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A Method for Transferring Derivatisation Reagent to Individual Airborne Sub-micrometer Particles

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ABSTRACT

The sampling and analysis of reactive compounds in aerosols present a challenging problem in the field of industrial hygiene. The use of reagents to transform the reactive compounds to stable forms, suitable for instrumental chemical analysis, is often necessary. It is thereby important that the reactive compounds are transferred to stable forms before reaction with moisture and other sampled contaminants occur. A specific problem with sub-micrometer particles is that methods based on inertial collection of these particles into liquid reagents have poor collection efficiencies due to the low mass of the sub-micrometer particles.

A device with which a reagent can be vaporised and then condensed onto sub-micrometer airborne particles, prior to the collection of them, has been constructed and tested for di-n-butylamine that is a suitable reagent when determining airborne isocyanates. The results show that the reagent can be condensed onto sub-micrometer particles so that the single particles are embedded in reagent droplets. Typical mass ratios between reagent and particle that can be achieved in each droplet are in the range 10^2 - 10^5 . This minimises the risk of chemical changes due to moisture and other components in sampling/analysis of reactive components in aerosols prior to the derivatisation. The growth of the sub-micrometer particles to 5-10 μm facilitates the collection with techniques based on inertial impaction.

INTRODUCTION

Today there is an increasing concern about the indoor air quality in industrial, office and home environments. Reactive and irritating compounds in the air are important constituents to consider in health effect assessments. There have been many investigations of reactive low molecular weight compounds like formaldehyde, but for reactive compounds that partition between gas and particle phase there are still several methodological problems (Soderholm 1995).

In order to analyse reactive compounds in the environment, they normally have to be transferred to a stable form as soon as possible after sampling. The most commonly used technique for this process is called derivatisation, where the reactive compound reacts with a specific reagent to a stable derivative. Sources of errors from the derivatisation process are for example the occurrence of reactions with other compounds in the sampled aerosol and poor reagent transport into particles collected on a sampling substrate. In addition, low collection efficiencies for sub-micrometer particles when using standard techniques as sorbent tubes and impingers can underestimate exposures. (ACGIH 1995, Spanne 1999). Sub-micrometer particles have too low mass to be sampled with conventional inertial techniques and often the particles carrying most of the mass have too low diffusivity to be collected with devices based on collection by thermal diffusion.

Thermal degradation products of polyurethane in workplace air (Karlsson *et al.* 1998) constitute typical reactive pollutants for which there is a need for improvements of sampling and analyti-

cal techniques. Many types of hazardous isocyanates in both gas phase and in sub-micrometer particles are emitted when polyurethane is heated. The condensation device presented here was developed initially with a focus on that particular problem.

The purpose of this work was to develop and evaluate a method capable of supplying a reagent to particles prior to collection and thereby, in addition to the immediate start of the derivatisation reaction, increase their size so that they easily can be collected with inertial particle collectors. This procedure minimise the influence of sampling on the chemical composition in the particles before the derivatisation reaction has taken place. Furthermore, this increase the collection efficiency for sub-micrometer particles compared with passing the particles directly through an impinger, which is a standard method for collecting particles into liquid reagents.

DESIGN OF THE DEVICE

A device facilitating sampling and derivatisation of reactive compounds in sub-micrometer particles was developed, where a derivatisation reagent is supplied to the particles before collection. The device presents a method to supply a derivatisation reagent directly to particles in an aerosol.

The evaporation-condensation device is shown in Figure 1. It works as the corresponding part of a conductive-cooling-type condensation particle counter (Willeke and Baron 1993). The device consists of a heated evaporation chamber (B) and a condensation chamber (C), which is held at a lower temperature. In the evaporation chamber,



Figure 1.

a) Photograph of the device showing:
A: aerosol inlet,
B: condensation chamber,
C: aerosol outlet.
b) Schematic diagram of the device showing the flow of air and reagent through the inlet (A), through the condensation chamber (B), and through the outlet (C).

the walls are filled with the reagent. The reagent is supplied from a reservoir. Air is passed through the inlet (A) and through the condensation chamber (B) where the reagent is supplied. The amount of reagent transferred to the particles depends on the flow rate of the reagent and the flow rate of the aerosol. The level of saturation is achieved depending on the reagent rate and the temperature difference between saturation and the ambient temperature, which is constant by e-

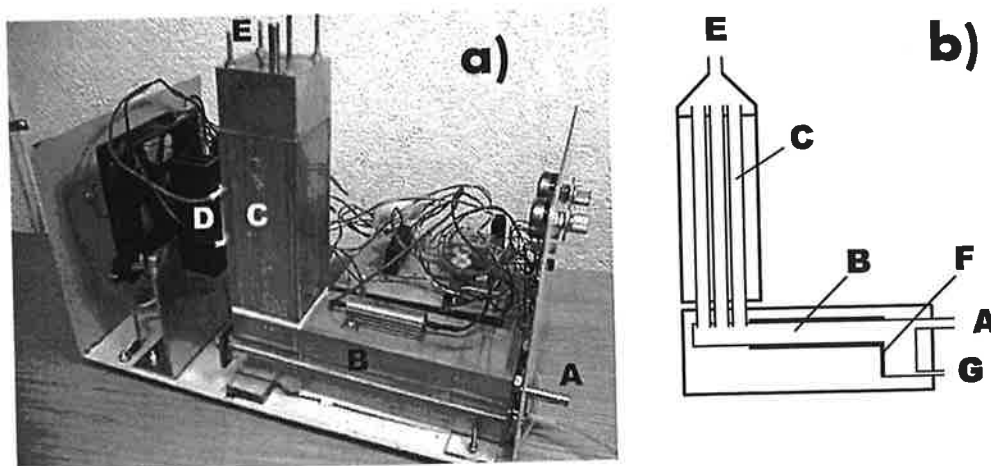


Figure 1.

a) Photograph of a working prototype of the condensation device, stripped of its insulation. A: aerosol inlet, B: evaporation chamber with a resistive heater attached to the top, C: condensation chamber, D: heat sink of the Peltier element cooling the condensation chamber, E: aerosol outlet.

b) Schematic diagram of the same condensation device. The aerosol passes into an inlet (A), through the evaporation chamber (B) that is covered with a wick (F) to which the liquid reagent is supplied from a reagent reservoir (G), and then into the condensation tubes (C).

the walls are covered with a wick (F), filled with the liquid reagent. The wick is supplied from a reagent reservoir (G). Air is passed into the device through an inlet (A) and then through the evaporation chamber where it is saturated with reagent, which vaporises from the wick. The amount of reagent vapour transferred to the air depends on the temperature of the heated saturation chamber, the flow rate and the vapour pressure of the reagent. Air and vapour are transported to the condensation chamber where the air is supersaturated with reagent as the temperature decreases. The level of super-saturation that can be achieved depends mainly on the flow rate and the temperature difference between saturator and condenser. These temperatures can be adjusted and held constant by electronic control units.

When sampled aerosol is passed into the device, the aerosol particles are mixed with the vapour in the evaporation chamber. The aerosol, now with reagent vapour added to it, then enters the cooled condensation chamber where reagent vapour condenses on the particles. The particles are thereby individually embedded in reagent and grow in size so a visible droplet cloud is emitted. The droplets can easily be collected in for example an impinger or impactor or on a filter.

Dibutylamine (DBA) has been found as a suitable reagent for the determination of isocyanates in airborne particles (Spanne 1996). As there is a need to determine airborne isocyanates in different environments in order to avoid exposures giving rise to adverse health effects, dibutylamine was chosen as the

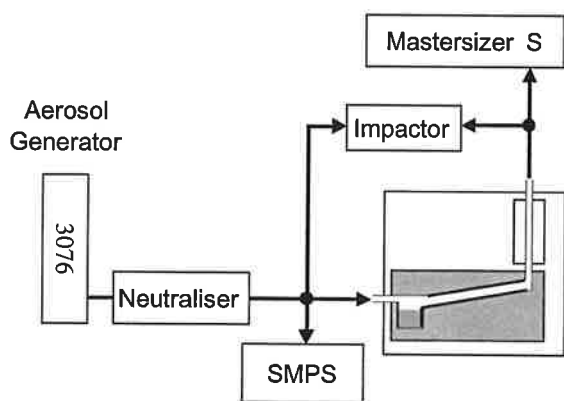


Figure 2.

Experimental set-up for the characterisation of the device with dibutylamine as reagent.

reagent to initially be evaluated in the device.

MATERIALS AND METHODS

In order to evaluate the device, it was tested in an experimental set-up, shown in Figure 2. A fluorescein test aerosol was generated using a nebulizer (Atomizer model 3076; TSI Inc., St. Paul, MN, USA) from a saturated fluorescein solution in acetone, diluted 1:100 with ethanol. The test aerosol is electrically neutralized with a 10 mCi Kr-85 β source. The size distribution and concentration of the original aerosol was measured with a Scanning Mobility Particle Sizer model 3934, consisting of an Electrostatic Classifier model 3071 and a Condensation Particle Counter model 3022A (TSI Inc., St. Paul, MN, USA). The size distribution of the enlarged particles from the condensation sampler was measured with a Fraunhofer diffraction instrument

(Mastersizer S with a 300 mm lens; Malvern Instruments Ltd., Malvern, UK).

All chemicals used were of technical grade and fluorescein, was obtained from Sigma-Aldrich, Steinheim, Germany.

The saturator in the condensation device was held at 52°C and the condensation tubes at 10°C.

Samples of the test aerosol were taken using a 2-stage single-jet impactor with jet nozzle diameters of 2.2 and 1.0 mm, resulting in a 50 % particle cut-off diameter of 3.4 and 1.0 μm , respectively. The sample flow rate was 1.5 l min^{-1} . Teflon filters (Zefluor™ supported PTFE, pore size 2 μm ; Gelman Sciences, Ann Arbor, Michigan, USA) were used on the impaction plates and for the final filter. The fluorescein was extracted from the filters with 3 ml ethanol and measured with a fluorometer (model TD-700; Turner Designs, Sunnyvale, CA, USA).

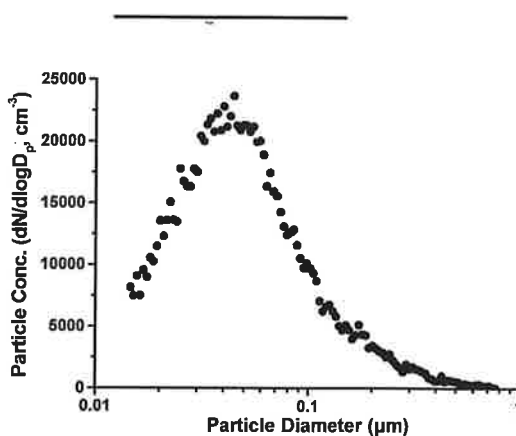


Figure 3.

Particle size distribution of the fluorescein test aerosol before passing the condensation device, measured with an SMPS-system.

RESULTS

The size distribution of the fluorescein aerosol before the SMPS-measurement of the aerosol is shown in Figure 3.

The size distribution of the aerosol after exiting the condensation device was measured with the SMPS-system for different flow rates. The results and the calculated particle diameters were 5.2, 1.0 and 0.74 μm .

Results from the collected particles on the final filter after the reagent was added to the particles, the amount of fluorescein larger than 1 μm was 99.3 % was 1 μm .

DISCUSSION

The size distribution calculated from the data given by the Mastersizer S. No results are given by the measurements with the SMPS-system.

Table 1.

Sampling of the condensation device. Results are given in μm .

Sample

After the condensation device
Before the condensation device

RESULTS

The size distribution of the generated fluorescein aerosol was measured with the SMPS-instrument. The size distribution of the aerosol used for the tests is shown in Figure 3.

The size distribution of the droplets exiting the condensation chamber was measured with the diffraction instrument for different flow rates through the device. The results are shown in Figure 4 and the calculated count median diameters were 5.2, 6.6 and 8.6 μm for 2.1, 1.0 and 0.74 l min^{-1} , respectively.

Results from the analysis of the collected particles in the impactor and on the final filter are shown in Table 1. After the reagent was condensed onto the particles, 70 % of the collected amount of fluorescein was in particles larger than 3.4 μm and more than 99.3 % was in particles larger than 1 μm .

DISCUSSION

The size distribution in Figure 4 is calculated from the volume equivalent diameter given by the Malvern Master-sizer S. No relevant concentration data is given by the instrument, as the measurements were made at the very low

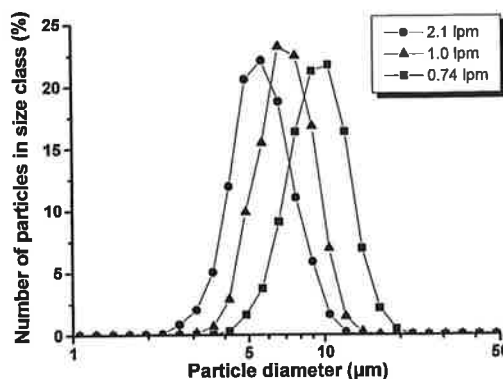


Figure 4.

Particle size distribution of the droplets with fluorescein particles and reagent after passing the condensation device at three different flow rates, measured with a Fraunhofer diffraction instrument.

end of the instruments concentration range. Quantitative data was achieved by impactor measurements. The theoretical loss of particles due to diffusion was 50 % for 1.2 nm particles and 5 % for 8.1 nm particles (Gormley and Kennedy 1949).

The temperatures of vaporisation and condensation were chosen to give a high supersaturation in order to demonstrate the feasibility of the method. The theoretical saturation ratio (partial pres-

Table 1.

Sampling of the fluorescein aerosol with an impactor, before and after passage through the condensation device. Samples were taken during 3 minutes at a flow rate of 1.5 l min^{-1} . Results are given in $\mu\text{g fluorescein m}^{-3}$.

Sample	Impactor stage no.			Sum
	1 ($d_{50}=3.4 \mu\text{m}$)	2 ($d_{50}=1.0 \mu\text{m}$)	Final filter	
After the condensation device	10.5	4.3	0.1	14.9
Before the condensation device	0.7	3.5	25.4	29.6

sure of the reagent at saturation temperature divided by the partial pressure at condensation temperature) in the condensation chamber was 12.7 compared to 6.8 in the TSI 3022A CPC. These values were obtained from interpolation of literature data (Lide 1995). As the homogenous nucleation is not a problem in this application, a high saturation ratio can be used.

The Kelvin diameter corresponding to the theoretical supersaturation in the condensation chamber was 2.9 nm.

Future work to develop the condensation device should be focused on examinations of flow rates and supersaturation ratios in order to minimise losses and maximise collection efficiency for suitable collection devices while maintaining sufficient growth of particles of the desired size range to be sampled and analysed. The use of a turbulent mixing CPC technique as described by Mavilev and Wang (2000) might work particularly well for this application as a short residence time will minimise diffusion losses.

Furthermore, the device should be tested for other reagents suitable for analysis of reactive hazardous air pollutants.

CONCLUSIONS

A condensation device with ability to transfer the reagent dibutylamine to sub-micrometer particles was constructed. The use of the device facilitates an immediate start of the derivatisation process and particle collection with inertial samplers.

The ability of the method to transfer a liquid reagent to airborne particles was demonstrated. This method increases

the possibilities to suppress unwanted reactions in the particles competing with the derivatisation reaction that may occur after the collection of airborne reactive particles. The growth of the particles facilitates the collection with inertial devices like impingers and impactors.

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