

Electronic Supplementary Information (ESI)

Manuscript title:

Arsenic exposure through groundwater to the rural and urban population in the Allahabad-Kanpur track in the upper Ganga plain

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Determination of total arsenic in contaminated groundwater after KBrO₃ oxidation.

Arsenic contaminated groundwater on analysis shows arsenic as As^{III} and As^V. Total arsenic analysis in contaminated groundwater could be done (a) by reducing all arsenic to As^{III} or (b) by oxidizing all arsenic to As^V followed by suitable instrumental methods.

For reducing total arsenic to As^{III}, normally reagents in use are (i) KI/HCl or KI/Ascorbic acid. But the method widely in use for determination of total arsenic in water is after reduction to As^{III} by KI/HCl (*Perkin Elmer MHS-10, 1978*). The limitation of this method is that for complete reduction from As^V to As^{III} the sample has to be kept for about 60 minutes after the addition of reagents thus preventing the instant analysis of the water samples.

We also observed that in this procedure of reduction, satisfactory results are obtained at lower concentrations but a complete conversion from As^V to As^{III} does not occur at higher concentrations (above 500 μg L⁻¹). Hence, dilution is needed and more time is required for those samples having As concentration above 500 μg L⁻¹.

For analysis of large number of samples every day for total arsenic, it was felt reduction technique is not convenient, so an alternative method was required.

Literature survey showed that for instantaneous on line oxidation of As^{III} to As^V, KBrO₃ was used followed by photometric measurement (*Dasgupta et al. 2002*). We used KBrO₃ oxidation method for routine analysis of total arsenic from groundwater arsenic contaminated areas of Ganga Meghna Brahmaputra Plain (*Sengupta 2006*).

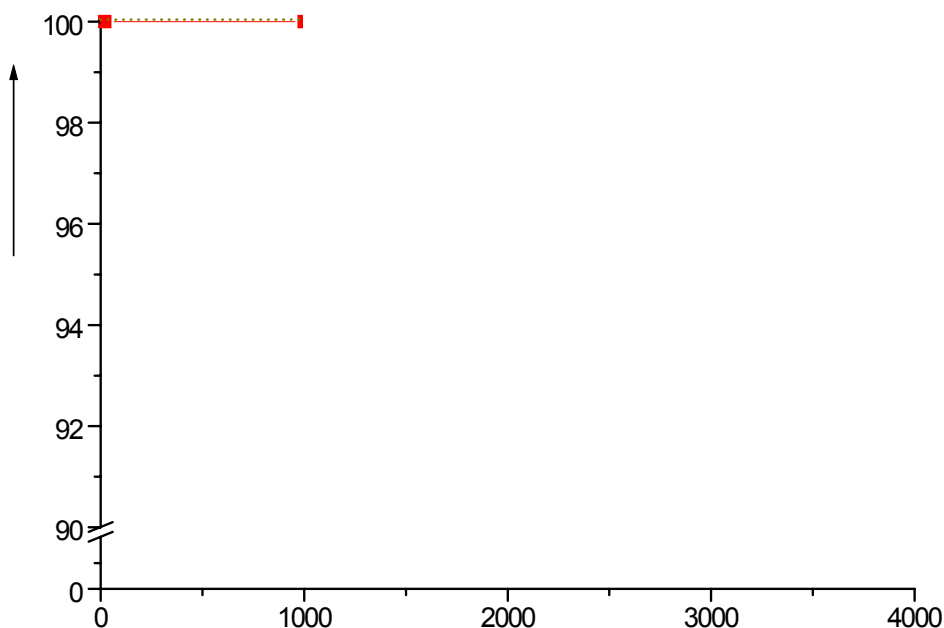
Procedure:

To each 10 ml of water sample containing both As^{III} and As^V at different concentrations, one drop of 2% (w/v) KBrO₃ solution was added and can be measured immediately against known standard arsenic by FI-HG-AAS. **ESI Figure I** shows, that only 1 drop of 2% KBrO₃ is enough to oxidize As^{III} to As^V completely up to 1000 μg L⁻¹ and almost 97% conversion was observed up to 4000 μg L⁻¹.

Effect of pH on the KBrO₃ oxidation method:

We have studied the efficiency of KBrO₃ method in oxidizing As^{III} to As^V at various pH ranges. It was observed that KBrO₃ method works well within the pH ranging from highly acidic pH (corresponding to 8N HNO₃) to below pH-3. On further increasing the pH, ferric hydroxide precipitates.

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ESI Figure 1: Conversion of As As^{III} to As^V after addition of 1 drop, 2% potassium bromate as oxidizing agent.

Use of field-kit for arsenic determination based on Mercuric Bromide Stain Method

Beginning in 1997 the World Bank, UNICEF, WHO and other international aid agencies came forward to combat the gruesome groundwater arsenic situation in Bangladesh. A unanimous decision was taken to test all the hand tube wells to gauge the magnitude of the calamity. Both in Bangladesh and West Bengal, India, it was decided to use field test kits to determine the arsenic concentration in hand tube wells and to color tube wells having arsenic less than $50 \mu\text{gL}^{-1}$ green and those above $50 \mu\text{gL}^{-1}$ red. The field-kits used at that time were based on the principle of mercuric bromide stain method (*Greschonig and Irgolic, 1997*). Concentration of arsenic was determined by visual identification of the color matching with standard. The most important limitation of using these field kits is visual identification of the color especially in the lower range. The accuracy of the bromide stain method was evaluated in a round robin exercise, and it was reported that the arsenic concentrations for a solution of arsenite at $50 \mu\text{gL}^{-1}$ in distilled water had a relative standard deviation (RSD) of 75% (*Greschonig and Irgolic, 1997*). It was further reported (*Greschonig and Irgolic, 1997*) that the mercuric bromide stain method was incapable of producing quantitative meaningful results with $\text{RSD} \leq 10\%$ below a concentration $150 \mu\text{gL}^{-1}$ of arsenic. Hussam et. al. (1999) reported that the Merck field kit “is not only inadequate to screen water samples containing less than $100 \mu\text{gL}^{-1}$ of arsenic, but also provides

toxic arsine gas that may be a health hazard". Several researchers criticized (Hussam *et al.* 1999, BGS 1999, Pande *et al.* 2001, Rahman *et al.* 2002, Kinniburgh and Kosmus 2002, Deshpande and Pande 2005, Jakariya *et al.* 2007) use of such field-kits to measure arsenic concentrations at the level 10 and $50\mu\text{gL}^{-1}$ and coloring the hand tube-wells safe and unsafe. However, two publications reported suitability of such type of field-kit for measurement of arsenic even in the low arsenic concentration range (van Geen *et al.* 2005, Steinmaus *et al.* 2006) and used them in arsenic contaminated areas. The publication of van Geen *et al.* 2005, was strongly criticized (Mukherjee *et al.* 2005).

In our comparative study of several field-kits based on mercuric bromide stain method with FI-HG-AAS from 2866 field samples (hand tube-wells), we reported (Rahman *et al.* 2002) that false detection was within 10% from 70 to less than $600\mu\text{gL}^{-1}$ of arsenic. Based on the above findings we used the Hach field-kit (as it was readily available to us) to know the area in Allahabad-Kanpur track in upper Ganga plain where hand tube-well water samples contained arsenic concentration above $70\mu\text{gL}^{-1}$. On our way from Allahabad to Kanpur in upper Ganga plain track, we measured couple of hand tube-well water samples from villages by the Hach field-kit first and if the field-kit showed higher arsenic concentration to couple of samples from a village, we collected more water samples from there for our laboratory analysis. In this publication, we have no desire to make a comparative study of Hach field-kit with our FI-HG-AAS technique.

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