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**DEVELOPMENT AND APPLICATION OF A LOW-FLOW
THERMODENUDER AND ITS COMPARISON WITH A COMMERCIALY
AVAILABLE MODEL**

**ENTWICKLUNG UND ANWENDUNG EINES NIEDRIG-FLUSS
THERMODENUDERS UND VERGLEICH MIT EINEM
HANDELSÜBLICHEN MODELL**

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Abstract

This report describes the development and application of a thermodenuder (TD). Such an instrument enables near real-time measurements of total volatile and non-volatile particle concentrations in engine exhausts by conditioning exhaust emission samples in the ultrafine particle regime of diesel and petrol engines. The TD is designed to strip-off the volatile and semi-volatile fraction (short-chained hydrocarbons) attached to the surface of particles by thermal desorption. As we were unable to improve the performance of a commercially available thermodenuder (TSI model 3065), we developed an alternative instrument. Innovative aspects of this instrument include the direct heating system (based on a galvanically separated power unit) and the registration of the gas temperature. Both features keep the temperature gradient stable and, at the same time, prevent unexpected sample transformations due to uncontrolled condensation and nucleation under supersaturated conditions. The TD is suitable for use with instruments like SMPS (Scanning Mobility Particle Sizer), has the potential to monitor existing devices (incl. stoves) with respect to future environmental standards, aids in the maintenance and proper functioning of existing fossil fuel powered engines, and it can even be employed as a tool to improve the design of combustion engines.

Keywords: thermodenuder, thermodesorption, submicrometer particles, ultrafine particles, volatile- and semi-volatile hydrocarbons, carbonaceous particles, soot.

Zusammenfassung

Der vorliegende Bericht beschreibt die Entwicklung und die Anwendung eines Thermodenuders (TD). Dabei handelt es sich um ein Instrument welches in nahezu Echtzeit die Messung der gesamten, flüchtigen, und nicht-flüchtigen Partikel-Konzentrationen in der ultrafeinen Grössenklasse erlaubt, die von Verbrennungsanlagen ausgehen. Das Konzept des TDs ist derart gestaltet, dass durch thermische Desorption die flüchtige und semi-flüchtige Fraktion (überwiegend kurzkettige Kohlen-Wasserstoff-Moleküle) sich von der Oberfläche der festen Partikelfraktion löst und abgefiltert wird. Da es nicht möglich war, das Trennverhalten eines im Handel erhältlichen TDs (TSI-Modell 3065) zu verbessern, wurde der Bau eines alternativen Instrumentes angestrebt. Der innovative Aspekt des neuentworfenen Konzeptes umfasst die direkt beheizte Desorberstufe (basierend auf einer galvanisch getrennten Stromversorgung) und die direkte Erfassung der Aerosol-Kerntemperatur. Diese Besonderheiten verhindern, dass es zu unerwünschten Temperaturschwankungen innerhalb der Heizstufe kommt und infolge dessen durch unbeabsichtigte Rekondensation bei übersättigten Bedingungen in der Absorptionsstufe die Aerosolzusammensetzung verfälscht. Dieses Instrument eignet sich für den Einsatz in Kombination mit einem SMPS (Partikelmobilitäts-Klassifizierer). Der TD kann dazu genutzt werden um vorhandene Verbrennungsanlagen hinsichtlich Umweltverträglichkeit zu untersuchen bzw. als Analyse-Hilfsgerät um bestehende Verbrennungsmaschinen hinsichtlich ihres Abgasverhaltens zu verbessern.

Schlüsselwörter: Thermodenuder, Thermodesorption, Submikrometer Partikel, Ultrafeine Partikel, flüchtige und semi-flüchtige Kohlen-Wasserstoffe, Kohlenstoffhaltige Partikel, Russ.

1. Introduction

Conditioning of combustion aerosol prior to scanning is essential in order to obtain reproducible size distributions with an SMPS system (BURTSCHER et al. 2001b). Especially in combustion exhaust, the volatile and semi-volatile fraction also referred to as the "wet" fraction, is readily condensed onto larger solid particles by processes known as adiabatic cooling. Removal of the volatile or "wet" fraction with a thermodenuder is therefore essential to obtain a more reproducible "dry" particle size spectrum (BURTSCHER et al. 2001b). Furthermore, the removal of the adsorbed volatile fraction not only reveals the true nature of the particle's size spectrum of the non-volatile fraction, but it also enables determination of the total, volatile, and solid particle concentrations of combustion engine exhaust.

The stripping mechanism is easily achieved by first heating it to a preset temperature - typically to 250°C (ABDUL-KHALEK & KITTELSON 1995, MIKKANEN et al. 2001). This will cause the volatile fraction to desorb and evaporate from the solid particle fraction. Then the heated gas and particle load is pushed along into a cooler section

where the heated volatile fractions adsorb onto the cooler surface and thus are trapped by the charcoal-pellets.

1.a TSI Low-Flow Thermodenuder Model 3065 (TSI-TD)

The commercially available TSI instrument (model 3065 Low-Flow Thermodenuder, TSI Inc. which is actually manufactured in Germany by Topas GmbH TDD 590) revealed some major disadvantages. Most of the hardware constituting the aerosol-conducting pathway is made of glass. The desorber section of the instrument uses a 6.35 mm (1/4") in diameter and 120 mm long convoluted stainless steel tube welded onto a 100 mm long glass "bottleneck" that enlarges to form a shoulder piece holding the stainless-steel grid pipe required to keep the charcoal-pellets from collapsing into the aerosol pathway. It is important to mention that the steel-glass interface within the desorber stage reveals a slightly thicker diameter than the steel or the glass section. It is 13 mm in diameter, whereas the glass extension holding the steel grid-pipe at the very end of the desorber section measures already 20 mm. These variations in diameter are crucial in order to understand the temperature profiles outlined further below. Heating for the desorber section is achieved indirectly by using a heater tape that is wrapped around both the stainless steel pipe and the glassware attached to it. The thermocouple used to operate the instrument's heater control loop is inserted in-between the aerosol-conducting tubing and the heater tape.

The adsorber section of this instrument has an outer diameter of about 100 mm and covers a length of approximately 700 mm. It is capable of holding up to 6 L of activated charcoal pellets. According to the specifications, the instrument is suitable for flow rates between 0.2 - 2 L/min, with optimal flow at 0.5 to 1 L/min at a desorptive temperature range covering ambient temperature all the way up to 400°C.

1.b QUT Low-Flow Thermodenuder (QUT-TD)

The alternative model built at the University's workshop at QUT is modular in design thus allowing rapid access to key elements of the instrument. Rather than using different types of material, the aerosol-conducting pathway is made entirely of stainless steel. The aerosol-conducting tubing over its entire length maintains a diameter of 12.7 mm (1/2"). The desorber section is likewise made of a convoluted stainless steel pipe and covers a total length of 370 mm of which 300 mm are used for the actual heating purpose. Heating is achieved by having the proximal end (aerosol inlet) isolated against the grounded housing and applying a low voltage (4.8 V_{AC}) capable of drawing a load current of 55 A across the entire length of the convoluted desorber pipe (fig. 1). This amount of directly generated caloric energy (roughly 260 W) enables rapid heating of the aerosol. Crucially, the gas temperature is detected at the exit of the desorber pipe shortly before the heated gas enters the adsorber stage. The 500 mm long adsorber section can house about 5.5 L of

activated charcoal pellets. In addition the adsorber stage is fitted with cooling loops and extra thermocouples to analyse the temperature gradient within the adsorber stage (fig. 1). Contrary to the TSI-TD design, all thermocouples used are positioned in a way to register aerosol core temperatures within the aerosol-conducting pathway. During the course of instrument testing, it was found that the QUT-TD is able to handle flow rates of 1 to more than 3 L/min.

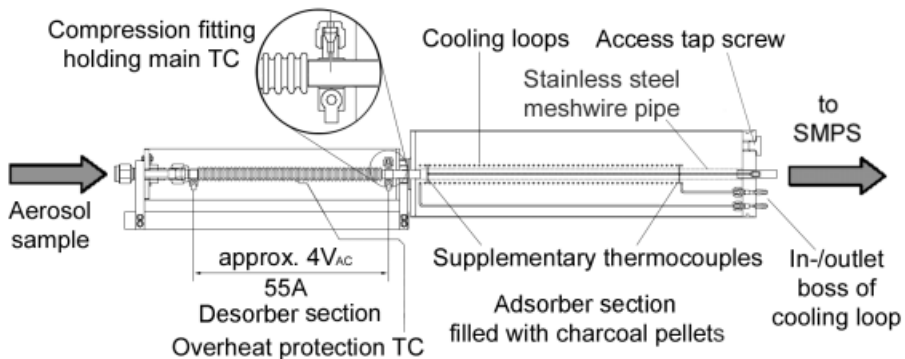


Figure 1: Schematic of the interior of QUT-TD. Care was taken to maintain a constant overall aerosol-conducting inner pipe diameter of both the desorber (heater) and the adsorber (cooler) stage. A total of 4 thermocouples (2 TCs for the heater and 2 TCs for the cooler) have been fitted.

2. Experimental Design

Both instruments have been analysed regarding their temperature profiles across the desorber stage and ultimately tested with several types of ultrafine aerosols in order to make a comparison possible.

2.1 Temperature Profiles

The desorber's temperature gradient was recorded by using a 0.5 m long and 1mm thick thermocouple (TC) attached to a Fluke 80TK TC module plugged onto a Fluke 75 digital multimeter. A tiny metal cage was used to keep the TC in the centre-most position within the aerosol-conducting pathway. For a given temperature, the TC was gradually inserted into the desorber stage (in intervals of 10 mm) past the desorber section and further, deep into the proximal section of the adsorber (altogether approx. 400 mm). Temperature profiles have been recorded for flow rates ranging from 0.3 to 3 L/min (TSI-TD) and 1 to 3 L/min (QUT-TD), using a temperature range starting from 150 to 400°C (in steps of 50°C). Flow was

generated using a venturi suction system while the rate was measured prior and after each temperature scan with a Gilibrator bubble flow meter. All temperature measurements have been performed with an empty adsorber stage; i.e. the charcoal has been removed to avoid unnecessary contamination.

2.2 Adsorption Efficiency – TSI-TD versus QUT-TD

To determine instrumental behaviour it was necessary to run several trials involving various test aerosols. The first tests utilized a non-volatile NaCl aerosol (determination of penetration efficiency) that has been followed by trials using a Condensation Monodisperse Aerosol Generator (CMAG model 3475, TSI Inc.). This aerosol generator, which operates with DEHS was used to determine separation efficiencies. All test scans have been made following a protocolled time series while each individual test trial consisted of at least 5 single scans.

For the penetration efficiency tests a sodium-chloride solution, with a concentration of 20 mg/L, was nebulised. The penetration efficiency should be measured both at room temperature and at operating temperature to distinguish thermophoretic losses from intrinsic losses in the thermodenuder. Downstream of the nebulizer, a diffusion dryer removes the water from the droplets to produce particles with a CMD of about 60 nm. As only a NaCl aerosol was used for the penetration efficiency trials, both the screen bypass and the saturator bypass arrangements of the CMAG were fully open. Once penetration efficiency was established the same setting was used to run test trials involving DEHS (fig. 2).

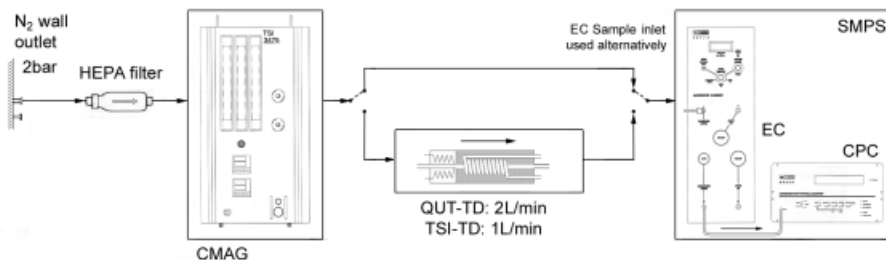


Figure 2: Schematic diagram of the instrumental setup to determine adsorption efficiency. CMAG: Condensation Monodisperse Aerosol Generator; TD: Thermodenuder; SMPS: Scanning Mobility Particle Sizer; EC: Electrostatic Classifier; CPC: Condensation Particle Counter.

3. Results and Discussion

Temperature Profile: Although the TSI-TD's manual explicitly allows flow rates up to 3 L/min and 2 L/min according to the corresponding web site (TSI, 2003), it was found during intensive testing that the TSI-instrument showed optimal results only within a very narrow flow-window of around 1 L/min. The combined effect of both the glass-metal interface, the various thickness' of the heater section itself, and the loosely packed heater tape are the main reasons why the temperature profiles in the lower and higher flow ranges revealed very inhomogeneous profiles (see fig. 3). Increasing the flow to 1.5 L/min resulted in a pronounced M-shaped temperature profile; this pattern became even more pronounced at flow rates of 2 L/min and extremely distorted at flow rates of 3 L/min. Residence times at 2 L/min are reduced to 200 ms and 130 ms respectively at 3 L/min pushing the heated air bolus far below the threshold temperature value of 250°C even when the instrument is operated at maximum desorber temperature of 400°C.

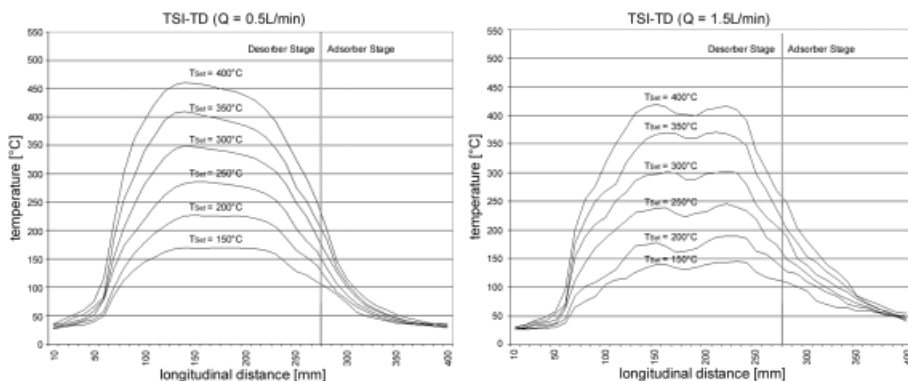


Figure 3: Temperature profile of the TSI-TD at various flow rates. At a flow-rate of $Q = 0.5$ L/min (left) the heated bolus of air it is not pushed fast enough to the adsorber stage and as a result cools off while still within the desorber stage, while a flow rate exceeding 1 L/min (right) results in very distorted temperature profiles.

A flow-rate of 0.3 L/min resulted in a residence time of about 1.3 sec. Given the particular design of the desorber stage, a 400°C hot aerosol bolus cools down rapidly falling even below the 250°C threshold while still within the desorber section. Only by increasing the flow to at least 0.5 L/min (760 msec residence time), the 400°C hot bolus enters the adsorber stage with 250°C.

With the current design of the QUT-TD, this instrument is not restricted to the upper temperature limit of 400°C. With the overheat protection device set to 650°C it was not attempted to operate the QUT-TD at flow rates smaller than 1 L/min mainly to

avoid damage of essential parts within the desorber stage when increasing the temperature even further. Thus, the QUT-instrument returns optimal desorption results when a flow rate of at least 1.5 L/min is maintained. On the other hand this instrument is capable in dealing with flow rates exceeding 3 L/min - but was not tested any further. Given the larger aerosol-tube diameter, the residence time at 1.5, 2, and 3 L/min are 1.5, 1.1, and 0.76 sec respectively. With any of the given flow rates, this instrument is able not only to maintain the threshold temperature upon reaching the adsorber stage, but it does so already when the heater is set to a desorber set-point temperature of 250°C.

With the optimum flow rate for the TSI-TD found to be 1 L/min, corresponding to a residence time in the desorber stage of 0.38 sec, it was compared to the temperature profile of the QUT-TD. As this instrument showed ideal patterns in the 1-3 L/min flow regime, a test aerosol flow rate of 2.5 L/min corresponding to a residence time of 0.9 sec, was chosen (right image in fig. 4). As can be seen from this figure, the QUT-TD with its predominantly positive sloping temperature gradient easily reached the required threshold temperature of 250°C with a preset desorber temperature of likewise 250°C; whereas, the TSI-instrument with a rather more plateau-like temperature profile and operated with its optimal flow rate was found to be 60°C below that required threshold value.

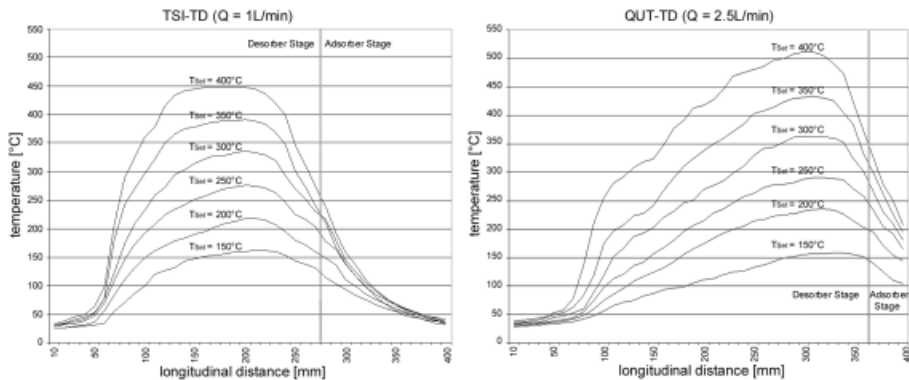


Figure 4: Comparison of the temperature profiles of both TDs. The TSI-TD (left) falls approx. 60°C short of the threshold temperature of 250°C (line of intersection between desorber and adsorber stage). It just meets this criterion with a preset heater temperature set to the maximum of 400°C. The QUT-TD (right) passes this criterion but does so already at a desorber temperature of 250°C.

DEHS-Trial: DEHS is a fairly large hydrophobic molecule with a molecular mass of 427 g/mol and a boiling point of 266°C at STD-conditions (LEROY 1950). Exposing both TDs to a high concentration of sodium-chloride particles onto which DEHS is condensed onto (heterogeneous nucleation; RISTOVSKI et al. 1998), enables proper evaluation of the desorption characteristics of these instruments. Figure 5 shows the spectra of the DEHS-condensed NaCl-aerosol generated by the CMAG before and after routing it through both TDs. With the TSI-TD, the removal of DEHS from the salt seeds took place only at temperatures above 350°C; such a peak shift could not even be obtained with the highest temperature setting of 400°C. Contrary, the QUT-TD managed to induce this peak shift to lower particle diameters already with temperatures around 350°C. For temperatures above 350°C the obtained size distribution after the QUT-TD corresponded to the previously measured recorded penetration efficiency NaCl spectra.

The same figure also reflects the better separative properties of the QUT-TD with a desorber temperature of 350°C. By generating a double-peaked size spectrum, the TSI-TD with a desorber set-point temperature of 400°C had difficulties in making this clear shift towards the smaller sized and stripped NaCl range.

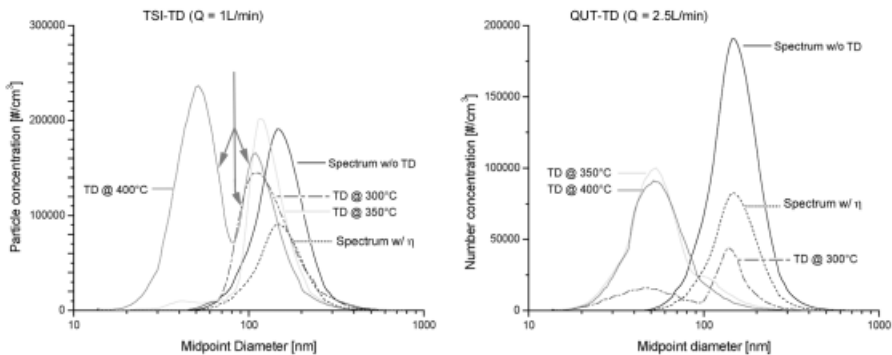


Figure 5: Size Distribution of DEHS-NaCl aerosol. The continuous black line represents the “raw” aerosol bypassing the TDs. The dashed black line represents the calculated “raw” aerosol routed through the TDs based on a NaCl penetration efficiency trial (Spectrum w/o TD from which the penetration losses are subtracted). The dash-dotted line represent the actual scan at 300°C, the light grey line 350°C, and the dark grey line 400°C.

4. Conclusion

Even with a preset heater temperature of 400°C, the design of the TSI-TD’s heater stage makes it very difficult to keep the desorber temperature above the required threshold temperature of 250°C. Already WEHNER et al. (2002) pointed out that the

small dimensions of the desorber stage, resulting in short residence times, is the main reason for the incomplete desorptive properties. Along with the steep drop below the required desorption temperature, efficient removal of the volatile fraction was achieved only partially. Consequently, recondensation of the desorbed volatile fraction onto the solid particle fraction must have occurred still within the desorber stage. An increase in flow (>1 L/min) slightly compensated for this steep temperature drop, but resulted in an inhomogeneous temperature profile within the heater stage. Such M-shaped temperature fluctuations within the desorber stage as a result of the different thermal properties of steel and glass -- especially at that interface -- should be avoided as the observed temperature depression forces the volatilised material to recondense back onto the solid aerosol phase, which cannot be thermally dissolved in the remaining timeframe when exposed to the subsequent thermal peak (BURTSCHER et al. 2001a; WEHNER et al. 2002).

The enlarged “shoulder piece” within the TSI-TD holding the stainless steel grid pipe for the adsorber reaches into the desorber stage. In fact, this grid-pipe at the distal end of the desorber stage acts as a heat sink by further depressing the already lowered exit temperature at the desorber-adsorber interface. In comparison, the temperature profile of the QUT-TD reaches the recommended thermal desorption threshold already with a preset heater temperature of 250°C. This threshold temperature is maintained throughout the various tested flow rates. This thermal response is mainly achieved by the direct heating concept and the aerosol-core temperature sensing thermocouple placed at the exit of the desorber stage (fig.1).

The difference between the two instruments is most obvious with the NaCl-DEHS aerosol where a distinct peak shift of the heterogeneously nucleated aerosol occurs from the larger to the lower diameter range; something which is easily achieved with the QUT-TD at a desorber temperature of 350°C, whereas the TSI-TD only partially satisfies that condition even though the desorber stage was heated up to the maximal possible temperature of 400°C.

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