Zn	Zn	620	—	—	70	—
Pb	Pb	1050	—	—	n.d.	—
Cr	$Cr(CO)_6$	110	—	230	5	—
Cr_2O_3	$Cr(CO)_6$	110	O_2/O_3	950	n.d.	—
PbBrCl	PbBrCl	515	—	—	11	13
PbS	PbS	580	—	—	20	13
$PbSO_4$	PbS	540	O_2	600	2	13
CoS	CoS	680	—	—	7	—

n.d. = not determined

conditions on a laboratory scale a 90 cm high quartz stack of 5 cm internal diameter was built (Figure 7).

It is equipped with 7 outlets as measurement points, which can be closed by quartz plugs when not used.

The stack has two heating zones (resistance heating), so that the temperature in the first zone—up to 900 °C—is close to the temperature in a real combustion chamber. The second heating zone is exhibiting a negative temperature gradient —controlled by the heating voltage (Figure 8)—so that the cooling rate of the hot aerosol is comparable to the one observed under real conditions:

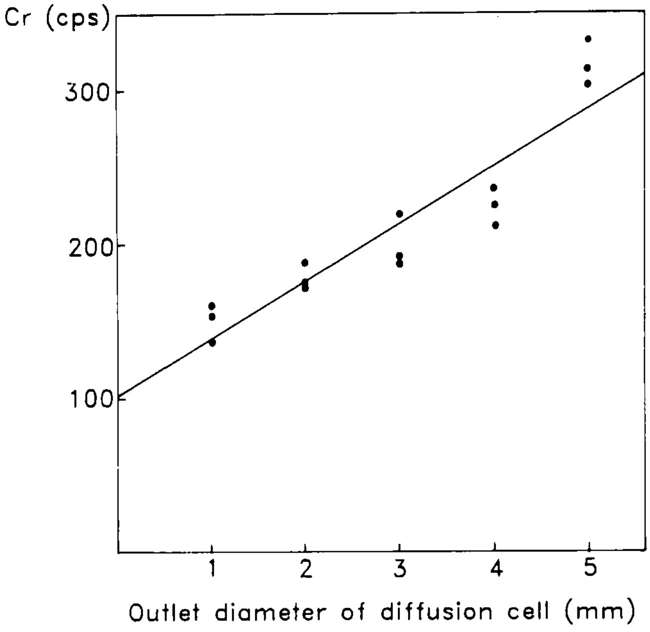

Figure 5 Effect of the aperture of the pierced plate on the generation of chromium aerosol. Sampling time 3 min.

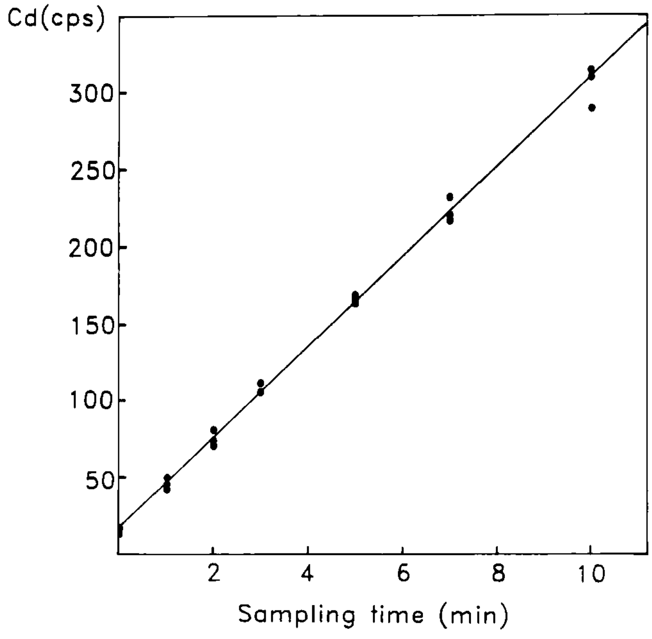

Figure 6 Stability of generator output as a function of time (cadmium).

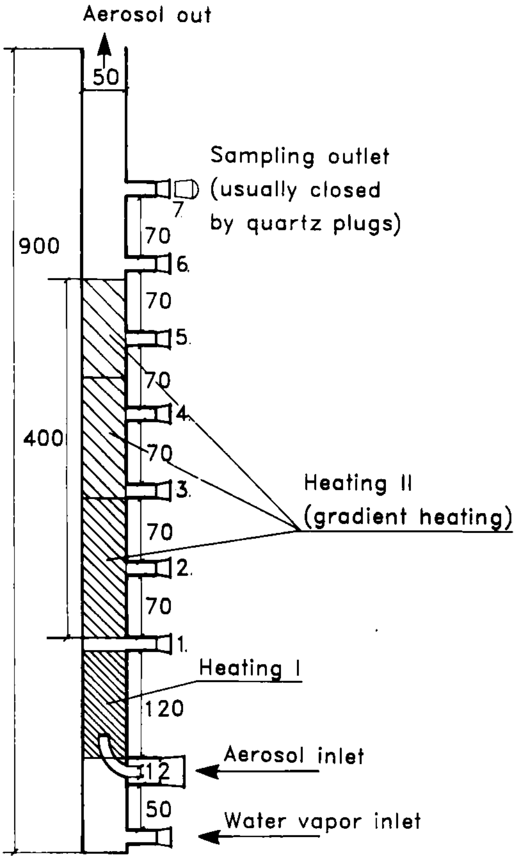

Figure 7 Scheme of laboratory stack made of quartz glass. (Dimensions in mm).

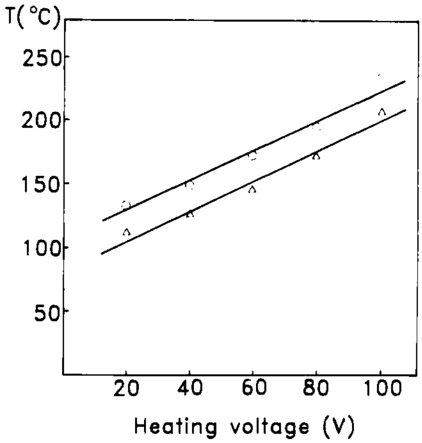

Figure 8 Temperature at measurement point 5 as a function of heating voltage. Temperature in heating zone I = 820 °C; Q = 300 l/h
○ = dry gas
△ = humidified gas (50 g H_2O/m^3)

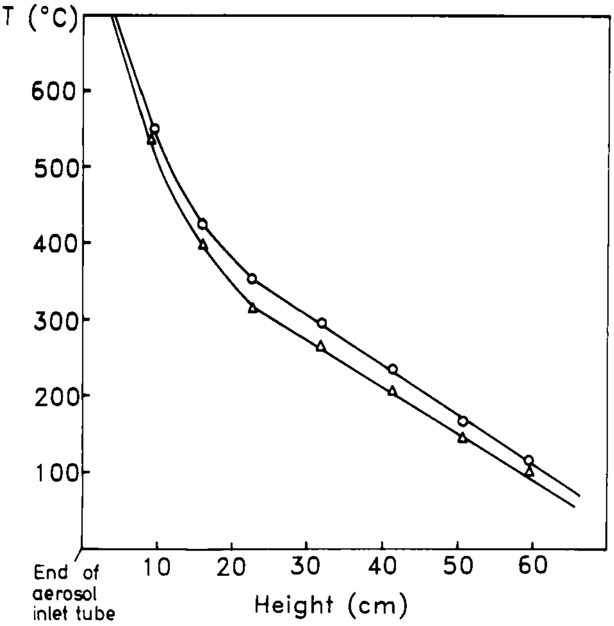

Figure 9 Temperature profile in the stack. Heating voltage 100 V. Temperature in heating zone I 820 °C. Q = 300 l/h
○ = dry gas
△ = humidified gas (50 g H_2O/m^3)

$$\left(\frac{\Delta T}{\Delta t}\right) \text{lab. stack} \approx \left(\frac{\Delta T}{\Delta t}\right) \text{real stack.} \tag{5}$$

The total flow rate in the stack employed in these experiments was 300 l/h. The "stack gas" could be humidified by mixing the aerosol flow from the metal generators in heating zone I with humidified N_2 (flow 100 l/h) (see Figure 7).

Denuder measurements were carried out at measurement point 5 at which the temperature can be varied between 100–300 °C (normally 200 °C, Figure 8). Humidity of the stack gas was varied between 0–50 g H_2O/m^3. At 50 g H_2O/m^3 temperature was about 25 °C lower compared to dry gas at measurement point 5.

Temperature as a function of stack height at constant heating voltage is presented in Figure 9.

MEASUREMENT OF HEAVY METAL AEROSOL BY DENUDER TECHNIQUE

The scheme of the collection system connected to the quartz stack is presented in Figure 10. A coated borosilicate glass tube (length 50 cm, i.d. 0.6 cm) was used as a denuder. It was connected to a 37 mm diameter filter holder. Both denuder tube and filter holder were mounted in a tubular oven which was kept at 200 °C.

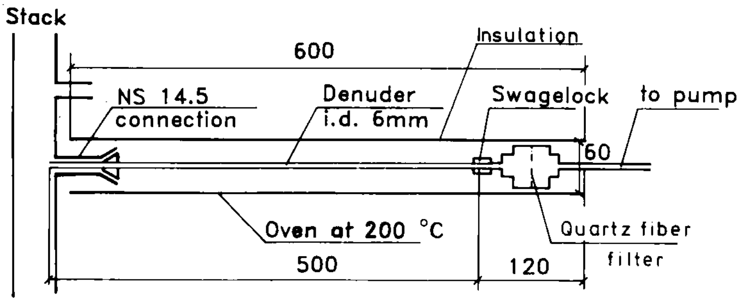

Figure 10 Denuder test system connected to the laboratory stack. (Dimensions in mm).

Experiments were carried out using Cd metal aerosols. For collection of Cd vapour denuders with a coating of elemental silver were employed, leading to Cd deposition at the walls.

The denuders were prepared from glass tubes of 50 cm length, which were coated by reducing Ag^+ from 0.1 M Ag_2SO_4/NH_3-solution using HCHO as a reducing agent according to the following procedure: One end of the glass tube was closed by an Eppendorf^R vessel (1.5 ml, polypropylene) and 2 ml of Ag_2SO_4/NH_3-solution (5% NH_3) were pipetted through the other end followed by 100 µl of NH_3-solution (25%) and 100 µl of HCHO-solution (35%). This was repeated 6 times so that the tube was full, except 5–10% of the total volume. This rest was left uncoated to avoid collection of metal vapour through turbulent deposition (see eq. 4). After the filling the tube was immediately heated up to 90 °C and a layer of elemental silver was formed on its inner wall.

After sampling the Ag-coating was eluted with 2 ml of concentrated HNO_3 (Merck suprapur^R) and the solution diluted with bidistilled water for analysis.

The whole laboratory sampling system for Cd measurements is presented in Figure 11. Particulate Cd was collected by the back-up filter (Munktell MK 360.37 mm). Denuder efficiency investigations were made by using a cold trap (solid CO_2 + acetone) and 3 absorption bottles (3 M HNO_3, suprapur) in series. Each part of the system and also the connecting PTFE tubes were analyzed separately by using flameless AAS. The flow rate employed in the measurements varied between 30 and 120 l/h. The temperature in all experiments was ≈850 °C in heating zone I and 200 °C at measurement point 5. Denuder efficiency was calculated from the following mass balance:

$$E_{\text{den}} = \frac{100\, m_{\text{den}}}{m_{\text{den}} + m_{\text{coldtrap}} + m_{\text{abs}} + m_{\text{tubing}}}\,\% \qquad (6)$$

where m = mass of Cd^0.

RESULTS AND DISCUSSION

Deposition of particulate Cd onto denuder walls was investigated by taking filter

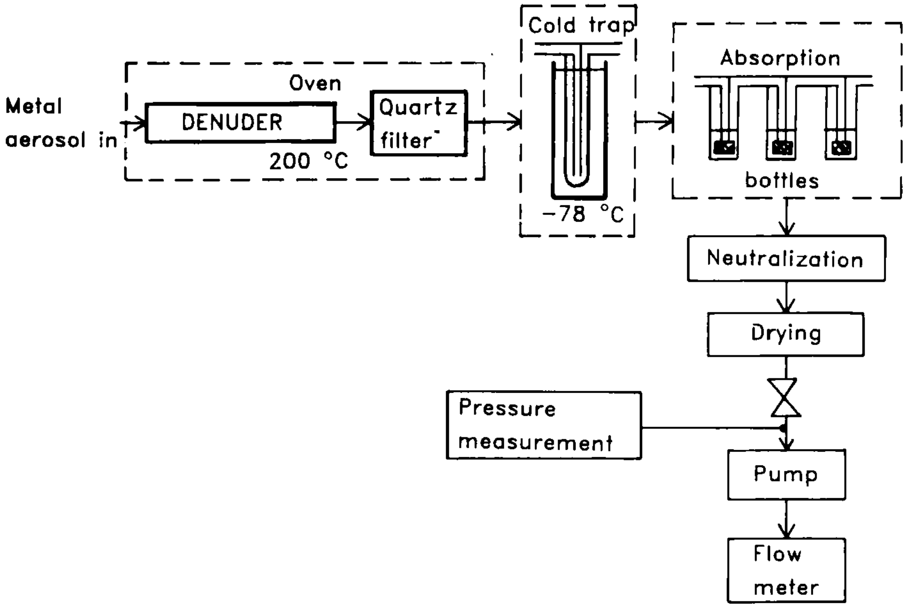

Figure 11 Laboratory sampling system for Cd measurement. Absorption liquid 3M HNO_3. Neutralization agent 1M NaOH and drying agent silica gel.

Table 2 Collecion efficiencies of Ag-denuders for measurement of Cd^0-vapor. Sampling time 10 min.

Sampling flow rate l/h	*H_2O content g/m³*	*Denuder*	*Cold trap*	*Cd µg/m3*		*Denuder efficiency %*
				Abs bottles	*PTFE tubes*	
30	0	400	—	0	—	>99
30	50	170	8	28	3.3	81
60	0	330	—	0	—	>99
60	50	550	4	43	0.7	92
90	0	330	7	9	1.2	95
120	0	240	1.3	0	0.2	99

samples directly from the stack with a probe mounted near the measurement point 5, and after the denuder tube (back-up filter) at measurement point 5, when the stack was not heated. Obviously no particle losses occurred, in the denuder, because no statistically significant difference could be noticed between the two filter measurements. About 10% of the amount of particulate Cd was found in the denuder. This means that also without stack heating part of the Cd was still in the gas phase.

When stack heating was on almost all the Cd could be found in the denuder, i.e. 8–9 times the amount found on back-up filter.

The efficiency of Ag-denuders for collection of Cd^0-vapor was calculated according to the mass balance equation (6). Efficiencies are shown in Table 2.

Diffusion in the denuder was investigated by cutting the tube into 8 sections

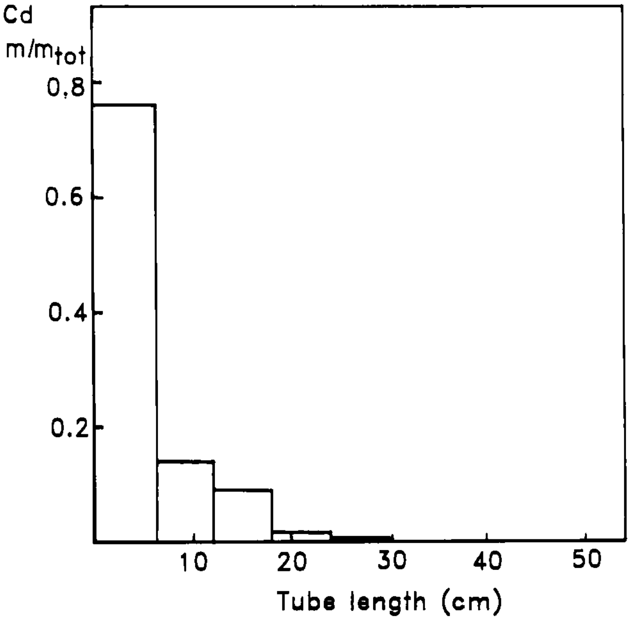

Figure 12 Deposition of Cd in different sections of the denuder tube. Flow rate 60 l/h; m_{tot} = total amount of Cd in all sections of the denuder tube.

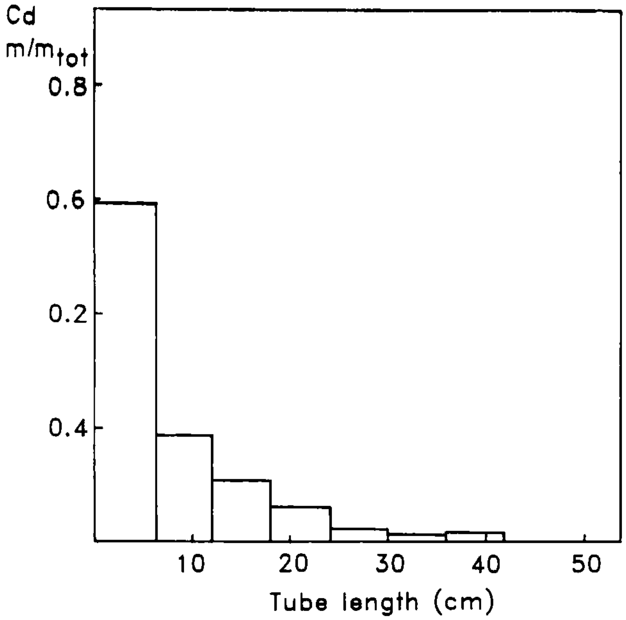

Figure 13 Deposition of Cd in different sections of the denuder tube. Flow rate 90 l/h; m_{tot} = total amount of Cd in all sections of the denuder tube.

after sampling and analyzing each section separately. This experiment was made at three different flow rates: 60, 90 and 120 l/h. The results are shown in Figures 12–14.

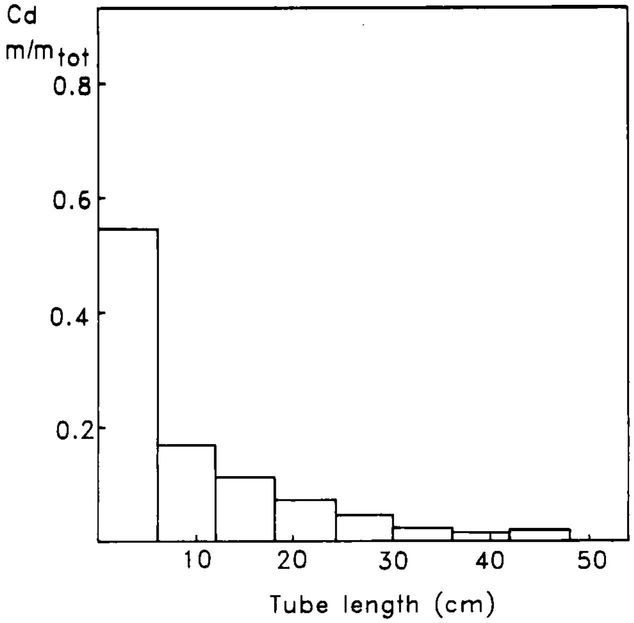

Figure 14 Deposition of Cd in different sections of the denuder tube. Flow rate 120 l/h; m_{tot} = total amount of Cd in all sections of the denuder tube.

Using the data of the sections analyses it was possible to calculate the diffusion coefficient of Cd^0 at 200 °C according to the Gormley–Kennedy equation as reformulated by Durham and Spiller.[15]

$$G_j = 0.819 T_i (e^{3.657 D_i dt_x r^{-2}} - 1) \cdot e^{-3.657 D_i t_j r^{-2}} \tag{7}$$

G_j	amount deposited in jth denuder section
T_i	total amount entering the denuder
D_i	gas diffusion coefficient at the experimental conditions
dt_x	axial displacement time for transport through the length of a section of the denuder
t_j	axial displacement time for travel of the gas from the inlet through section j, $j > 1$
r	radius of the cylindrical diffusion denuder.

Because the plot of ln (G_j) vs t_j gave a straight line it can be assumed that the deposition of Cd^0 in denuders is limited by gas phase diffusion to the denuder wall. The value of $(0.42 \pm 0.04)\,cm^2/s$ for D_i was calculated from the slope of the line.

The stability of the denuder sampling was investigated by using different sampling times. The amount of Cd found was always a linear function of sampling time as is shown in Figure 15.

The real conditions in stack gases are often so complicated that many parameters have to be taken into account. Further experiments are needed to

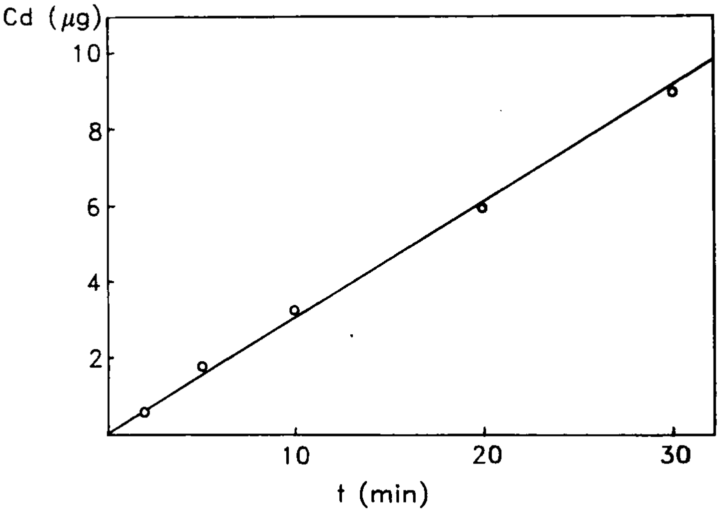

Figure 15 Amount of Cd found in a denuder as a function of sampling time.

investigate the influence of reactive trace gases (SO_2, NO_x) on denuder collection efficiency. Cyclones or impactors have to be used for preseparation of larger particles under real conditions.

As these first experiments have shown, Ag-denuders seem to offer an efficient and sensitive possibility for measurement of elemental Cd in gaseous and particulate form. A detection limit of $0.2\,\mu g/m^3$ can be reached by combining denuder sampling with flameless AAS and employing sampling times of 30 min and flow rates of 60 l/h.

Under the same sampling and analysis conditions the detection limit of only $5\,\mu g/m^3$ could be reached by using conventional absorption bottles (50 ml HNO_3). Besides having the lower detection limit, the denuder technique also avoids many errors inherent in stack sampling procedures since the sampling may take place directly in stack at flue gas temperature.

Acknowledgement

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