

## ENHANCEMENT OF TRACE METAL ATOMIC ABSORPTION SIGNALS THROUGH THE OPTIMIZATION OF PHYSICAL FACTORS ATTENDANT ON ASPIRATION RATES

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(Received March 24, 1985; revised December 23, 1985)

An optimization scheme based on instrumental components controlling the aspiration rates of water sample solutions in the flame atomic absorption technique is proposed. The methodology adopted stems from the quantitative study of the effect of such factors as fuel/oxidant flow rates, burner-slit, length, radii of aspiration and sampling capillaries, aspiration temperature and addition of organic solvent to the aqueous samples. The method is applied to the estimation of silver, copper, chromium, iron, strontium, zinc, cadmium, lead and mercury concentrations in drinking waters without the use of a preconcentration step. An overall hundred-fold enhancement in the absorption signals is achieved at a fairly high S/N ratio. The method is quantitative with a precision of  $\pm 1\%$  at the detection level of the individual trace metals.

### INTRODUCTION

In recent years precise quantitative estimations of elements and compounds harmful to human health have resulted from increasing efforts to enhance the sensitivity of the relevant measuring techniques. This is specifically true for atomic absorption analysis of heavy metals in water samples of varied nature. Except under the most unusual circumstances, the flame atomic absorption method necessitates a preanalysis concentration step [1,2,3] to this effect. Although it is not difficult to obtain an enrichment factor of  $10^{-2}$ – $10^{-3}$  for the conventional  $1$ – $10^{-3}$  ppm sample range, yet the concentration ranges of most heavy metal constituents of different waters usually lie outside the atomic absorption analytical range. In addition, the preconcentration steps involve the use of special methodology and chemicals under specified conditions not ordinarily amenable to analytical convenience. For example, the electrodeposition and freeze-ash drying methods convert the sample to a form that is difficult to deal with subsequently for atomization [4]. Similarly, the shortcoming associated with the direct evaporation method, is that it needs large sample volumes. The oldest separation/preconcentration methods based on precipitation and crystallization have also limited and specific application as is the case with ion exchange and chromatographic methods [4]. The chelation/solvent extraction methods, though very specific, is very popular among the water analysts [5,6]. Flameless atomization too is quite sensitive but flexible technique for the estimation of mercury in waters [7,8,9,10].

It is a well established fact that analytical signal enhancement through the use of organic solvents in flame atomic absorption method is partly due to a decrease in solution viscosity [11]. This physical property thus has a direct bearing on the feed rates of samples to be aspirated into the flame. It, therefore, may be inferred that a signal optimization can be achieved by a control on those instrumental components/parameters which govern, directly or indirectly, the viscosity of the sample solution. Furthermore, since solution viscosity is quantitatively related to the flow parameters in the atomic absorption system, complete optimization of instrumental components may warrant a considerable improvement in the overall signal enhancement. An attempt has been made in the present investigation to bring out quantitative role of such physical factors as the fuel/oxidant flow rates, length and radius of aspiration capillary, burner-slit length, solution temperature and an added organic solvent to the sample. It turns out that the signal optimization based on these factors is an auxiliary means to augment the additional enhancement of atomic absorption signals over and above those obtained through preanalysis chemical methods referred to above. The scheme developed in this work warrants hundred-fold signal enhancement and an overall reduction in detection limit of the same order of magnitude without any involvement of the 'chemical type'. Analytical data for the estimated concentrations of silver, copper, chromium, iron, strontium, zinc, cadmium, lead and mercury are reported in drinking water samples based on the above method.

## EXPERIMENTAL

A Hitachi atomic absorption spectrophotometer (Model 170-10), equipped with a single-slot, premix burner was used for the optimization study. The first step to this effect consisted in cutting down the length of the sample capillary from 16.0 cm to 8.0 cm. Then a 0.018 inch (I.D) capillary was installed in the aspirator unit replacing its 0.012 inch capillary, thus increasing the diameter by a factor of 1.5. Acetylene and oxidant (air) flow rates were then optimized to get maximum enhancement in absorption signals. The burner with a 10.0 cm slit length was replaced by the one with 5.0 cm slit length. A constant thermostat bath (LAUDA, Thermo-temp) was used to control the viscosity or, for that matter, the feed flow rate of the sample as a function of temperature. The accuracy limit of the thermo-temp unit used was  $\pm 0.10^\circ$ . The temperature range selected was from  $15.0^\circ$  through  $55.0^\circ$  for various samples. Acetone was used as an added organic solvent for the enhancement of signals. Standard solutions were run under identical conditions established for the samples. All measurements were made at a bandpass of 0.4 nm. The overall absorption sensitivity for each trace metal was then measured collectively in terms of the above cited parameters as absorption peak height (mm).

## DISCUSSION

The data on the optimizations of physical factors attendant on sample aspiration rates appear in Table 1 and Fig. 1 through Fig. 3. Listed in Table 1 are the fuel and air flow rates that yield optimum signal sensitivity for the listed trace metals. It turns out that lowest fuel/air flow rates are required for silver and cadmium while chromium, lead and mercury yield optimum signals at

about double the fuel/air flow rate for silver and cadmium. The case of strontium is unique in that it requires the maximum fuel/air flow rate for its signal optimization. As the analytical signal enhancement arises because of an increase in the transportation rate of the solution into the burner, it is observed that the absorption sensitivity is considerably improved as a function of increasing temperature in the case of all the trace metals. Fig. 1 demonstrates this fact whereby an enhancement factor of two to three was achieved by increasing the sample temperature from  $15^\circ$  (laboratory temperature) to  $55.0^\circ$  in a proper thermo-

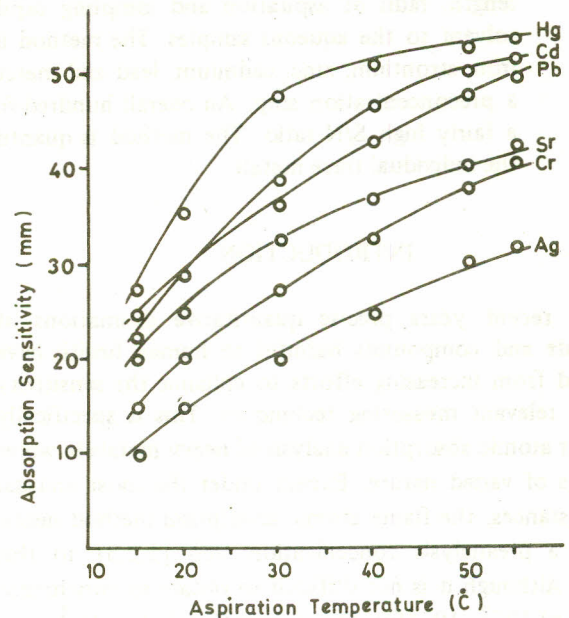


Fig. 1 Absorption sensitivities vs. aspiration temperature for various trace metals.

Table 1. The fuel/air flow rates and lower detection limits achieved under optimization of instrumental components

Trace metal	Fuel		Air		Lower detection limit (ppb)
	Flow (l / min)	Pressure (kg/ cm <sup>2</sup> )	Flow (l/min)	Pressure (kg/ cm <sup>2</sup> )	
Silver	1.35	0.20	4.45	1.00	0.015
Copper	2.00	0.28	5.35	1.20	0.005
Chromium	2.36	0.35	8.00	1.80	0.020
Iron	2.70	0.40	6.66	1.50	0.010
Strontium	4.05	0.60	8.90	2.00	0.030
Zinc	1.70	0.25	8.00	1.80	0.010
Cadmium	1.35	0.20	4.45	1.00	0.004
Lead	2.70	0.40	8.00	1.80	0.050
Mercury	2.02	0.30	6.66	1.50	0.0004

stat bath. The observed increase in absorption sensitivity as a function of aspiration temperature is more marked in the case of mercury and cadmium. Between 15-55° the density differential of water is equivalent to about 52% decrease in the viscosity value, which, in turn, corresponds to an increase in the flow rate of the aspirated solution by a factor greater than two. This fact may be judged through the well-known quantitative relationship between the fluid flow,  $F$ , and the viscosity,  $\eta$ , of the solution, given by  $F = f[r^4 / l \eta]$ , where  $r$  and  $l$  are radius and length of the capillary. Thus a reduction of  $l$  to  $\frac{1}{2} l$  would double the flow rate,  $F$ , which, in turn, should double the population density of ground-state atoms in the flame zone. Also an increase in the radius,  $r$ , would drastically increase the flow rate since by simply doubling  $r$  the flow rate should increase by a factor of sixteen. This was confirmed by cutting down the capillary by half of its original length and the overall absorption sensitivity was found to be almost doubled. Similarly, the diameter of the aspiration capillary was changed from 0.012 to 0.018 inch thereby yielding an enhancement in absorption signals by an average factor of about four as compared with a theoretically expected factor of about five. The obvious reason for this observed 20% decrease in the enhancement factor is a possible swamping of the flame at higher feed rates. As a decrease in the burner slit length amounts to an increased exposure of aerosol droplets in the path of the flame, the use of a burner with slit-length of 5.0 cm in place of one having a slit-length of 10.0 cm gave twice as much absorption.

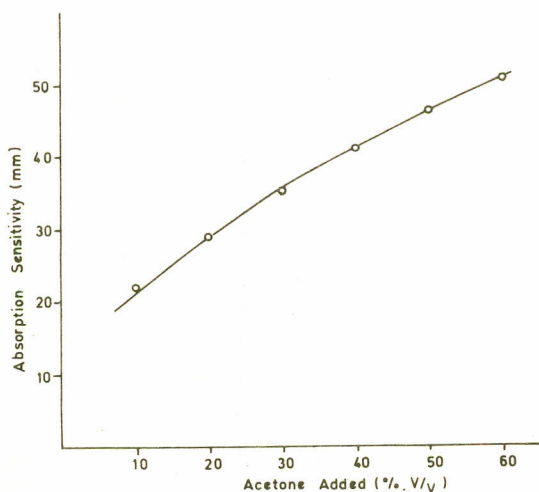


Fig. 2. Absorption sensitivity for silver as a function of acetone added (%)

In Fig. 2 is shown the typical enhancement of absorption signals obtained for silver by the addition of varying amounts of acetone to the aqueous samples. The observed increase in sensitivity is mainly due to a decrease in solution viscosity as seen earlier. Thus, viscosity is the primary solution parameter controlling atomization and affecting the flow rates directly via droplet size formation [11]. The absorption sensitivity for silver at laboratory temperature increases by a factor of four on the addition of 60% acetone (v/v). This might as well be true for other organic solvents having viscosities less than that of water. Therefore, use was made of such solvents as acetaldehyde, butyl acetate, diethyl ketone, ethyl acetate and methyl acetate. The concentration dependence of absorption is typical of each solvent. A viable use may, therefore, be made of these solvents at 30-40% (v/v) concentration.

The proposed method thus warrants an overall enhancement factor of  $10^2$  through the control of the above cited components. The proposed signal enhancement procedure has functional dependence on aspiration rate. Thus, it may be used in any make of the atomic absorption spectrophotometer that incorporates a suction-based aspirator, a premix-slit burner and a mechanical/auto disperser. Excellent calibration curves (Fig. 3) with a high precision

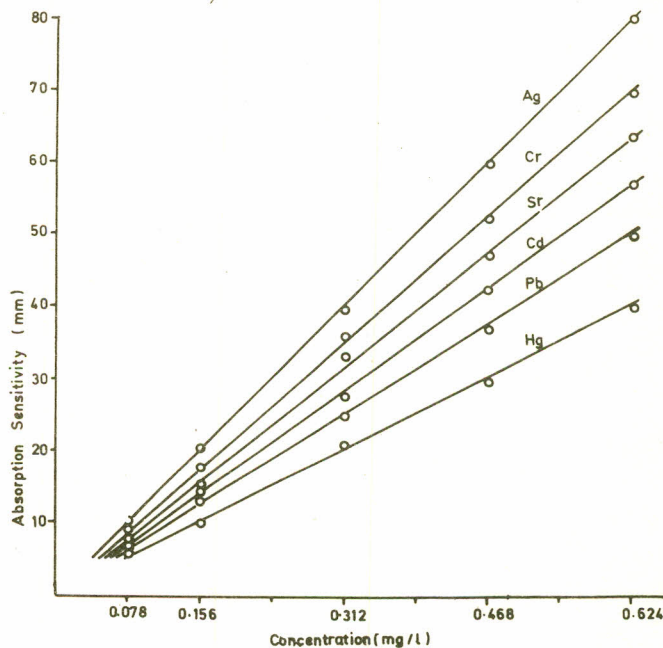


Fig. 3. Standard working curves for various metals aspirated at 50°

of  $\pm 1\%$  have been obtained within a working concentration range of 0.078-0.624 mg/l for various trace metals. The method is well suited to the quantitative estimation of all the major trace metals in waters of varied nature without

a prior preconcentration step. The lower detection limits achieved for various trace metals are given in Table 1 at 2S confidence level.

*Acknowledgement.* One of us (M. A.) would like to thank the Quaid-i-Azam University for financial support and access to laboratory facilities to carry out this work.

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