Quantifying uncertainty in the measurement of arsenic in suspended particulate matter by Atomic Absorption Spectrometry with hydride generator

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Abstract
Arsenic is the toxic element, which creates several problems in human being specially when inhaled through air. So the accurate and precise measurement of arsenic in suspended particulate matter (SPM) is of prime importance as it gives information about the level of toxicity in the environment, and preventive measures could be taken in the effective areas. Quality assurance is equally important in the measurement of arsenic in SPM samples before making any decision. The quality and reliability of the data of such volatile elements depends upon the measurement of uncertainty of each step involved from sampling to analysis. The analytical results quantifying uncertainty gives a measure of the confidence level of the concerned laboratory. So the main objective of this study was to determine arsenic content in SPM samples with uncertainty budget and to find out various potential sources of uncertainty, which affects the results. Keeping these facts, we have selected seven diverse sites of Delhi (National Capital of India) for quantification of arsenic content in SPM samples with uncertainty budget following sampling by HVS to analysis by Atomic Absorption Spectrometer-Hydride Generator (AAS-HG). In the measurement of arsenic in SPM samples so many steps are involved from sampling to final result and we have considered various potential sources of uncertainties. The calculation of uncertainty is based on ISO/IEC17025: 2005 document and EURACHEM guideline. It has been found that the final results mostly depend on the uncertainty in measurement mainly due to repeatability, final volume prepared for analysis, weighing balance and sampling by HVS. After the analysis of data of seven diverse sites of Delhi, it has been concluded that during the period from 31st Jan. 2008 to 7th Feb. 2008 the arsenic concentration varies from 1.44 ± 0.25 to 5.58 ± 0.55 ng/m3 with 95% confidence level (k = 2).

1. Background
In chemical metrology most of the important decisions are based on the quality and the reliability of results of quantitative analysis. In this context it is also important to have reliability of the results in the international trade and analytical results should be acceptable to all users within the country or outside the country. This can be achieved by the estimation of uncertainty in the measurements as per ISO/EURACHEM guidelines [1-5]. In this regard ISO has published “Guide to the expression of uncertainty in measurement (GUM)” in 1995 in collaboration with BIPM, IEC, IFCC, IUPAC, and OIML. Since last decades there is an increasing interest in arsenic study in the environment because of its toxicity to plants, animals and human beings. The major contamination sources of such toxic metals in the air are natural (volcanoes) as well as anthropogenic like industries [6,7]. The industrial sectors like metal smelting, refining sector contributes major sources of contamination in the environment. The arsenic in atmosphere is generally found associated with fine particles (<2 μm), as arsenate (+5 oxidation state) and arsenite (+3 oxidation state). Recent study shows that lung cancer is significantly higher in the areas where...
The arsenic concentration is 1.77 ng/m³ or more [8]. Such studies become important when experimental results conclude that lung cancer is significantly higher in the areas where arsenic concentration is 1.77 ng/m³ or more. In the measurement of arsenic by AAS-HG there are several interference due to transition metal ions, which forms hydride during reaction with sodium borohydride, sodium hydroxide and hydrochloric acid [9-12]. So it is important to measure all the possible sources of uncertainty in measurement before make any conclusion. As the determination of arsenic with the uncertainty in an environmental sample is a tedious job as there are so many parameters from sampling to final value, which influences the result.

The evaluation of the uncertainty at every step of the experiment is one of the requirements of the standard ISO/IEC17025 for certain test methods to get accreditation. In the last several years uncertainty measurement have been carried in different materials by using different techniques [13-16], but there are hardly studies related to such complex matrix in environmental samples.

For the measurement of arsenic and uncertainty measurement in SPM samples by AAS-HG, we have collected seven samples of SPM on cellulose filter paper through HVS in diverse sites of Delhi. The locations of sampling site are marked in map of Delhi given in Figure 1. The Figure 2 represents the SPM concentration during the sampling period. There are several sources of uncertainty in chemical metrology like incomplete definition, sampling, environmental conditions, uncertainties of masses, volumes, equipment, reference values, measuring equipment approximation, assumptions incorporated in experimental methods, random variations, etc. The uncertainty is of two types ‘Type A’ (evaluated using statistical analysis of a series of observations) and ‘Type B’ (evaluated using other means than the statistical analysis of a series of observations). So in proposed study, an attempt has been made to choose such a complex matrix for the evaluation and expression of uncertainty in measurement of arsenic in SPM samples by AAS-HG, following documents published by ISO/IEC 17025:2005, EURACHEM guideline and GUM document.

2. Results and discussion

The arsenic concentration varies from country-to-country and depends mostly upon the industrial and transport emission. In Delhi the arsenic concentration were found to be from 1.44 ± 0.25 to 5.58 ± 0.55 ng/m³ at seven

Figure 1 Locations of sample collection for arsenic measurement in Delhi.
different sites in proposed period. The maximum concentration of arsenic was found at Ashram zone (S-1 site; 5.58 ± 0.55 ng/m³) and minimum concentration was found at Pitampura and NPL zone (S-4, S-7; 1.44 ± 0.25 ng/m³). The high concentrations of arsenic at Ashram is mainly due to transport, industry and thermal power plant near by ashram and in Loni Road area which is densely populated zone, the house hold activities, industrial and transport contribute towards more arsenic contamination in the air. In Spain a study has been carried out in the year 2001 and 2002 in PM2.5 and an average concentration of 6.4 ng/m³ has been reported which, is more than the concentration of arsenic observed from various sites of Delhi. In another study of Yoshikawa concluded that lung cancer is significantly higher in the areas where arsenic concentration is 1.77 ng/m³ or more. So it is evident from the proposed study that five site out of seven sites of Delhi have more arsenic then the reported value. So these are the highly risky zones due to high level of arsenic content in the air.

The precise and accurate determination of arsenic in SPM sample is a tedious job due to huge losses during sample digestion process and due to vaporizing nature. At the same time evaluation of combined uncertainty in such a complex matrix is very complicated as there are various parameters, which contribute uncertainty in the entire process. On determining the uncertainty for arsenic content measurement we were redundantly meticulous in identifying all uncertainty sources. In a routine determination of uncertainty we recommended that it is possible to be much less pedantic, and only reveal and realistically quantify the most significant components. The uncertainty components, which contribute a negligible value, could be ignored from the calculation of combined uncertainty value. The uncertainty components, which are found to contribute significant value during the subsequent computations they can be quantified more precisely and final combined uncertainty, can be recalculated. In the determination of arsenic concentration with uncertainty budget in environmental sample there are five major sources, which directly influence the final results those are \( |C_{\text{As}}|, |V_{\text{Test}}|, |W_{\text{TSPM}}|, |V_{\text{HVS}}| \) and \( |W_{\text{ANA}}| \). The repeatability under \( |C_{\text{As}}| \) is the major component, which contributes maximum uncertainty in arsenic determination. Repeatability depends upon various factors like volume of sample and acid taken for measurement in hydride generator. So we should take proper precautions during analysis. The reference standard stock solution is also other crucial parameters. So for the calibration of the instrument the standard stock solution must be off having low uncertainty. The Flow rate is also parameter which contributes uncertainty in HVS sampling, as flow rate get changed by several factors such as oily nature of the sample, presence of photochemical smog, wood smoke may block the filter paper and cause a rapid drop in air flow. Besides these high humidity and dense fog can cause the filter to become wet and thus airflow reduces through the filter paper. Sampling through HVS is another contributor for uncertainty in arsenic determination.

### 3. Conclusion

A generalized scheme for planning a measurement and a simple, practical approach to estimate and combining
uncertainties has been demonstrated for the determination of arsenic in SPM samples. The results show that the arsenic concentration varies $1.44 \pm 0.25$ ng/m³ to $5.58 \pm 0.55$ ng/m³ with variation of sites with 95% confidence level. The experimental result shows that the heavy traffic site and industrial site are the major sources for the contamination of arsenic in environment.

4. Experimental Section

4.1 Instruments and Apparatus

Atomic Absorption Spectrometer (AAS) of Analytik Jena make Vario-6 with a hydride generator accessory was used for the analysis of arsenic. The arsenic measurements were carried out at 193.7 nm wavelength at optimum conditions of acids, temperature and reducing agent. The pipette of 5 mL and volumetric flask of 50 mL capacity used were of Borosil glass works India Limited. The pipettes and volumetric flasks were calibrated prior to analysis by National Physical Laboratory-India (National Metrology Institute of India) following international standard procedure and protocol. All the acid digestion and dilution work was carried out in cleaned laminar flow bench equipped with the proper exhaustive system. The sampling of SPM was carried out using High Volume Sampler (HVS-410, Make: Envirotech) and was collected on pre-desiccated cellulose filter papers. No chemical treatment of cellulose filter paper were carried out before sampling, but the filter paper were dried for 3 hrs in an oven at 105°C before sampling to remove moisture if any and to get constant weight. Flow rate of HVS was kept about 1.0 ± 0.2 m³/min. and the sampling time was eight hours.

4.2 Reagents

Nitric acid (69%), Hydrochloric acid (35%) of GR grade (Guaranteed Reagent), which were further purified by sub boiling point distillation in a quartz glass device, Hydrogen Peroxide (50%), Sulphuric acid (98%) all E. Merck (India) make were used. De-ionized water (18 mega ohm resistivity) prepared from Millipore milli-Q element water purification system, USA was used throughout the process. The reference standards stock solution of 1.0 mg/litre (BND 301.03) of arsenic was used prepared by NPL-India. The stock solution was diluted upto working range of AAS-HG for arsenic and these solutions were used for the calibration of the AAS-HG instrument.

4.3 Sampling Site and Description

New Delhi is located 160 km south of the Himalayas at latitude 28°24' to 28°53'N and longitude 76°20'E to 77°20'E with an altitude of about 216 meter above mean sea level. Delhi’s climate is mainly influenced by its inland position and the prevalence of continental air during major part of the year. Delhi has three distinct seasons: summer, monsoon and winter. For the proposed study seven different sites were selected namely Ashram (S-1), which is a heavy traffic zone and thousands of vehicles crossing this junction per hour, Azadpur (S-2) is a thickly populated residential area in North West Delhi district. It is India’s largest wholesale market for vegetable and fruits called the Azad Market. Due to several industries in this area it is consider as industrial zone also. Loni Road (S-3) is densely populated area and also a traffic zone, Pitampura (S-4) is neither a heavy traffic zone nor a industrial zone, so we have considered this as an ambient zone, Highway no. 56 (S-5) is a traffic zone, Naraina (S-6) is an industrial zone, it also includes Mayapuri industrial area and NPL (S-7) is considered to be mixed zone. Two sides of NPL are surrounded by ridge area whereas other two sides are surrounded residential area, with traffic movement. The SPM samples were collected between 9 am to 6 pm because of the major operational activities carried out during daytime and in the night time the filter paper get moist due to dew and flow rate of HVS also decrease sharply after heavy loading of SPM. The sampling was carried out between 31st Jan. 2008 to 7th Feb. 2008.

4.4 Sample digestion procedure

For the determination of arsenic two replicates of 18 × 11.5 cm size (known weight at deposited area) of all the seven sites were taken into a separately cleaned air tight poly tetra fluoro ethylene (PTFE) vessel. To these vessels 15 mL of sub boiled nitric acid, 5 mL of hydrogen peroxide and 5 mL of de-ionized water were added and it was closed tightly with PTFE vessel lid. The PTFE vessels-containing samples were kept for overnight at room temperature to oxidized arsenic and released from SPM samples. These steps minimize the risk of losing of arsenic during digestion. After keeping the PTFE vessel for overnight, 4 to 5 drops of sulphuric acid was added to each vessel and PTFE vessel was kept on hot plate by covering with Teflon lid at 100°C for 15-20 minutes and then heated at 150°C -160°C. Further the lid of the PTFE vessel was opened and it was heated again after addition of 10 mL of hydrochloric acid. Further in syrupy condition the samples were heated again with 5 ml hydrochloric acid to ensure the complete removal of nitric acid. Finally the solutions were boiled once again with 15 ml 1:1 de-ionized water and hydrochloric mixture. After digestion the whole content in the vessel was transferred into 100 mL capacity quartz centrifuge tube and centrifuged at 5000 rotations per minute for 2-3 minutes to separate solid particles from the solutions. The supernatant liquid was transferred in to a glass beaker. The remaining residue in the vessel was washed several times with hot water to ensure complete transfer of digested sample from the vessel. Further the solutions
were heated at 75°C for 45 minutes with 10 mL of 25% potassium iodide and 15 mL of 25% ascorbic acid solution to convert As (V) to As (III). The final solutions were made 50 mL by de-ionized water. In the final solution arsenic was determined by AAS-HG using respective standards and principal resonance line (193.7 nm) after reducing arsenic in the presence of sodium borohydride (3%), sodium hydroxide (1%) and hydrochloric acid (5%) using electro thermal heating at 900°C. Mean absorbance values of six readings of two replicates (three each) were taken into the consideration for calculation of the concentration of arsenic. Procedural blank for cellulose filter paper without sample was also done to check the blank levels for arsenic and correction applied wherever required. The details of the procedure are published elsewhere [17].

4.5 Determination of concentration of arsenic in SPM sample

In the determination of arsenic in SPM samples major sources of the uncertainty have been included in the calculation of combined uncertainty according to the EURACHEM/GUM guidelines. The concentration of arsenic $C(M_{As})$ in the SPM samples has been evaluated using AAS-HG technique by following equation.

$$C(M_{As}) = \frac{C_{AS} \times V_{TEST} \times W_{TPSM}}{V_{HVS} \times W_{ANA}} \text{ ng/m}^3$$

(1)

Where; $C(M_{As}) = \text{Concentration of arsenic in SPM (ng/m}^3\text{)}$; $C_{AS} = \text{Concentration of arsenic analyzed from AAS-HG in } \mu\text{g/litre}$; $V_{TEST} = \text{Volume made of the test sample after wet digestion process in mL}$; $W_{TPSM} = \text{Total weight of SPM deposit on 18 cm } \times 23 \text{ cm filter paper(area taken for analysis (gm))}$; $V_{HVS} = \text{Volume of the air processed through HVS (m}^3\text{)}$; $W_{ANA} = \text{Weight of SPM deposited on 18 cm } \times 11.5 \text{ cm filter paper area taken for analysis (gm)}$.

In this manuscript we have taken some important contributions that are stated above in equation-1. The parameters which contributed towards the uncertainty are also shown in ‘Fish- bone or Cause and effect or Ishikawa diagram in Figure 3.

Table 1 Various evaluated components for the determination of arsenic in SPM samples

| Sample I.D. | Concentration of arsenic obtained from AAS-HG after reducing blank (μg/litre) | Concentration of Arsenic in ng/m³ [C₆₈⁺] | Volume made for test samples (Table 2) [V.TEST] | Volume of air processed through HVS at STP (m³) [V₆₈] | Total weight of SPM deposited on 18 cm x 23 cm filter paper (gm) [W₆₈] | Weight of SPM deposited on 18 cm x 11.5 cm filter paper area taken for analysis (gm) [W₁₁₅] |
|-------------|-------------------------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| S-1         | 27.52 ± 1.28*                                   | 5.58 ± 0.271                    | 50 ml                           | 493.52                          | 0.2210 ± 0.0021                 | 0.1105 ± 0.0042                 |
| S-2         | 13.33 ± 0.87*                                   | 3.21 ± 0.182                    | 50 ml                           | 414.97                          | 0.1116 ± 0.0041                 | 0.0568 ± 0.0081                 |
| S-3         | 19.92 ± 0.97*                                   | 4.36 ± 0.212                    | 50 ml                           | 457.16                          | 1.3088 ± 0.0004                 | 0.6544 ± 0.0007                 |
| S-4         | 6.62 ± 0.65*                                    | 1.45 ± 0.112                    | 50 ml                           | 456.65                          | 0.1406 ± 0.0033                 | 0.0703 ± 0.0065                 |
| S-5         | 8.03 ± 0.73*                                    | 1.70 ± 0.122                    | 50 ml                           | 471.24                          | 0.1896 ± 0.0025                 | 0.0948 ± 0.0049                 |
| S-6         | 9.82 ± 0.83*                                    | 2.37 ± 0.131                    | 50 ml                           | 414.78                          | 0.2404 ± 0.0019                 | 0.1202 ± 0.0038                 |
| S-7         | 5.62 ± 0.59*                                    | 1.44 ± 0.113                    | 50 ml                           | 391.63                          | 0.7760 ± 0.0006                 | 0.3880 ± 0.0012                 |

*± Value obtained for six determinations of two replicates (three each).

*² and *³ = details of uncertainty in weighing in Table 9.
In accordance with GUM [4], the combined uncertainty for the mathematical model, which is a product or quotient form, is given by:

\[
\left[ \frac{u_c(y)}{y} \right]^2 = \sum_{i=1}^{N} \left[ p_i \frac{u(x_i)}{x_i} \right]^2
\]  

(2)

The sensitivity coefficient = \( p_{iy}/x_i \). Where \( p_i \) is the power of the terms in the equation (1).

\( p_1 \) for \( C_{AS} = +1 \);
\( p_2 \) for \( V_{TEST} = +1 \);
\( p_3 \) for \( W_{TSPM} = +1 \);
\( p_4 \) for \( W_{ANA} = -1 \) and \( p_5 \) for \( V_{HVS} = -1 \);

The combined uncertainty is given by:

\[
\left[ \frac{u_c(M_{As})}{M_{As}} \right]^2 = \left[ \frac{u_{CAS}}{CAS} \right]^2 + \left[ \frac{u_{VTEST}}{V_{TEST}} \right]^2 + \left[ \frac{u_{WTSPM}}{W_{TSPM}} \right]^2 + \left[ \frac{u_{WANA}}{W_{ANA}} \right]^2 + \left[ \frac{u_{VHVS}}{V_{HVS}} \right]^2
\]  

(3)

The uncertainty evaluation in every step of the experiment has been discussed in the following sub-sections:

5.0 Uncertainty components in the measurement of concentration of arsenic obtained from AAS-HG \([C_{AS}]\)

Referring to Figure 4, the major sources of the uncertainty for \( C_{AS} \) are due to reference standard stock solution, repeatability, dilution in 50 mL volumetric flask from stock solution to working range and 5 mL capacity pipette used for dilution.

5.2 Uncertainty evaluation due to repeatability

The repeatability has also been considered for the determination of arsenic. The concentration of the arsenic was determined experimentally by analyzing six determinations of two replicates (three each). The standard deviation in values obtained by AAS-HG and repeatability has been calculated by using following EURACHEM guide. The details are given in table 3.

5.3 Uncertainty in 50 mL volumetric flask used for dilution from 1.0 mg/L (1000 \( \mu \)g/L) to working range

The final volume of standard arsenic solution made was 50 mL after several dilutions. The major uncertainties were due to temperature variation and calibration accuracy as per manufacturer’s specification. The details are given in Figure 5 and table 4.

The uncertainty associated with the use of the volumetric flask of 50 mL capacity at a temperature other than the calibration temperature (temperature difference) is given by:

\[
u(V_T) = V \times \Delta T \times 2.1 \times 10^{-4}
\]  

(4)

Table 3 Uncertainty in repeatability of values obtained from AAS

| Sample I.D. | Concentration of arsenic in SPM samples in ng/m\(^3\) (x) | Standard uncertainty u(x) | Combined uncertainty due to \([C_{AS}]\) from section 5.0 |
|-------------|------------------------------------------------|--------------------------|--------------------------------------------------|
| S-1         | 5.58 ± 0.271*1                                   | 0.272                    |
| S-2         | 3.19 ± 0.182*1                                   | 0.183                    |
| S-3         | 4.34 ± 0.212*1                                   | 0.213                    |
| S-4         | 1.44 ± 0.112*1                                   | 0.113                    |
| S-5         | 1.69 ± 0.122*1                                   | 0.123                    |
| S-6         | 2.33 ± 0.131*1                                   | 0.132                    |
| S-7         | 1.42 ± 0.113*1                                   | 0.114                    |

*1 ± = uncertainty in repeatability in concentration measurement of arsenic.
Where \( V \) is the volume of volumetric flask and \( \Delta T \) is temperature difference

The same effect of temperature has been considered three times in the measurement of arsenic and the values have been calculated using equation (4): 50 mL volumetric flask used for dilution from stock solution to working range (refer to table 4), 5 mL pipette used for dilution (refer to table 5) and again 50 mL volumetric flask used for making volume after wet digestion of sample (refer to table 6).

5.4 Uncertainty due to 5 mL pipette used for dilution

5 mL aliquot was taken by 5 mL pipette for making dilution upto 50 mL. The main uncertainties were due to temperature variation and calibration accuracy as quoted by the manufacturer. The effect of temperature on 5 mL pipette has also been considered as per section 5.2. The details are given in Figure 6 and table 5.

Combined uncertainty due to section 5.0 \([C_{AS}]\) has been calculated by the sum of subsection 5.1, 5.2, 5.3 and 5.4 as follows.

\[
\text{Combined uncertainty of } [C_{AS}] = \sqrt{(\text{uncertainty due to reference standards stock solution})^2 + (\text{Uncertainty due to repeatability})^2 + (\text{Uncertainty due to 50 mL volumetric flask})^2 + (\text{Uncertainty due to 5 mL pipette})^2}
\]

So substituting values from table 2, 3, 4 and 5 combined uncertainty due to \([C_{AS}]\)

\[
\begin{align*}
\sigma(C_{AS}) \text{ for S-1} &= \sqrt{(0.012)^2 + (0.271)^2 + (0.01)^2 + (0.0018)^2} = 0.272 \\
\sigma(C_{AS}) \text{ for S-2} &= \sqrt{(0.012)^2 + (0.182)^2 + (0.01)^2 + (0.0018)^2} = 0.183
\end{align*}
\]

Similarly the combined uncertainty for sample S3-S7 is calculated.

Table 5 Uncertainty due to five mL pipette used for dilution up to 50 mL

| Uncertainty component | Distribution | Standard Uncertainty ± \( \mu(x) \) |
|-----------------------|--------------|----------------------------------|
| Calibration accuracy  | Normal ± 0.02 mL | 0.02/2 = 0.01 |
| Effect of temperature | Rectangular $5 \times *3 \times 2.1 \times 10^{-4}$ | $0.0032/\sqrt{3} = 0.0018$ |

For every dilution the uncertainty will change, this change is very negligible; therefore for simplicity we have considered the uncertainty of first dilution even after performing the dilution second times. So combined uncertainty due to \([C_{AS}]\) by substituting values from Table 2, 3, 4 and 5.

\[
\begin{align*}
\sigma(C_{AS}) \text{ for S-3-5} &= \sqrt{(0.012)^2 + (0.271)^2 + (0.01)^2 + (0.0018)^2} + 0.272 \\
\sigma(C_{AS}) \text{ for S-6-7} &= \sqrt{(0.012)^2 + (0.182)^2 + (0.01)^2 + (0.0018)^2} + 0.183
\end{align*}
\]

Similarly combined uncertainty for sample S3-S7 has been calculated and the final values are given in table 3.
6.0 Uncertainty evaluation in 50 mL volumetric flask used in making volume after wet chemical digestion \([V_{TEST}]\)

The known weight of the sample was processed through wet chemical route and final volume was made 50 mL. Referring to Figure 7, the sources of uncertainty for \([V_{TEST}]\) are due to calibration uncertainty and effect of temperature variation on 50 mL volumetric flask. The uncertainty associated with temperature for 50 mL volumetric flask is carried out as per section 5.3. The details are given in Figure 7 and table 6.

\[
\text{Combined Uncertainty in 50 mL volumetric flask} = \sqrt{(0.01)^2 + (0.018)^2} = 2.06 \times 10^{-2}.
\]

7.0 Uncertainty evaluation due to volume of air processed through high Volume sampler \([V_{HVS}]\)

Referring to Figure 8 the sources of the uncertainty for \([V_{HVS}]\) are due to the uncertainty due to flow rate of air through HVS, time recording by stop watch, ambient pressure measurement and measurement of temperature of the site.

7.1 Uncertainty due to flow rate of air through HVS

The volume of air sampled through HVS has been calculated on the basis of equation-5 and volume of air processed at standard temperature and pressure (STP) is calculated by using equation-6 given below.

\[
\text{Volume of air sampled} = \text{Time (min)} \times \text{Flow rate (m}^3/\text{min}) = 500 \times 1.1 = 550 m^3
\]

\[
\text{Volume of air processed through HVS at STP} = \frac{V_1 \times P_1 \times T_1}{T_2 \times P_2}
\]

Where, \(V_1\) - Total volume of air processed through HVS, \(P_1\) - Atmospheric pressure on the date of measurement (mm of mercury; table 7); \(T_1\) - Standard temperature (273); \(T_2\) - working temperature [temperature of the sampling site °C + standard temperature] and \(P_2\) - Standard pressure (760 mm of mercury). Substituting value from table (7) in equation-6

\[
\text{Volume of air processed through HVS at STP} = 550 \times 745.65 \times 273 \times (25.5 + 273) \times 760 = 493.52 (m^3).
\]

The detail of uncertainty due to flow rate of air is given in table 8.

7.2 Uncertainty due to ambient pressure measurement

The onsite pressure of the atmosphere was measured in millibar (mbar) by using ambient pressure measurement instrument and the value measure was converted in mm of mercury unit by multiplying mbar value by 0.75. The details are given in table 8.

7.3 Uncertainty in time recording due to Time Tracker Recorder

The total time was recording by using inbuilt time tracker recorder in the HVS used for processing the atmospheric air. The details are given in table 8.

7.4 Uncertainty in measuring temperature of the site

The onsite temperature of the open atmosphere was measured by calibrated thermometer three times in a
day and average of three values were used for calculation of total volume of air processed at STP. The details are given in table 8.

\[
\text{Combined uncertainty due to } \left[ V_{\text{HVS}} \right] = \sqrt{\text{Uncertainty in flow rate of HVS}^2 + \text{Uncertainty in time tracker recorder}^2 + \text{Uncertainty in ambient pressure measurement}^2 + \text{Uncertainty in temperature of the site}^2}
\]

Putting values in above from table 8 the combined uncertainty due to HVS;

\[
\left[ V_{\text{HVS}} \right] = \sqrt{(0.1)^2 + (0.025)^2 + (0.3)^2 + (1.5)^2} = 1.533
\]

8.0 Uncertainty evaluation due to balance used for weighing the blank and SPM deposited filter paper \([W_{\text{TSPM}}]\) and \([W_{\text{ANA}}]\)

The analytical balance used is Mettler Toled AX 204 with accuracy ± 0.1 mg. The details are given in Figure 9 and table 9.

The total weight of the SPM deposited on filter paper and weight of the filter paper used for wet digestion process was calculated as below. Taking example of sample-1.

(I) Total area of the cellulose filter paper used for sampling = 20.3 cm × 25.4 cm = (515.6 cm\(^2\))

(II) Total area of the filter paper used for deposition (18 cm × 23 cm) = 414 cm\(^2\)

(III) Total weight of the cellulose filter paper used for sampling (515.6 cm\(^2\)) = 4.255 g

(IV) Empty weight of the filter paper of same deposit area (414 cm\(^2\)) = 3.4164 g

(V) Formula for calculation of weight on 414 cm\(^2\) area = 

\[
\frac{\text{weight of (20.3 cm × 25.4 cm) × Area of (18 cm × 23 cm)}}{\text{Area of (20.3 cm × 25.4 cm)}} = \frac{4.255 × 414}{515.6^2} = 3.4164 g
\]

(It has been considered that the thickness of the cellulose filter used is uniform through out the area. On this basis we have calculated the weight of the deposit area (414 cm\(^2\)).

(VI) Total suspended particulate matter deposit on the filter paper (414 cm\(^2\)) = 3.6374 g

(VII) Weight of the SPM deposited (V-IV) = 0.2210 g

(VIII) Weight of the SPM deposited area (18 cm × 11.5 cm) taken for analysis = 0.1105 g

The weight calculation for other samples (S-2 to S-7) were done in same way as given above for sample-1.

9. Calculation of concentration and associated uncertainty of arsenic in S-1 sample

The concentration of arsenic in the seven SPM has been determined by AAS-HG using equation-1. The
uncertainty associated with the concentration of arsenic has been calculated using the uncertainty components. Substituting the values from table 1 into equation-1, the concentration of arsenic (ng/m$^3$) in S-1 sample:

$$C(M_{As}) = 27.52 \times 50 \times 0.221 \times 0.1105 \times 493.52 = 5.58 \text{ ng/m}^3$$

The combined uncertainties in the determination of arsenic in case of sample S-1 was carried out using equation-3. Putting values from summary table 10, combined uncertainty;

$$u_c(M_{As}) = \sqrt{\left(u(C_{As})/M_{As}\right)^2 + \left(u(V_{TEST})/V_{TEST}\right)^2 + \left(u(W_{TEST})/W_{TEST}\right)^2 + \left(u(W_{ANA})/W_{ANA}\right)^2 + \left(u(V_{HVS})/V_{HVS}\right)^2}$$

For S-1, $u_c(M_{As})/5.58 = \sqrt{\left(0.272/5.58\right)^2 + \left(2.06 \times 10^{-2}/50\right)^2 + \left(0.424 \times 10^{-3}/0.221\right)^2 + \left(0.424 \times 10^{-3}/0.1105\right)^2 + \left(1.533/493.52\right)^2} = 0.049$

Therefore Concentration of arsenic for S-1 = 5.58 ± 0.55 ng/m$^3$

In the same way the concentration of arsenic in sample S-2 has been calculated. Putting values from table 1 concentration of arsenic is;

| Name of the site                           | Date of Sampling | Sampling starting time | Sampling end time | Flow rate of air sampled through HVS (m$^3$/min)* | Time (in min.) | Volume of air processed through HVS (m$^3$) | Atmospheric pressure measured on site (mbar) | Atmospheric Pressure in mm of mercury (mbar × 0.75) | Temperature of the sampling site (°C)* | Volume of air processed through HVS at STP (m$^3$) |
|--------------------------------------------|------------------|------------------------|-------------------|-----------------------------------------------|---------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|-----------------------------------------------|---------------------------------------------|
| Heavy traffic site; Ashram zone (S-1)      | 31-1-08          | 9.10 am                | 5.30 pm           | 1.0 ± 0.2                                      | 500           | 550                                         | 994.2 ± 0.55                                | 745.65                                      | 24 ± 3                                         | 493.52                                      |
| Industrial site; Azadapur zone (S-2);      | 1-2-08           | 10.0 am                | 5.00 pm           | 1.0 ± 0.2                                      | 420           | 462                                         | 995.2 ± 0.55                                | 746.40                                      | 24 ± 3                                         | 414.97                                      |
| Densely populated + Traffic site Loni Road (S-3); | 2-2-08          | 9.45 am                | 5.30 pm           | 1.0 ± 0.2                                      | 465           | 511.5                                       | 993.6 ± 0.55                                | 745.20                                      | 25 ± 3                                         | 457.16                                      |
| Ambient site Pitampura zone (S-4);         | 3-2-08           | 9.45 am                | 5.30 pm           | 1.0 ± 0.2                                      | 465           | 511.5                                       | 992.5 ± 0.55                                | 744.37                                      | 25 ± 3                                         | 456.65                                      |
| Traffic zone; Highway No. 56 (S-5);       | 4-2-08           | 10.30 am               | 6.30 pm           | 1.0 ± 0.2                                      | 480           | 528                                         | 995.5 ± 0.55                                | 746.63                                      | 26 ± 3                                         | 471.24                                      |
| Industrial site; Nariana zone (S-6);       | 5-2-08           | 9.15 am                | 6.00 pm           | 1.0 ± 0.2                                      | 425           | 467.5                                       | 996.3 ± 0.55                                | 747.22                                      | 26 ± 3                                         | 414.78                                      |
| Mixed site; NPL zone (S-7);               | 7-2-08           | 10.0 am                | 4.40 pm           | 1.0 ± 0.2                                      | 400           | 440                                         | 992.8 ± 0.55                                | 744.60                                      | 26 ± 3                                         | 391.63                                      |

*For the calculation of air processed through HVS the flow rate of HVS was taken 1.1 m$^3$/minute, while the temperature was taken 25.5 in case of S-1, S-2 and 26.5°C in case of S-3, S-4 and 27.5 in case of S-5 to S-7.

Table 8 Uncertainty in sampling of SPM by HVS

| Uncertainty components                           | Distribution | Calibration uncertainty reported in certificate | Standard uncertainty u(x) |
|------------------------------------------------|--------------|-------------------------------------------------|--------------------------|
| Uncertainty in flow rate of HVS at 95% confidence level | Normal, k = 2 (Type ‘B’) | 1.0 ± 0.2 (m$^3$/minute) | 0.2/2 = 0.1 |
| Uncertainty due to time (in minutes) recording by time tracker recorder at 95% confidence level | Normal, k = 2 (Type ‘B’) | 1.0 ± 0.05 (minute) | 0.05/2 = 0.025 |
| Uncertainty in ambient pressure measurement at 95% confidence level | Normal, k = 2 (Type ‘B’) | 994.2 ± 0.6 (mbar) | 0.6/2 = 0.3 |
| Uncertainty in measuring *temperature of the site at 95% confidence level | Normal, k = 2 (Type ‘B’) | 30 ± 3 (°C) | 3/2 = 1.5 |

Combined uncertainty due to $V_{HVS} = \sqrt{((0.1)^2 + (0.025)^2 + (0.3)^2 + (1.5)^2)} = 1.533$
And the combined uncertainty in the determination of arsenic in case of sample S-2 is carried out using equation-3. Putting values from summary table 10, the combined uncertainty;

\[
\frac{u(C_{As})}{C_{As}} = \sqrt{\left(\frac{0.183}{3.21}\right)^2 + \left(\frac{0.0047}{50}\right)^2 + \left(\frac{0.424 \times 10^{-3}}{0.1136}\right)^2 + \left(\frac{0.424 \times 10^{-3}}{0.0568}\right)^2 + \left(\frac{1.533}{414.97}\right)^2} = 0.058
\]

\[
C_{As} = 3.21 \times 0.058 = 0.196
\]

Therefore Concentration of arsenic for S-2 = 3.21 ± 0.39 ng/m³

Similarly combined uncertainties for concentration of arsenic in samples S-3 to S-7 have been calculated. Table 11 shows the analytical results of the arsenic with uncertainty at seven sites.

Table 10 Summary of combined uncertainty

| S.N | \(\frac{u(C_{As})}{C_{As}}\) | \(\frac{u(V_{TEST})}{V_{TEST}}\) | \(\frac{u(W_{TSPM})}{W_{TSPM}}\) | \(\frac{u(W_{ANAL})}{W_{ANAL}}\) | \(\frac{u(V_{HVSS})}{V_{HVSS}}\) |
|-----|------------------|------------------|------------------|------------------|------------------|
| S-1 | 0.272/5.58 | 2.06 \times 10^{-5}/50 | 0.424 \times 10^{-3}/0.2110 | 0.424 \times 10^{-3}/0.1106 | 1.533/493.52 |
| S-2 | 0.183/3.21 | 2.06 \times 10^{-5}/50 | 0.424 \times 10^{-3}/0.1136 | 0.424 \times 10^{-3}/0.0568 | 1.533/414.97 |
| S-3 | 0.213/4.36 | 2.06 \times 10^{-5}/50 | 0.424 \times 10^{-3}/1.3088 | 0.424 \times 10^{-3}/0.6544 | 1.533/457.16 |
| S-4 | 0.112/1.45 | 2.06 \times 10^{-5}/50 | 0.424 \times 10^{-3}/0.1406 | 0.424 \times 10^{-3}/0.0703 | 1.533/456.65 |
| S-5 | 0.123/1.70 | 2.06 \times 10^{-5}/50 | 0.424 \times 10^{-3}/0.1896 | 0.424 \times 10^{-3}/0.0948 | 1.533/471.24 |
| S-6 | 0.132/2.37 | 2.06 \times 10^{-5}/50 | 0.424 \times 10^{-3}/0.2404 | 0.424 \times 10^{-3}/0.1202 | 1.533/414.78 |
| S-7 | 0.114/1.44 | 2.06 \times 10^{-5}/50 | 0.424 \times 10^{-3}/0.7760 | 0.424 \times 10^{-3}/0.3880 | 1.533/391.63 |
Table 11 Results of arsenic with uncertainty in SPM analyzed by AAS-HG

| Name of the site          | SPM in μg/m³ | Concentration of arsenic in ng/m³ with combined uncertainty |
|---------------------------|--------------|----------------------------------------------------------|
| Ashram zone (S-1); Heavy traffic site | 395          | 5.58 ± 0.55                                               |
| Azadpur zone (S-2); Industrial site | 203          | 3.21 ± 0.38                                               |
| Loni Road (S-3); Densely populated +Traffic site | 2337         | 4.36 ± 0.43                                               |
| Pitampura zone (S-4); Ambient site | 251          | 1.45 ± 0.24                                               |
| Highway No.56 (S-5); Traffic site | 338          | 1.70 ± 0.22                                               |
| Nariana zone (S-6); Industrial site | 429          | 2.37 ± 0.27                                               |
| NPL zone (S-7); Mixed site | 347          | 1.44 ± 0.25                                               |

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Authors' contributions
NS participated in the design of the study, carried out sampling, wet digestion of the sample and written work. VNO has contributed in analysis of the arsenic analysis by AASH-PKG has given valuable suggestion during experiment as well written work. TA has calculation of various uncertainties, which have been identified in the digestion of the sample and written work. NK has contributed in writing the manuscript. TA has

Competing interests
The authors declare that they have no competing interests.

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