

Sampling and Analysis of Trace Elements emitted by Diesel Vehicles

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Abstract:

This paper compares a conventional sampling procedure from the constant volume sampling tunnel system to an especially designed flow proportional raw-gas sampling technique. Both techniques were applied in parallel for the determination of trace element emissions of a diesel engine in a series of tests. Based on these studies, the advantages and limitations of both methods will be discussed and their suitability will be assessed.

Introduction

Diesel engines emit fine soot particles which may cause or aggravate serious respiratory and cardiovascular health problems. Therefore, the analysis of particle size and number as well as a comprehensive chemical characterization of diesel emission is of increasing interest. An essential precondition for accurate and reliable results is a suitable sampling procedure which guarantees low contamination levels and excellent reproducibility.

This study compares two sampling methods for the characterization of total or particle bound metals in diesel emissions:

1. The conventional sampling based on filters placed after the constant volume sampling (CVS) system^[1], and
2. a flow proportional raw-gas sampling technique. The latter was designed to pump an undiluted exhaust gas sample through a washing bottle assembly (WB) with downstream back up filter at a rate which is kept proportional to the total exhaust gas and, thus, to yield a representative sample.

Experimental

Measurements were done at the exhaust of a diesel light-duty vehicle using conditions according to New European Driving Cycle (NEDC). Samples from the CVS were collected on quartz-fibre filters. Equally handled fieldblanks were taken to assess the background level of the sampling procedure.

For the flow proportional sampling the raw gas volume flow was measured at 1 Hz by an ultrasonic method (FlowSic). Simultaneous pressure and temperature measurements were used to obtain an instantaneous signal for the standardized raw exhaust flow. A proportional partial flow was drawn through the washing bottle assembly and the back-up filter.

Two separate washing bottle assemblies of the same type were used to sample ambient air simultaneously. These fieldblanks were taken to assess the background level of the new sampling technique. The bottles of the WB assemblies were filled with diluted acid in high purity quality such as Merck suprapur[®]. The downstream back-up filter-holder was equipped with a quartz-fibre filter. Figure 1 presents the principle of the sampling set-up for conventional CVS sampling on filters as well as the set-up of the flow proportional raw gas sampling using the especially designed washing bottle/back-up filter assembly (WB sampling).

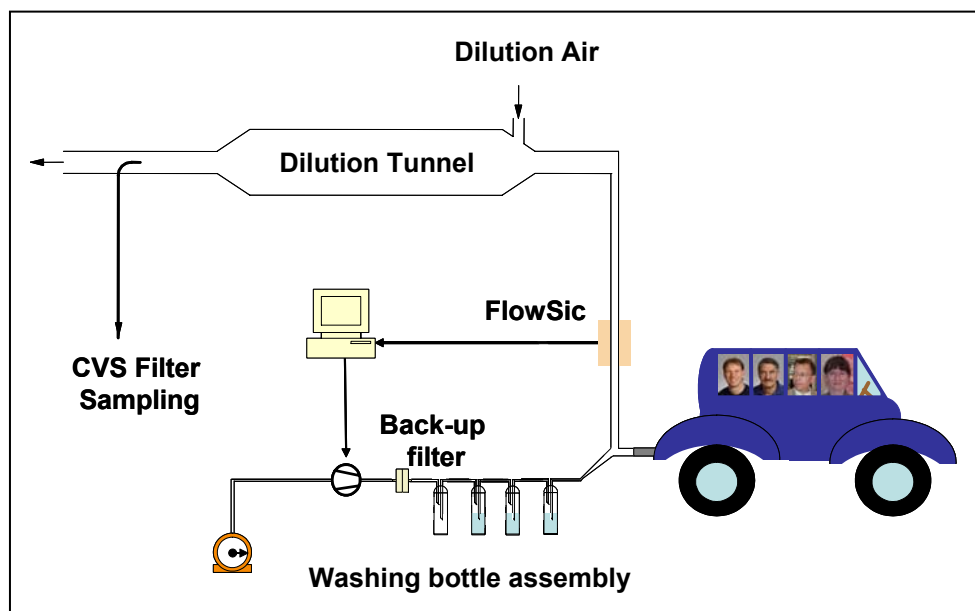


Fig. 1 Sampling set-up for conventional CVS sampling on filters, and for flow proportional raw gas sampling using washing bottle/back-up filter assembly.

All CVS and WB samples were taken simultaneously during four separate test runs (T1 - T4). Two parallel WB assemblies were provided for double determination. Acid solutions and back-up filter were analyzed separately and added for comparison with the CVS data. Metals were determined by inductively coupled plasma mass spectrometry (ICP-MS) after adequate sample preparation.

All filter samples were digested in a high performance microwave digestion unit. The samples usually show low aerosol masses and the concentration of the elements of interest are at ultra-trace levels. The acid mixture for the digestion depends on the elements of interest and filter type. The required low detection limits (DL) are only achievable by consequent optimisation of the sample preparation procedure. Only fresh acids in high purity quality gave adequate, contamination free results. Therefore, only high quality acids such as Merck suprapur and ultrapur quality and high-purity water (18.2

MΩ/cm) prepared by a Milli-Q Gradient A10 System (Millipore) were used for sample preparation. Previous studies also showed that only a control of vessels after cleaning digestion leads to appropriate detection limits. ^{3, 4, 5, 5]}

All acidic absorption solutions from the washing bottles were directly determined by ICP-MS. The spectrometers used in determinations of the aqueous solutions were a quadrupole-ICP-MS *ELAN 6000* (Perkin Elmer/Sciex) and a magnetic sector field ICP-MS *ELEMENT II* (ThermoFinnigan), both operated under standard hot plasma conditions. Standards were prepared from single and multi-element standards in ICP-quality (Merck and Alfa Aesar).

Results and discussion

Metal determination in emission aerosols is mostly limited by sampling procedure. Main reasons are high contamination risk and possible element losses during sampling. The conventional sampling procedure from the constant volume sampling (CVS) tunnel is advantageous with respect to handling. However, the aerosol is usually transported over a relatively long distance through steel pipes. The dilution of the sample by dilution air is another disadvantage because the detectable total concentration is decreased and the contamination risk increased.

The specially designed flow proportional sampling directly from the raw exhaust gas is more complex because it demands the rapid measurement of the normalized total exhaust volume flow and a fast control of the sampling pump over a very wide range of sample flow. However the sampling equipment can easily be cleaned and exchanged which is a major advantage over the CVS method. Finally the flow proportional sampling method is not only suitable for sampling of particle bonded metals but also for total metal content in the exhaust gas.

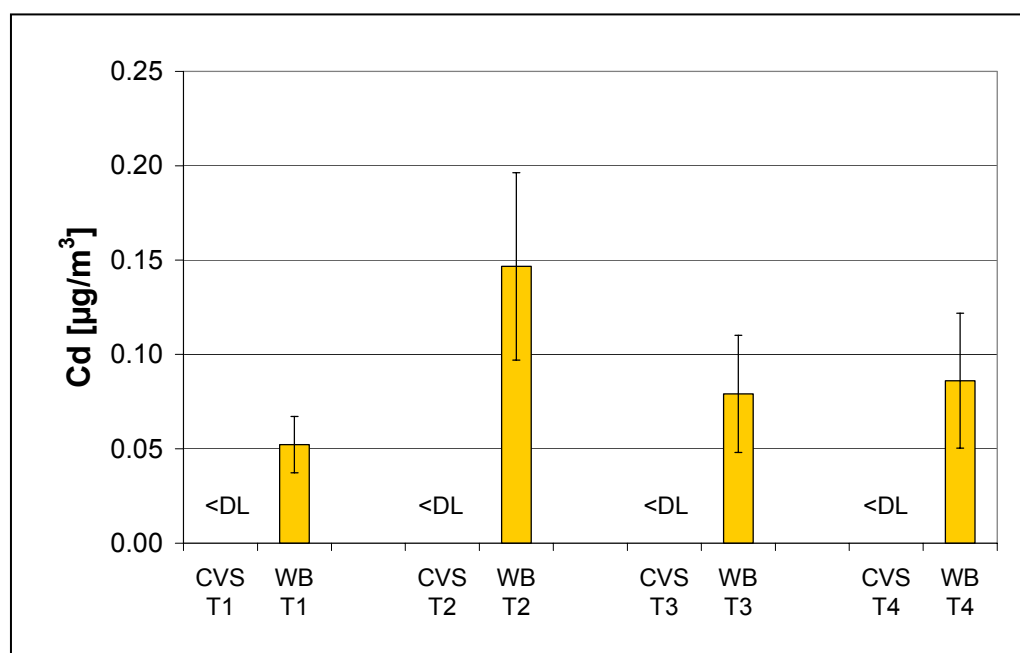


Fig. 2: Comparison for cadmium collected in parallel using CVS and WB sampling methods in four subsequent tests

Figure 2 shows the results for cadmium which represents elements that tend to form volatile species. The WB sampling gave higher results in all four tests whereas the CVS sampling results were mainly below detection limit. This leads to the assumption that the WB sampling directly from the raw gas seems to be advantageous if an element, such as cadmium Cd, tends to form volatile species. Cadmium was mainly detected in the diluted acid solutions of the washing bottles, while the concentrations on the filters were mostly below the detection limit.

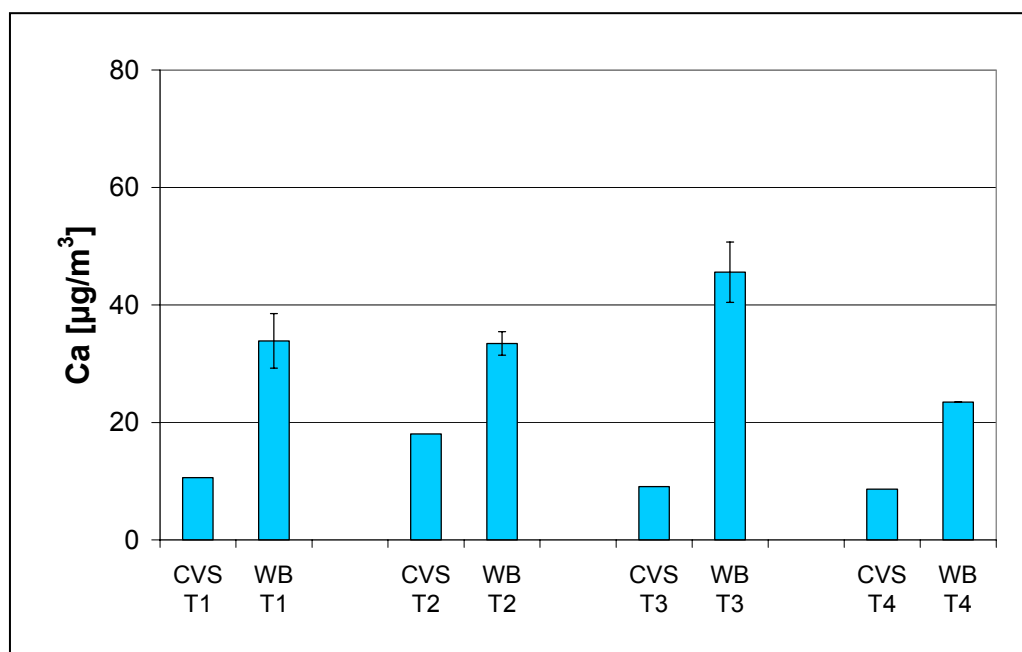


Fig. 3: Comparison for calcium collected in parallel using CVS and WB sampling methods in four subsequent tests

Figure 3 shows the results of calcium as an example for elements which occur mainly in particle bonded form, and which usually show no tendency to form volatile species. For these elements the results based on the two sampling techniques are in better agreement. However, the WB sampling technique tends to give slightly higher results. This might be caused by transport losses in the CVS system. The theory of transport mechanisms and deposition of sub-micron particles supports this theory.^[6]

Figure 4 summarizes the results for iron. Fe shows no systematic dependence on the sampling procedure. The first test gave slightly higher results in the WB sampling, while higher concentrations were determined based on CVS samples for tests T2 to T4. This might reflect the various possible iron sources such as fuel, engine, transport pipes, CVS, etc. which results in an indistinct concentration pattern.

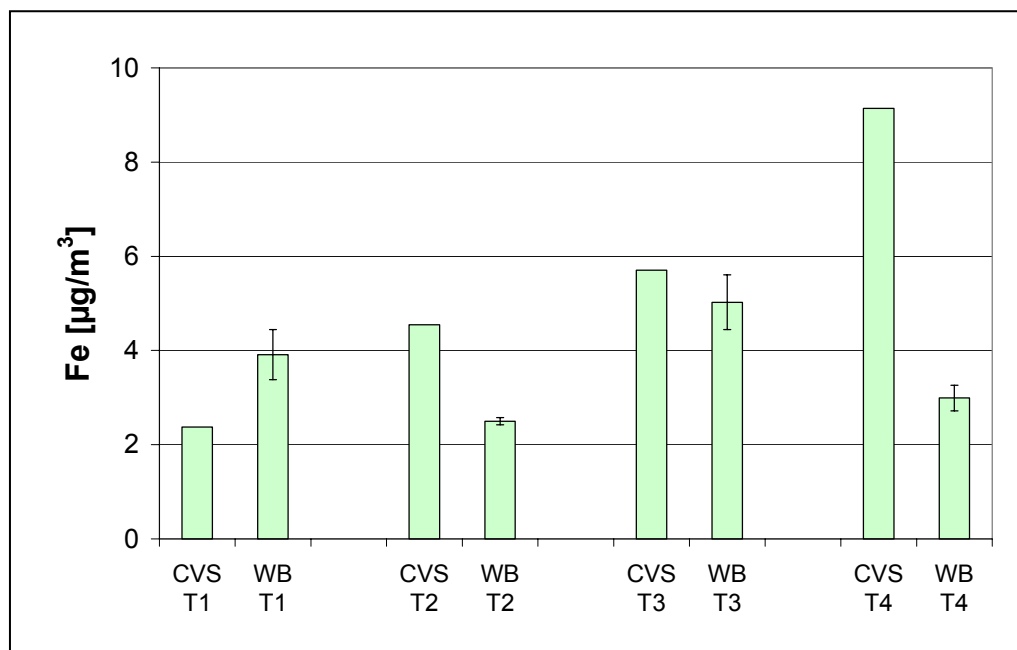


Fig. 4: Comparison for iron collected in parallel using CVS and WB sampling methods in four subsequent tests

Outlook

Further investigations should confirm these preliminary tests and enlighten possible reasons for differences such as transport losses or volatility. Moreover applicability and limits of the two techniques, including repeatability, reproducibility, and improvement potential should be investigated in more detail. One focus might be the current limitation to the CVS system when using ELPI for size fractionation. Further studies should show if a size classified information can also be obtained from a flow proportional sampling directly from the raw exhaust gas, i.e. by using field flow fractionation (FFF) as a possible fractionation method in combination with ICP-MS.

Conclusion

The comparison of the results for both sampling techniques leads us to conclude that the flow proportional raw gas sampling using a washing bottle assembly with downstream back-up filter has some advantages for the sampling of elements which readily form volatile species such as cadmium. Elements which form less volatile species, such as calcium and zinc result in better agreement. However, raw gas sampling still gives slightly higher values which might indicate transport losses in the CVS system. For some elements no clear trend was found, i.e. for iron. Omnipresent elements such as iron might originate from various sources such as engine, fuel, tubing and CVS which possibly results in higher variations. However, flow proportional raw-gas sampling with the washing bottle assembly is a valuable alternative to CVS filter sampling. It is especially suited for volatile species or elements that might be effected during transport to and in the CVS system.

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