

# Monitoring and Method development of Hg in Istanbul Airborne Particulates by Solid Sampling Continuum Source-High Resolution Electrothermal Atomic Absorption Spectrometry

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**Abstract.** In this work, a method has been developed and monitoring for the determination of mercury in PM<sub>2.5</sub> airborne particulates by solid sampling high-resolution continuum source electrothermal atomic absorption spectrometry. The PM<sub>2.5</sub> airborne particulates were collected on quartz filters using high volume samplers (500 L/min) in Istanbul (Turkey) for 96 hours every month in one year. At first, experimental conditions as well as the validation tests were optimized using collected filter. For this purpose, the effects of atomization temperature, amount of sample introduced in to the furnace, addition of acids and/or KMnO<sub>4</sub> on the sample, covering of graphite tube and platform or using of Ag nanoparticulates, Au nanoparticulates, and Pd solutions on the accuracy and precision were investigated. After optimization of the experimental conditions, the mercury concentrations were determined in the collected filter. The filters with PM<sub>2.5</sub> airborne particulates were dried, divided into small fine particles and then Hg concentrations were determined directly. In order to eliminate any error due to the sensitivity difference between aqueous standards and solid samples, the quantification was performed using solid calibrants. The limit of detection, based on three times the standard deviations for ten atomizations of an unused filter, was 30 ng/g. The Hg content was dependent on the sampling site, season etc, ranging from <LOD to 450±64 ng/g in Istanbul. In addition that direct determination of the Hg content in the samples, addition of AuNPs, AgNPs and Pd solution for amalgamation effects on the recoveries were investigated. The results were compared using statistical tests.

**Keywords:** Solid sampling, High-resolution continuum source electrothermal atomic absorption spectrometry, Mercury, PM<sub>2.5</sub> airborne particulate matters, amalgamation

## Introduction

Mercury in airborne particulate matter (APM) originates from both natural (crustal, aquatic, etc.) and anthropogenic sources (smelters, fossil fuel combustion, waste incineration, etc.). It is estimated that one third to two thirds of the total Hg released annually comes from human activities. The levels of Hg in the atmosphere (i.e., in the air that we breathe) are very low and usually do not pose any health risk; however, the steady release of Hg has resulted in current levels that are three to six times higher than the estimated levels in the pre-industrial atmosphere (Araujo 2011, Gelaude 2002, Grobecker 2006, Salvato 1996, Furtado da Silva 2006 ).

An attractive alternative for trace element determination in complex matrices might be the direct analysis without any sample preparation, using solid sampling graphite furnace AAS (SS-GF AAS), as has been proposed for the determination of mercury in environment, in biological samples and in polymers

(Araujo 2011). This technique essentially requires only a minimum of sample preparation, represents a minimum risk of contamination, provides highest sensitivity as no dilution is involved, does not use chemicals, maybe except for a modifier, and requires less time due to the absence of sample preparation. Nevertheless, SS-GF AAS might still encounter problems when volatile elements, but Araujo et al (2011) were accomplished this problem in the Hg determination by SS-GF AAS.

The aim of this study was to develop a alternative methods for Hg determination in airborne samples using direct determination and some nanoparticulates addition effects, avoiding sample dissolution.

## Materials and Methods

An Analytik Jena ContrAA 700 high-resolution continuum source atomic absorption spectrophotometer equipped with a transversely heated graphite furnace,

SSA600 solid sampling autosampler (Analytik Jena, Jena, Germany) and a 300W xenon short-arc lamp (XBO 301, GLE, Berlin, Germany) operating in a hot-spot mode as a continuum radiation source was used for all measurements. Measurements were carried out at 253.652 nm absorption line of Hg with 5 pixels (central pixel $\pm$ 1). All measurements were performed using pyrolytically coated graphite tubes with integrated PIN platform (Analytik Jena Part No. 407-A81.025). All measurements were carried out as triplicate.

Samples were collected on quartz filters using High Volume Air Sampler with PM2.5 collector. All reagents were analytical grade. High-purity water (resistivity 18.2 M $\Omega$ .cm) obtained by a TKA reverse osmosis and a TKA deionizer system (TKA Wasseraufbereitungssysteme GmbH, Niederelbert Germany) was used for all dilutions. Whenever necessary, ceramic knife was used to cut filters. The optimized graphite furnace program for the determination of Hg in airborne particulates by solid sampling technique is given in Table 1.

**Table 1.** Graphite furnace temperature programme for the determination of Hg in collected airparticulate samples.

Step No	Furnace Temperature (°C)	Heating rate	Hold (s)
1	60	10	1
2	95	10	6
3	1100	1000	10
4	1600	1600	5

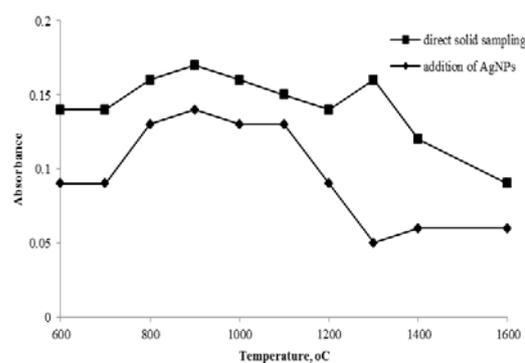
### Sample collection and preparation for analytical procedure

The empty quartz filters were dried until constant weight at 500 °C for 10 hours to remove some organic residues. The PM2.5 airborne particulates in Istanbul were collected on a quartz filter every month by a high volume air sampler with PM2.5 collector applying an air-flow rate of 500 L/h for 96 hours. The procedure was repeated every month once for one year. The traffic densities in sampling areas for the both cities was very high (The number of average motor vehicles during the day time in front of sampling stations of Istanbul were approximately 3800 per hour). The filter loaded with air-particulates were dried at 110 °C overnight. The empty filter masses were varied to 1.52 $\pm$ 0.01 g, and for collected filter masses were changed 1.63 $\pm$ 0.05 g. For determination of Hg, the filter with the sample was cut pieces below 1 mg and inserted in the platform for analysis.

### Results and Discussion

In order to investigate the effects of atomization temperatures on the sensitivity of the analyte simultaneously and optimize the graphite furnace program properly performing collected filter, the curves were obtained at different atomization temperatures

between 600 and 1600 °C with direct determination of the samples and addition to Ag/AuNPs and Pd solution. In the absence of any addition, the highest allowable temperature for Hg at almost all atomization temperatures was max at 900 °C. when the addition of the AgNPs the temperature was found stable between 800-1200 °C with low RSD values as seen in Fig 1 (and other solutions addition and effect not mentioned in this text).



**Fig. 1.** Atomization temperature for Hg determination in collected airborne samples by direct solid sampling and addition with AgNPs.

Another important parameter is for solid sampling is the effect of sample amount on the linearity and precision. It is likely that the analytes in high amount of sample could not be atomized effectively. In addition, when the platform was excessively overloaded, some losses may occur during the transferring of sample to the balance and furnace. The upper limit for the sample + filter by solid sampling AAS was around 1.8 mg at which the platform was almost brimful. At higher amounts, linearity, peak shapes and especially precision were deteriorated.

By applying the optimized parameters and using the aqueous and solid standards, the Hg concentration in the samples were changed between <LOD to 500 $\pm$ 64 ng/g by direct solid sampling for the monitoring the samples. The addition of nanoparticulates in the platform were compared with direct determination of samples without any addition and the results found with a good agreement. The advantages and disadvantages of the different methods using solid sampling were discussed.

### Conclusion

The study presents a method development Hg determination and the monitoring of PM2.5 mass, Hg concentration with by solid sampling high continuum source electrothermal atomic absorption spectrometry in airborne particulates collected from Istanbul.

The procedure for the acid digestion before cold vapor technique and preconcentration for the determination of Hg in air particulates is quite troublesome, time consuming and open to contamination and analyte losses. In addition, due to irreproducible blank values which are mostly very close to analyte concentrations in the samples,

the reliable results cannot not be reported. However, SS-HR-CS-GF AAS is free from all the above-mentioned risks and drawbacks. After optimization of experimental parameters, the Hg concentrations could be directly determined using solid calibrant and solution calibrant. The need of high number of sampling is not a disadvantage because by this way the distribution of the analyte in microscale, i.e. microheterogeneity of the collected sample could be identified. The quantifications with solid calibrants and addition of amalgamation solutions were found more reliable for better accuracy. On the other hand, monitoring of the Hg is important parameters for the environmental pollution.

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