APPLICATIONS FOR THE CATALYTIC STRIPPER

APPLICATION NOTE CI-0011

Background

Aerosol sampling is a complex topic applicable across multiple disciplines, from air quality, emissions control, Diesel and petrol research, alternative fuels, global warming research, to viral transport, filter testing, HVAC, and many more areas of science, industry, and technological research, too numerous to list.

Our Catalytic Stripper came to market to fill requirements for the measurement of solid aerosol, namely solid black carbon aerosol from internal combustion engines. However, the device can be used in all of the above research fields, and more.

The Catalytic Stripper (hereafter simply CS) is itself similar in principle to a thermal denuder, or evaporation tube, which is essentially a section of an aerosol inlet heated to a specific temperature. The key and critical difference of the CS is that it is *catalytically active*, so rather than just partitioning volatile material to the vapor phase, allowing it to condense onto the inner tubing walls or re-condense into aerosol, the non-solid fraction is exposed to a catalyst at elevated temperature, to chemically convert hydrocarbons and other non-solid material into non-reactive gaseous species. The result is that the aerosol emitting from the outlet of the CS will be the solid fraction of whatever entered the device.

The applications for such technology are numerous from emissions legislation, ambient soot (or particle number) monitoring, examining ashing properties of fuels, the brown carbon fraction of ambient aerosol, and for improving the calibration of many aerosol devices.

The below sections with give a brief description of some of the state-of-the-science research applications for the CS split into the following topics:

- **Ambient Air Measurement**
- **Vehicle Emissions**
- **Aircraft Emissions**
- **Marine Emissions**
- **Improving Calibration**
- **Filtration Efficiency Measurement**
- **Tobacco, E-cigarette, Marijuana Smoke Measurement**
- **Measuring Solid Particles in Liquids**

with referenced material at the end of each section.

Ambient Air Measurement

Soot particles are formed as by-products of incomplete combustion of carbon-containing fuels or biomass burning, next to other combustion products. They have recently received increased attention from the scientific community, society, and policy makers due to their role in global climate change, in compromising air quality, and their impact on human health.

Historically, both fundamental studies on microphysical properties of soot particles and air quality monitoring made use of filter-based absorption photometers and aethalometers (e.g. PSAP, COSMOS, MAAP). Another approach with filter-based thermal-optical instruments quantitatively retrieve the aerosol EC and OC fraction by heating the filter with specific temperature ramps in controlled atmospheres, following established protocols (e.g. OC-EC Analyser). There are numerous challenges in filter-based measurements, far beyond the scope of this application note, suffice to say that in the last few decades on-line instrumentation has become increasingly popular, retrieving real-time absorption (e.g. PAX, PASS, and CAPS), as well as refractive Black Carbon (rBC) mass concentrations (e.g. SP2).

Non-volatile BC particles can be mixed with volatile components, where volatile material condenses onto or envelopes BC particles, or volatile or semi-volatile OC and inorganic material formed via nucleation may exist as separate particles within the same aerosol. This is commonly referred to as the mixing state of the aerosol. Specifically, in an aerosol population comprised of both volatile and non-volatile material, the population is said to be “internally mixed” if all particles contain both species, and “externally mixed” if all particles are either one species or the other. In general, an aerosol population lies between these two extremes (Dickau et al., 2016). The aerosol mixing state affects optical and hygroscopic properties, and quantifying it is therefore important for studying an aerosol’s climate and health impacts.

The use of the CS within an ambient measurement setup presents an interesting array of potential configurations permitting the measurement of mixing state, and other interesting parameters such as the Mass Absorption Coefficient (MAC).

Catalytic Instruments GmbH & Co.KG • Zellerhornstrasse 7 • D-83026 Rosenheim
Tel: +49 8031 901 777-0 • Fax: +49 8031 901 777-5 • email: info@catalytic-instruments.com
www.catalytic-instruments.com

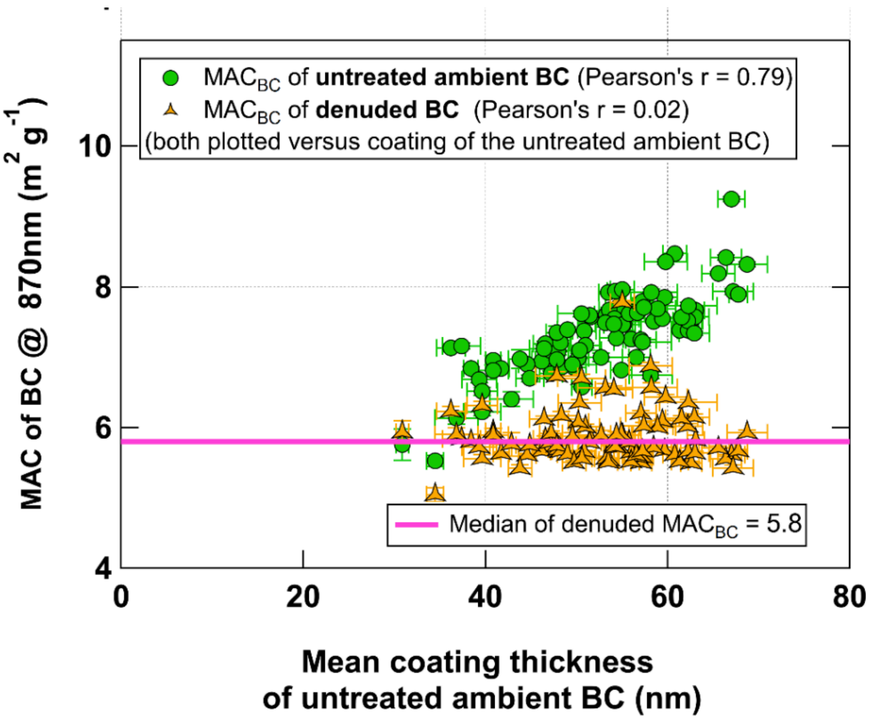

Figure 1: MAC_{BC} of ambient and CS "denuded" samples against the mean coating thickness of ambient rBC

Calibration of the SP2 is known to be improved with the use of a thermal denuder, even when using sources such as Aquadag and fullerene soot (Irwin et al., 2013). Prior to the invention of the CS, it became common to use a thermal denuder to reduce the uncertainty of SP2 measurements. With the CS, this uncertainty can be further reduced.

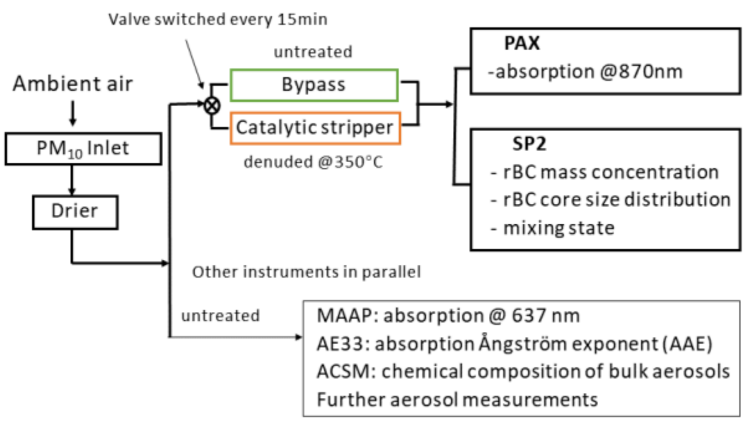

Figure 2: Taken from Yuan, J. et al. 2020

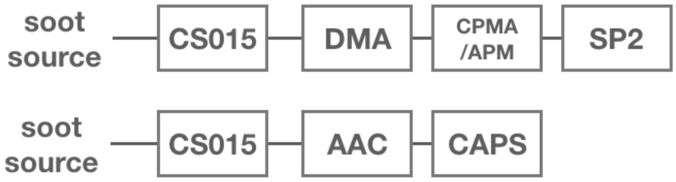

Figure 3: An example configuration for SP2 and CAPS calibration/measurements

Operating the CS in front of a Centrifugal Particle Mass Analyser (Cambustion; CPMA) or Aerosol Particle Mass Analyser (Kanomax; APM) will ensure that mass selection is of only the solid fraction. Thus, alternate scans between CS and non-CS will result in a derivation of the particle coating/mixing state.

Dickau, M., Olfert, J., Stettler, M., Boies, A. M., Momenimovahed, A., Thomson, K., Johnson, M. (2016). Methodology for Quantifying the Mixing State of an Aerosol. *Aerosol Science & Technology*, *50*(8), 759–772. https://doi.org/10.1080/02786826.2016.1185509

Irwin, M., Kondo, Y., Moteki, N., & Miyakawa, T. (2013). Evaluation of a Heated-Inlet for Calibration of the SP2. Aerosol Science and Technology, 47(8), 895–905. https://doi.org/10.1080/02786826.2013.800187

Park, K., Kittelson, D. B., & McMurry, P. H. (2003). A closure study of aerosol mass concentration measurements: Comparison of values obtained with filters and by direct measurements of mass distributions. *Atmospheric Environment*, *37*(9–10), 1223–1230. https://doi.org/10.1016/S1352-2310(02)01016-6

Yuan, J., Modini, R. L., Zanatta, M., Herber, A. B., Müller, T., Wehner, B., Poulain, L., Tuch, T., Baltensperger, U., and Gysel-Beer, M.: Variability in the mass absorption cross-section of black carbon (BC) aerosols is driven by BC internal mixing state at a central European background site (Melpitz, Germany) in winter, Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-41, in review, 2020.

Vehicle Emissions

Road Vehicles:

Current vehicle regulations in Europe and elsewhere in the world include limits for non-volatile particle number emissions with sizes larger than 23 nm, but this is likely to become more stringent in an EU push to improve air quality and reduce PN emissions. Proposed legislation is to sample particles down to 10nm, which is a challenge too great for just a thermal denuder (Giechaskiel B., 2020).

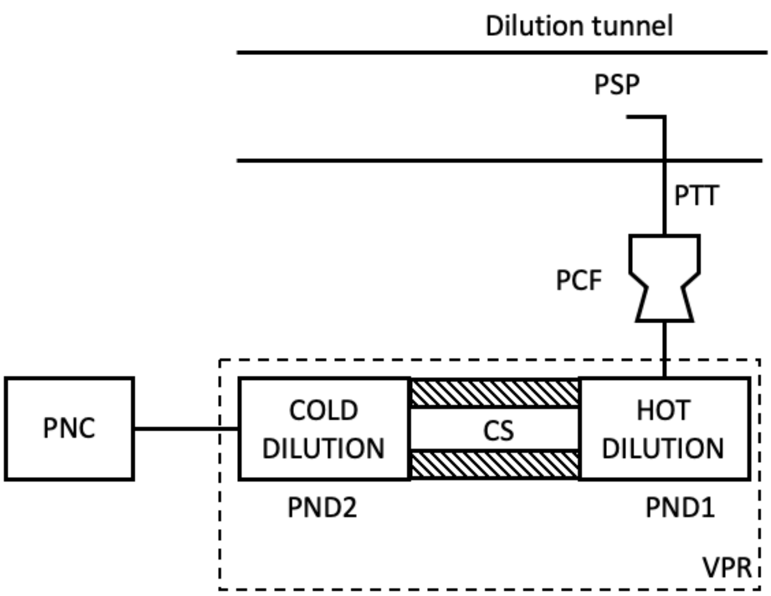

Figure 4: Schematic of the dilution tunnel measurement system in the updated PMP protocol

Acronym	Definition	Acronym	Definition
PSP	Particle Sampling Probe	VPR	Volatile Particle Remover
PTT	Particle Transfer Tube	PNC	Particle Number Counter
PCF	Particle pre-classifier	CS	Catalytic Stripper
PND	Particle Number Diluter	PND2	Particle Number Diluter 2

The review by Giechaskiel B., et al. (2020) summarises explicitly the benefits of using the CS for such important legislative measurements for emissions control, in particular highlighting the issues associated with thermal denuders.

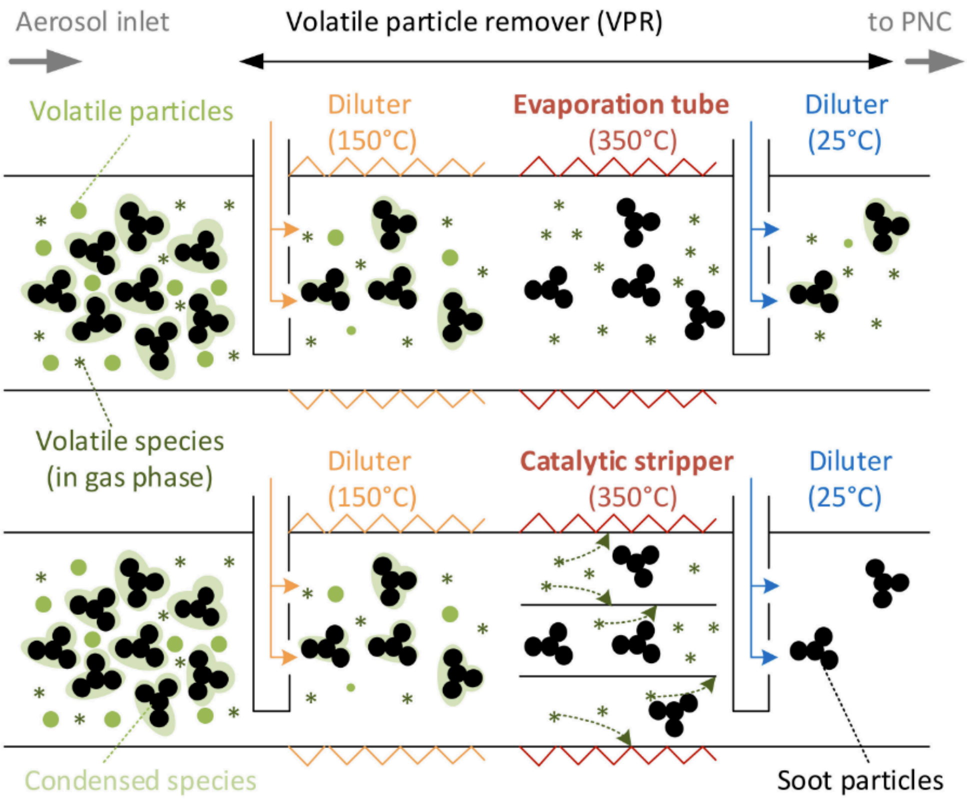

Figure 5: Schematic of volatile particle removers based on evaporation tube (upper panel) and catalytic stripper (lower panel). PNC = particle number counter. Giechaskiel B., 2020

Prior to the legislated measurement, researchers within the automotive industry have been using CS for a number of years. The TSI Engine Exhaust Particle Measurement system (EEPS) and Cambustion Differential Mobility Spectrometer (DMS500) can both be operated with integrated CS.

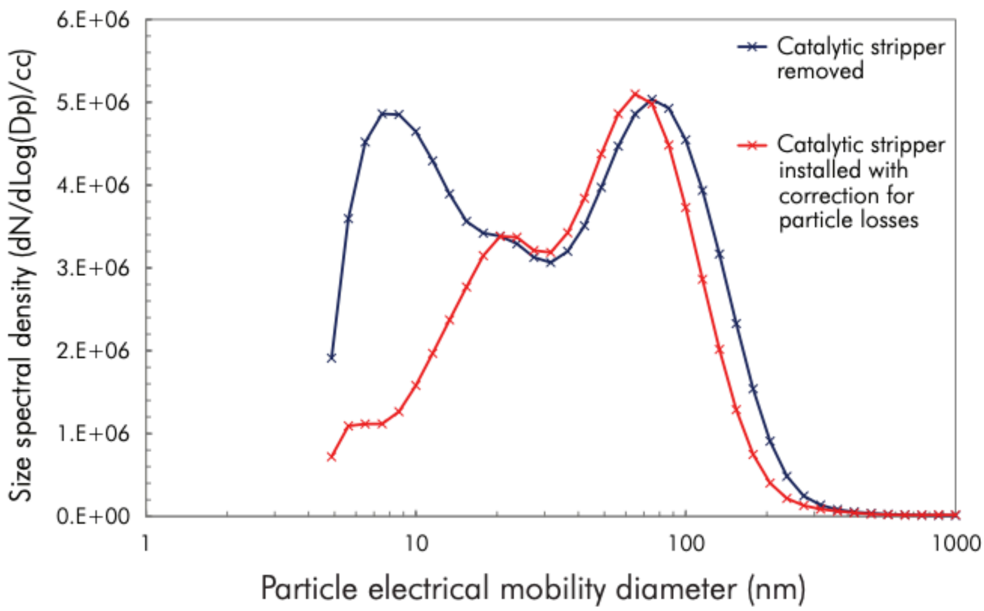

Figure 6: DMS500 with optional CS accessory showing the volatile fraction below 20nm, from GDI particles sampled upstream of turbocharger during WLTC

Focsa, C., Duca, D., Noble, J. A., Vojkovic, M., Carpentier, Y., Pirim, C., … Rieker, M. (2020). Multi-technique physico-chemical characterization of particles generated by a gasoline engine: Towards measuring tailpipe emissions below 23 nm. *Atmospheric Environment*, *235*, 117642. https://doi.org/10.1016/j.atmosenv.2020.117642

Giechaskiel, B., Melas, A. D., Lähde, T., & Martini, G. (2020). Non-Volatile Particle Number Emission Measurements with Catalytic Strippers: A Review. *Vehicles*, *2*(2), 342–364. https://doi.org/10.3390/vehicles2020019

Kittelson, D. B., Watts, W. F., Savstrom, J. C., & Johnson, J. P. (2005). Influence of a catalytic stripper on the response of real time aerosol instruments to diesel exhaust aerosol. *Journal of Aerosol Science*, *36*(9), 1089–1107. https://doi.org/10.1016/j.jaerosci.2004.11.021

Khalek, I. A., & Bougher, T. (2011). Development of a Solid Exhaust Particle Number Measurement System Using a Catalytic Stripper Technology. *SAE International Journal of Engines*, *4*(1), 2011-01–0635. https://doi.org/10.4271/2011-01-0635

Liu, Z., Swanson, J., Kittelson, D. B., & Pui, D. Y. H. (2012). Comparison of Methods for Online Measurement of Diesel Particulate Matter. *Environmental Science & Technology*, *46*(11), 6127–6133. https://doi.org/10.1021/es3003537

Ntziachristos, L., Amanatidis, S., Samaras, Z., Giechaskiel, B., & Bergmann, A. (2013). Use of a Catalytic Stripper as an Alternative to the Original PMP Measurement Protocol. *SAE International Journal of Fuels and Lubricants*, *6*(2), 2013-01–1563. https://doi.org/10.4271/2013-01-1563

Otsuki, Y., Takeda, K., Haruta, K., & Mori, N. (2014). A solid particle number measurement system including nanoparticles smaller than 23 nanometers. *SAE Technical Papers*, *1*. https://doi.org/10.4271/2014-01-1604

Swanson, J., Kittelson, D., Giechaskiel, B., Bergmann, A., & Twigg, M. (2013). A Miniature Catalytic Stripper for Particles Less Than 23 Nanometers. *SAE International Journal of Fuels and Lubricants*, *6*(2), 2013-01–1570. https://doi.org/10.4271/2013-01-1570

Swanson, J., Watts, W., Kittelson, D., Newman, R., & Ziebarth, R. (2013). Filtration efficiency and pressure drop of miniature diesel particulate filters. *Aerosol Science and Technology*, *47*(4), 452–461. https://doi.org/10.1080/02786826.2012.763087

Aircraft Emissions

Further to automotive emissions, aircraft emissions of particulate matter (PM) during the landing and take-off (LTO) cycle are regulated by the International Civil Aviation Organization (ICAO) through a limit on the engine smoke number (SN) (ICAO 2008). The primary objective of the regulation, introduced in 1981, was to reduce plume visibility and no engines tested since 1990 exceed the regulatory limit (EASA 2012). The SN is a filter-based optical method that quantifies the change in reflectance of a filter after sampling a given mass of engine exhaust (SAE 1997). Stettler et al., (2013) made use of a CS to remove the organic constituents of aircraft emissions to correlate the SN directly to black carbon concentration.

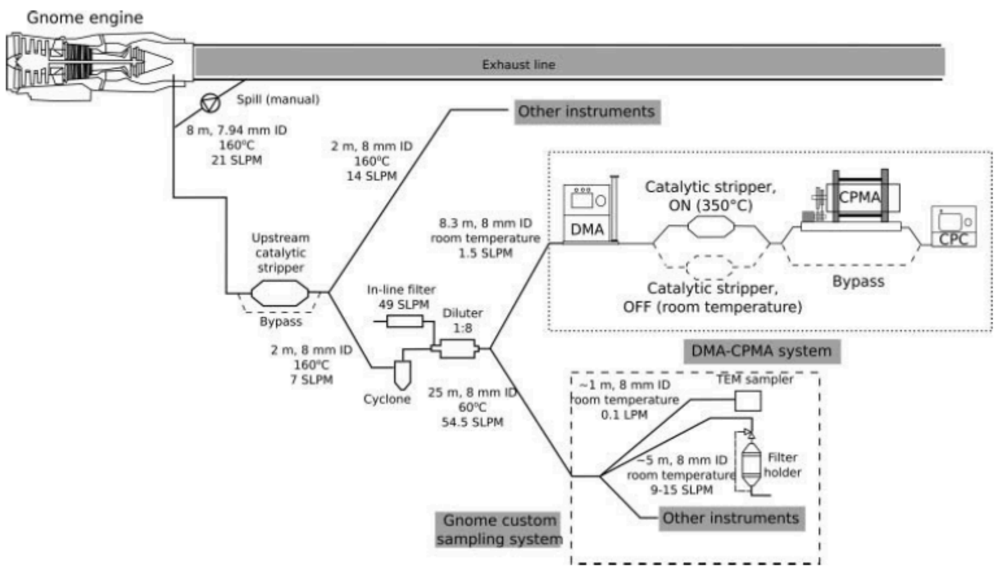

Figure 7: Experimental setup for measurements of the volatile mass fraction and volatile particle number fraction, showing the sampling system and the DMA-CPMA setup (Olfert et al., 2017)

Olfert et al., (2017) present work using the catalytic stripper to determine the effective density and volatility of particles sampled from a "gnome" helicopter gas turbine engine. Prior to Olfert et al. (2017), Johnson et al. (2015) presented a novel method of determining particle effective density and mass-mobility exponent of aircraft turbine aerosol, using a CS upstream of a CPMA for mass selection and modified DMS500 for particle size distribution information. Lobo et al. (2015) also present measurement of aircraft engine non-volatile PM emissions, using a CS as part of the VPR system.

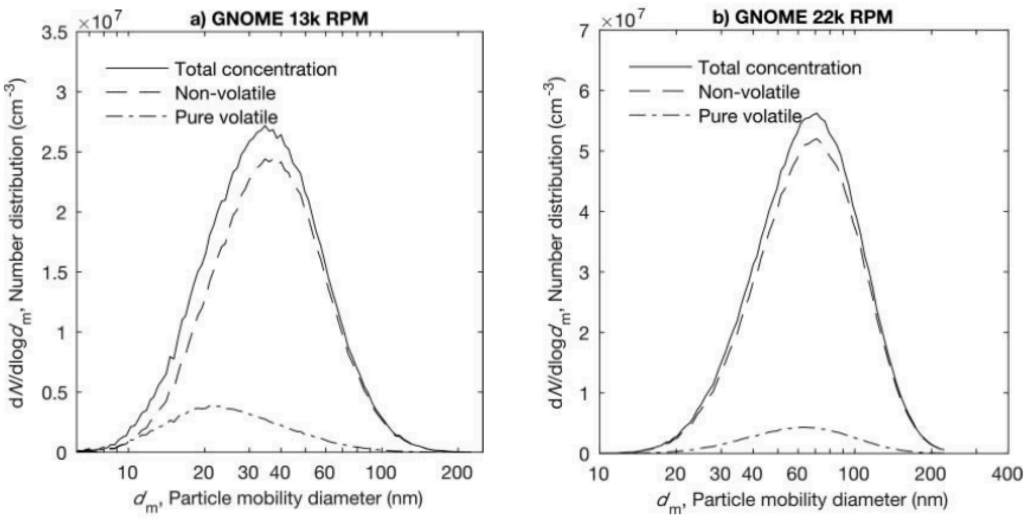

Figure 8: Number distributions from the Gnome engine at different RPM, using a CS to determine the volatile and solid fractions (Olfert et al., 2017)

Boies, A. M., Stettler, M. E. J., Swanson, J. J., Johnson, T. J., Olfert, J. S., Johnson, M., … Rogak, S. N. (2015). Particle Emission Characteristics of a Gas Turbine with a Double Annular Combustor. *Aerosol Science and Technology*, *49*(9), 842–855. https://doi.org/10.1080/02786826.2015.1078452

Johnson, T. J., Olfert, J. S., Symonds, J. P. R., Johnson, M., Rindlisbacher, T., Swanson, J. J., … Wang, J. (2015). Effective Density and Mass-Mobility Exponent of Aircraft Turbine Particulate Matter. *Journal of Propulsion and Power*, *31*(2). https://doi.org/10.2514/1.B35367

Lobo, P., Durdina, L., Smallwood, G. J., Rindlisbacher, T., Siegerist, F., Black, E. A., … Wang, J. (2015). Measurement of Aircraft Engine Non-Volatile PM Emissions: Results of the Aviation-Particle Regulatory Instrumentation Demonstration Experiment (A-PRIDE) 4 Campaign. Aerosol Science and Technology, 49(7), 472–484. https://doi.org/10.1080/02786826.2015.1047012

Lobo, P., Condevaux, J., Yu, Z., Kuhlmann, J., Hagen, D.E., Miake-Lye, R.C., Whitefield, P.D., Raper, D.W., “Demonstration of a Regulatory Method for Aircraft Engine Nonvolatile PM Emissions Measurements with Conventional and Isoparaffinic Kerosene fuels”, Energy and Fuels, Vol. 30, No. 9, 7770-7777, 2016. http://dx.doi.org/10.1021/acs.energyfuels.6b01581

Olfert, J. S., Dickau, M., Momenimovahed, A., Saffaripour, M., Thompson, K., Smallwood, G., … Johnson, M. (2017). Effective Density and Volatility of Particles Sampled from a Helicopter Gas Turbine Engine. *Aerosol Science and Technology*, 0–0. https://doi.org/10.1080/02786826.2017.1292346

Stettler, M. E. J., Swanson, J. J., Barrett, S. R. H., & Boies, A. M. (2013). Updated Correlation Between Aircraft Smoke Number and Black Carbon Concentration. *Aerosol Science and Technology*, *47*(11), 1205–1214. https://doi.org/10.1080/02786826.2013.829908

Marine Emissions

Maritime transport emits around 940 million tonnes of CO2 annually and is responsible for about 2.5% of global greenhouse gas (GHG) emissions (3rd IMO GHG study). In recent years, liquefied natural gas (LNG) has become a popular alternative to heavy fuel oils for use in marine engines due to its low cost and increasingly stringent emissions regulations from the International Maritime Organization (IMO). While natural gas (NG) combustion produces substantially less soot than other fossil fuels, its soot emissions are not negligible and have not been morphologically characterized (Trivanovic et al., 2019).

A CS015 catalytic stripper was used in the studies by Corbin et al. (2020) and Trivanovic et al. (2019) to measure the non-volatile PM fraction.

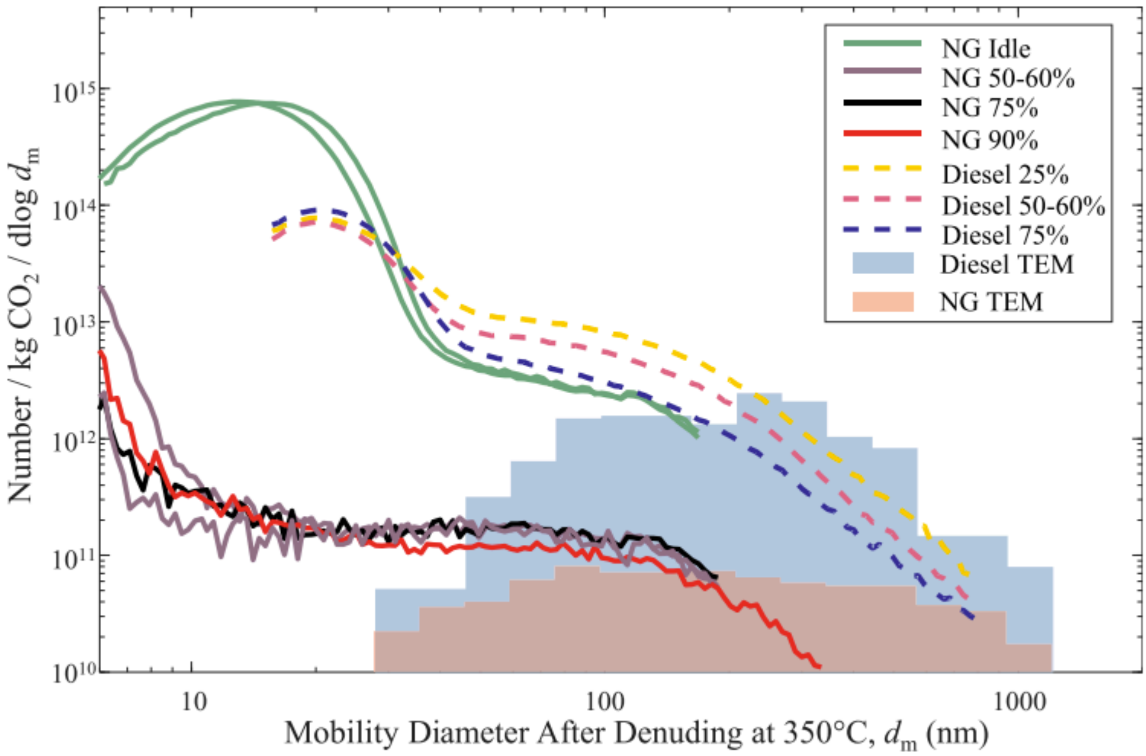

Figure 9: SMPS size distributions of PM catalytically denuded using a CS015 at 350°C (Trivanovic et al., 2019)

Jiang et al. (2018) performed a similar study measuring BC and fuels typically used in marine operations with a small marine engine.

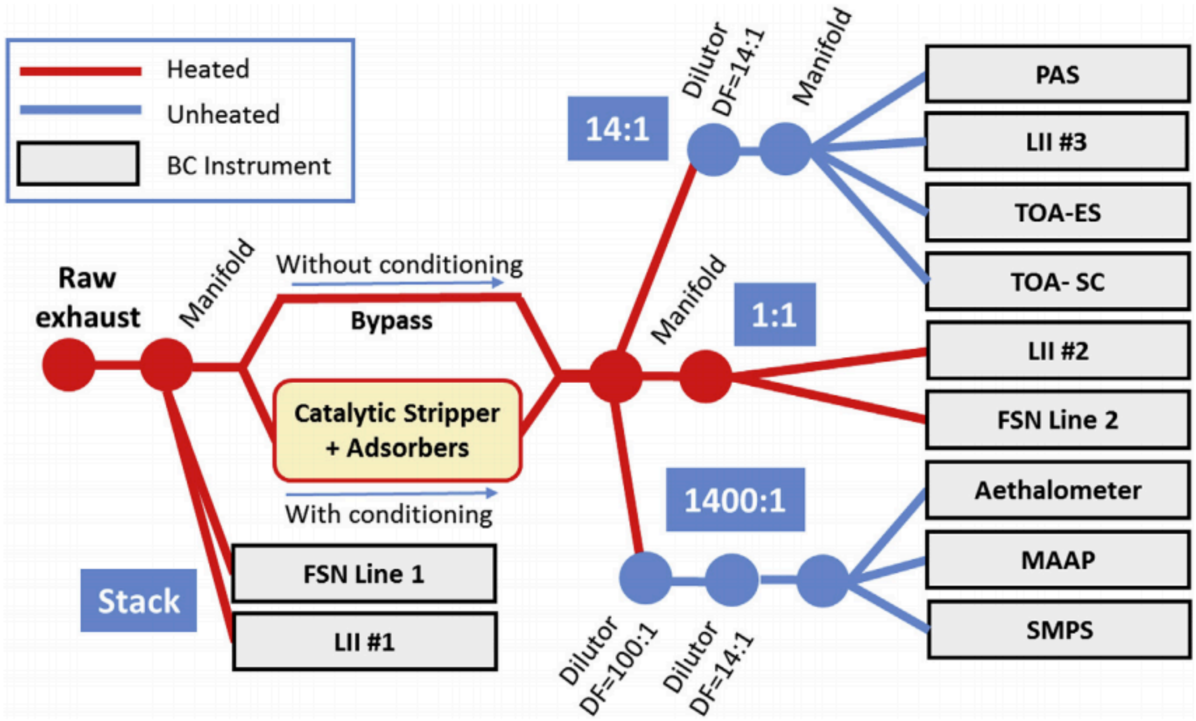

Figure 10: The experimental setup of Jiang et al. (2018), making use of a Catalytic Stripper to supply instrumentation with denuded non-volatile PM from the engine.

A key finding of this research was that the relative BC measured values were mostly independent of load and fuel, for the combinations studied.

The EU. in particular, is pressuring the IMO to take larger steps forward in improving maritime emissions, and research in this area is vital in driving positive changes in this cause.

Corbin, J.C., Peng, W., Yang, J., Sommer, D.E., Trivanovic, U., Kirchen, P., Miller, J.W., Rogak, S., Cocker, D.R., Smallwood, G.J., Lobo, P., Gagné, S., “Characterization of particulate matter emitted by a marine engine operated on liquefied natural gas and diesel fuels”, Atmospheric Environment, Vol. 220, 117030, 2020. https://doi.org/10.1016/j.atmosenv.2019.117030

Jiang, Y., Yang, J., Gagné, S., Chan, T. W., Thomson, K., Fofie, E., … Johnson, K. C. (2018). Sources of variance in BC mass measurements from a small marine engine: Influence of the instruments, fuels and loads. Atmospheric Environment, 182, 128–137. https://doi.org/10.1016/J.ATMOSENV.2018.03.008

Trivanovic, U., Corbin, J.C., Baldelli, A., Peng, W., Yang, J., Kirchen, P., Miller, J.W., Lobo, P., Gagné, S., Rogak, S.N., “Size and morphology of soot produced by a dual-fuel marine engine”, Journal of Aerosol Science, Vol.138, 105448, 2019. https://doi.org/10.1016/j.jaerosci.2019.105448

Improving Calibration

Calibration techniques themselves are seldom published, and as such it can be challenging to find information beyond user manuals. However, from a conceptual point of view, it is not difficult to imagine the benefits of using a catalytic stripper in various calibration setups for aerosol measurement.

As the CS removes non solid material from the aerosol sample, an obvious benefit is that if you are the user of fullerene soot, aquadag, a miniCAST, inverted burner, or similar soot generator, the CS will remove the OC fraction, improving the calibration of MAAP, PSAP, CAPS, SP2, etc, due to an improved accuracy from less interference from non-BC constituents.

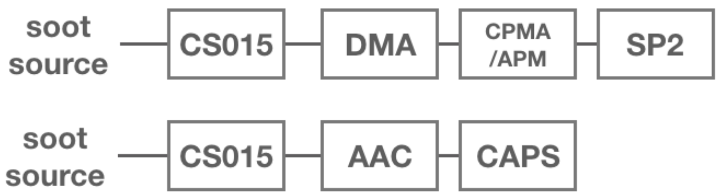

Figure 11: Example configurations for accurate calibration of SP2 and CAPS. Note, dilution and "exhaust" stages are emitted for clarity

The above diagram shows two example configurations for the calibration of the SP2 and CAPS instruments, but the same principle follows for many, many more instruments. The SP2 requires a pure BC source to empirically calibrate the peak height of the incandescence signal, and the CAPS requires pure BC for an accurate absorption measurement.

The CS015 will, in all instances, remove non-BC compounds from the soot source (e.g. aquadag, fullerene soot, miniCAST, inverted burner, Carbon Black, etc), such that the calibration of the instrument is with low uncertainty.

Titosky, J., Momenimovahed, A., Corbin, J., Thomson, K., Smallwood, G., & Olfert, J. S. (2019). Repeatability and intermediate precision of a mass concentration calibration system. *Aerosol Science and Technology*, *53*(6), 701–711. https://doi.org/10.1080/02786826.2019.1592103

Durdina, L., Lobo, P., Trueblood, M.B., Black, E.A., Achterberg, S., Hagen, D.E., Brem, B.T., Wang, J., "Response of Real-Time Black Carbon Mass Instruments to Mini-CAST Soot", Aerosol Science and Technology, Vol. 50, No. 9, 906-918, 2016. http://dx.doi.org/10.1080/02786826.2016.1204423

Filtration Efficiency Measurement

Filtration measurements are difficult to perform, but if the CS is used to eliminate variations in aerosol mixing state due to ambient conditions, by supplying a solid aerosol stream, improvements can be made to filter design in a more accurate manner. Most commonly performed with Diesel particulate filters, we expect to see an increase in studies related to breathing apparatus and respiratory disease following the 2020 COVID19 pandemic.

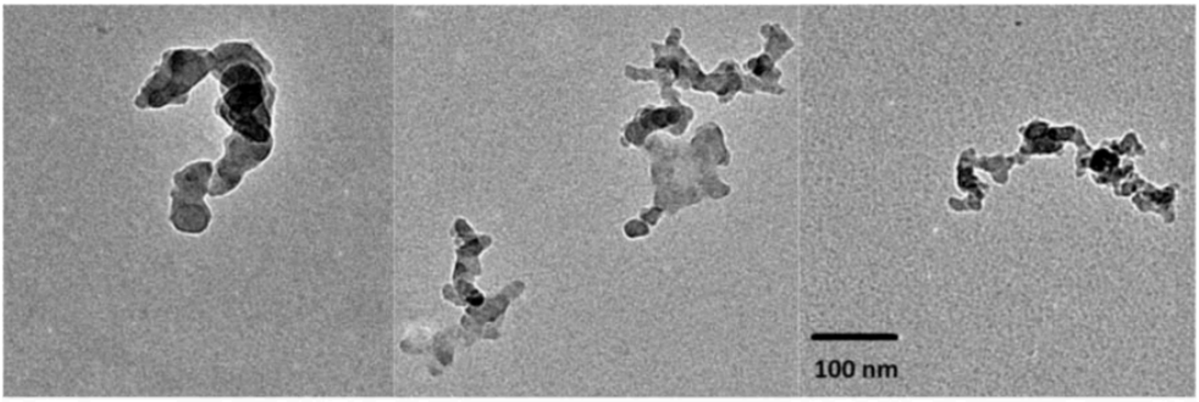

Figure 12: miniCAST soot particles, taken from Mamakos et al., 2013

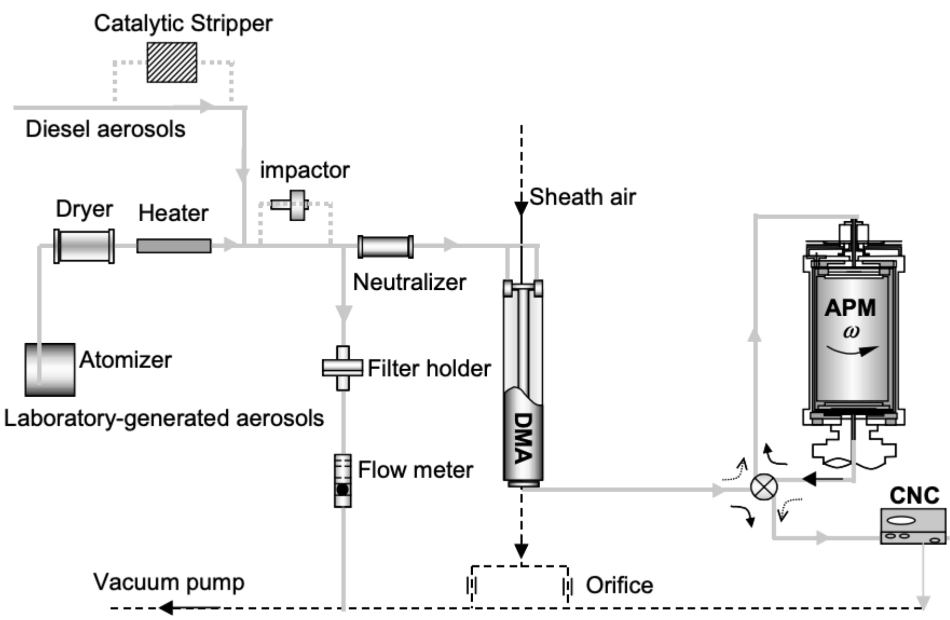

Figure 13: Taken from K. Park et al., 2003

Park, K., Kittelson, D. B., & McMurry, P. H. (2003). A closure study of aerosol mass concentration measurements: Comparison of values obtained with filters and by direct measurements of mass distributions. *Atmospheric Environment*, *37*(9–10), 1223–1230. https://doi.org/10.1016/S1352-2310(02)01016-6

Tobacco, E-cigarette, Marijuana Smoke Measurement

Recent increases in both e-cigarette and marijuana use (due it more widespread legalization) have necessitated the characterization of the billions of nanoparticles contained in each puff. Tobacco smoke offers a benchmark given that it has been extensively studied. Graves, B. M., et al. found tobacco and marijuana smoke particles to be quantitatively similar in volatility, shape, density and number concentration.

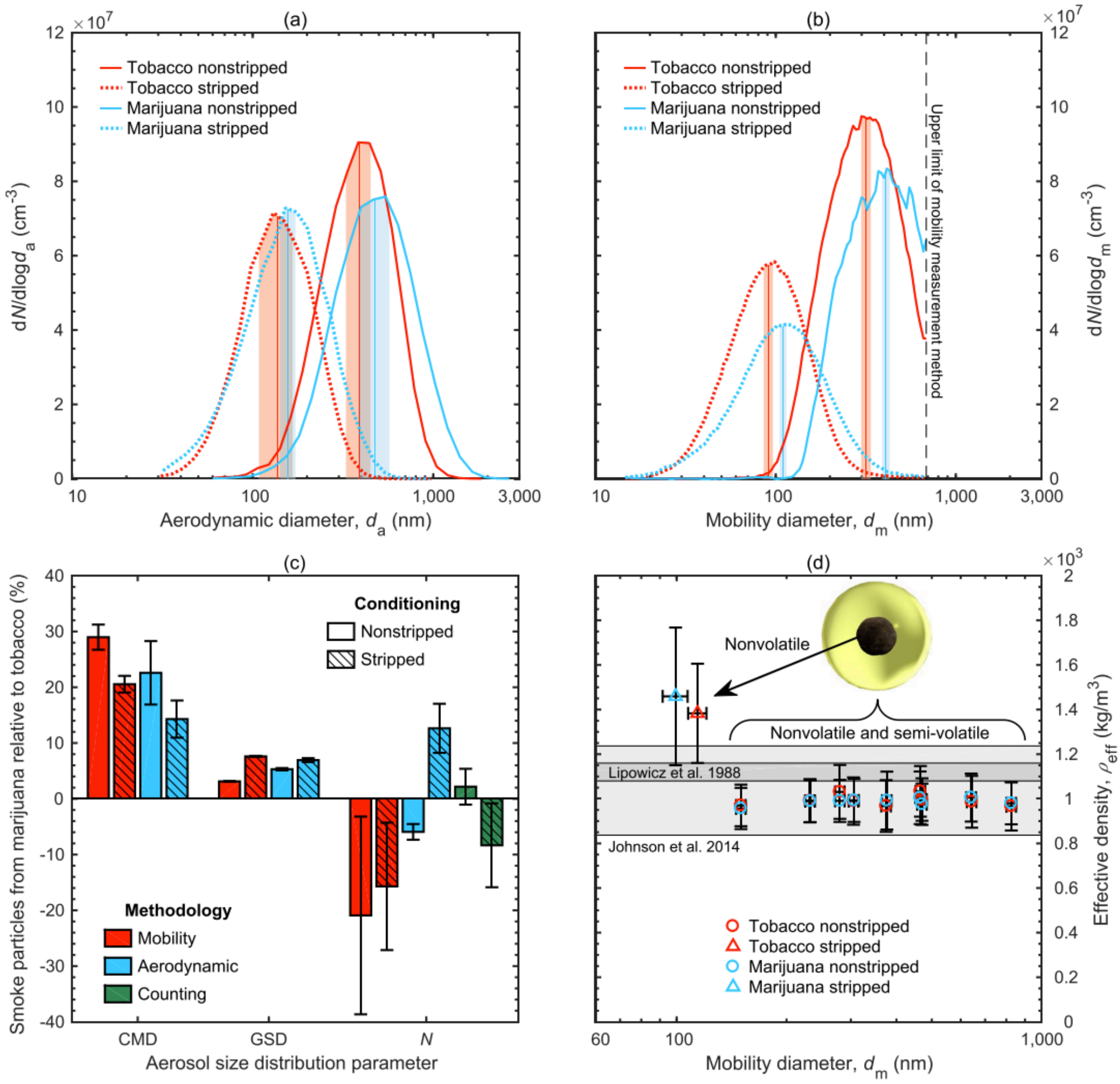

Figure 14: Taken from Graves B. M., et al., 2020.

Graves, B. M., Johnson, T. J., Nishida, R. T., Dias, R. P., Harynuk, J. J., Kazemimanesh, M. Boies, A. M. (2020). Comprehensive characterization of mainstream marijuana and tobacco smoke. *Scientific Reports*, *10*(1), 1–15. https://doi.org/10.1038/s41598-020-63120-6

Measuring Solid Particles in Liquids

A novel approach to measuring solid particles in liquids was adopted by Xiao et al. (2013), using a CS following a nebuliser as shown in the diagram below:

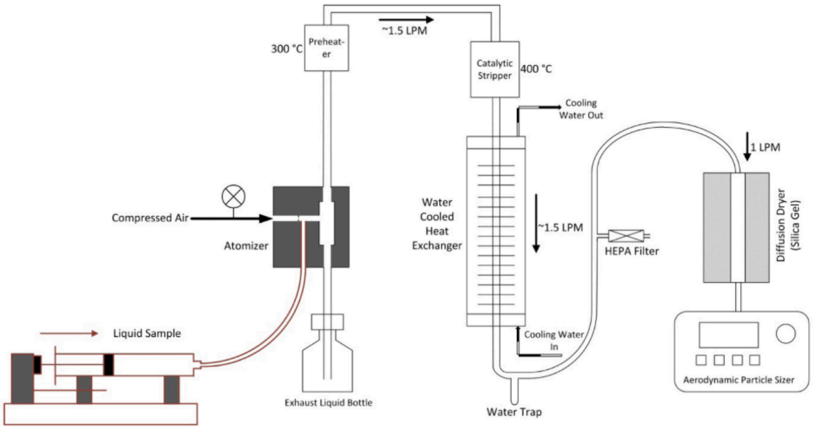

Figure 15: schematic diagram showing the experimental setup for measuring solid particles from a liquid sample

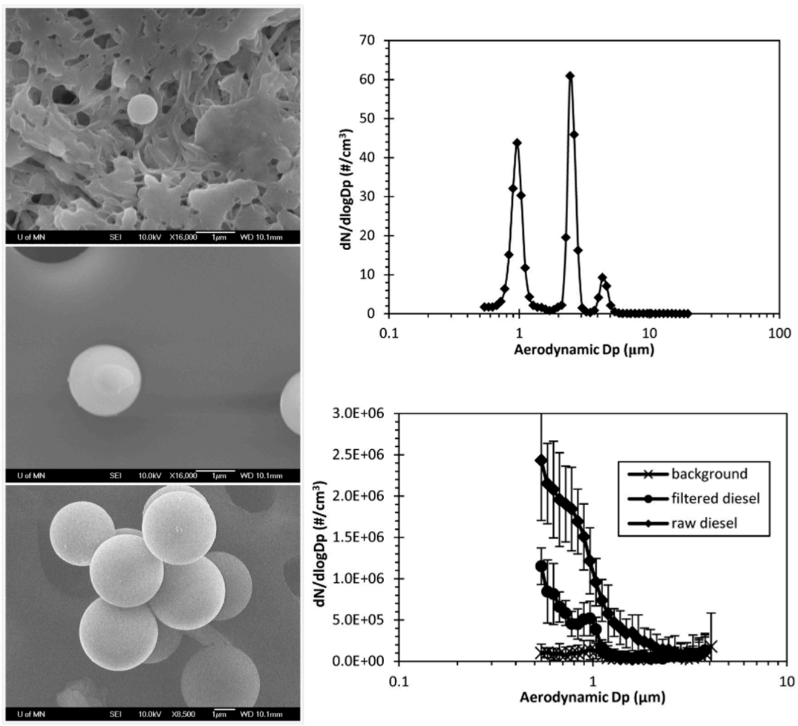

Figure 16: SEM images of seed particles, and aerodynamic size distributions of clean filtered diesel—top graph, and solid particle contaminant size distributions of raw diesel fuel, filtered fuel (filtered diesel) and 3-stage filtered fuel (background)—bottom graph

In this experiment, the CS was used to ensure the complete evaporation and oxidation of organic material, as the Diesel fuel aerosol naturally contains a significant amount of fuel droplets that must be removed in order to measure the contaminant size distribution.

There are numerous potential applications for this technique, such as studying BC in ice core samples, BC in rain water, further fuel contaminants and issues related to ashing.

Xiao, K., Pei, C., Swanson, J., Kittelson, D., & Pui, D. (2013). An Aerosolization Method for Characterizing Particle Contaminants in Diesel Fuel. SAE International Journal of Fuels and Lubricants, 6(3), 2013-01–2668. https://doi.org/10.4271/2013-01-2668

Summary

The CS is a an extremely useful tool for both improve calibrations through reduced uncertainty, as well as offering a unique insight into the properties of aerosol. Volatility can be probed, solid particle fractions studied, brown carbon quantified, and this is just the beginning.

New applications are being thought of continuously, and new papers released at an increasing rate.

Please contact us with your questions regarding how the Catalytic Stripper can be used to improve your measurements!
info@catalytic-instruments.com

Further Reading

Numerous Application Notes exist on our website, updated regularly, including a note on how particle losses have been fully characterised here.

References

A full list of references is updated regularly on our website.

Catalytic Instruments GmbH & Co.KG • Zellerhornstrasse 7 • D-83026 Rosenheim
Tel: +49 8031 901 777-0 • **Fax:** +49 8031 901 777-5 • **email:** info@catalytic-instruments.com
www.catalytic-instruments.com