

Determination of Trace Metals in Drinking Waters by a direct natural gas-acetylene mixed fuel Atomic Absorption method

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Summary: Using natural gas-acetylene mixed fuel system an atomic absorption spectrophotometric method is developed for the determination of trace metals in drinking waters. Optimum operating conditions are established in terms of fuel and air flow rates for the determination of sodium, potassium, zinc, nickel, cobalt, strontium and magnesium in drinking waters. Compared with the conventional acetylene-air method the proposed method provides an overall 25-40 percent increase in the absorption sensitivity with about 50 percent economy in acetylene consumption. The concentration data are reported at 2S confidence level for replicate measurements, together with lower detection limit for each trace metal estimated.

Introduction

In recent years, precise quantitative estimations of elements and compounds harmful to human health have received serious attention. This is specially true for atomic absorption spectrophotometry where improvement in electronic circuits and modification in sensitivity controlling parameters have resulted in the enhancement of detection limit. Besides design and auxiliary parameters the absorption sensitivity depends on the flame temperature. A flame burning in air forms an ideal means for converting a solution into the atomic form, and provides a remarkably stable environment for the absorption process. The first flames used in atomic absorption work were of the 'direct injection' type [1,2]. Willis [3] introduced the use of nitrous oxide in 1965 as an oxidant for the acetylene flame. This faster acetylene-nitrous oxide flame at 2867-2925°C produced absorption signals even for those elements which could not be analysed in the ordinary acetylene-air flame. It was shown later [4] that the use of nitrous oxide in con-

junction with acetylene involved no danger of flashback.

Certain improvements in burner geometry were suggested by Boling [5], and thus premix burners were introduced in 1967 [6]. The advent of a semi-flameless sampling system was developed for the analyses of environmental samples by Kahn [7] in 1972. In later years a great interest was developed in the flameless method because its sensitivity is two to three orders of magnitude better than that attainable with the conventional flame. In an attempt to produce high temperature, a graphite furnace was built by Lundgren and Johansson [8]. The temperature of the furnace was monitored through an infrared-sensitive detector.

An attempt has been made in the present investigation to find means for the improvement of atomic absorption signals by using a mixed fuel system comprising of about 10 percent natural gas mixed with acetylene. Optimum

conditions are determined for the flow of the mixed fuel and oxidant (air) to achieve the highest signal to noise ratio. The method is applied for the estimation of sodium, potassium, zinc, nickel, cobalt, strontium and magnesium in local drinking waters.

Experimental

A Hitachi atomic absorption spectrophotometer (Model 170-10), equipped with a 0.5 x 100mm single-slot burner, was used in conjunction with the auxiliary arrangement shown in Figure 1. The high vacuum, two-way quickfit stopcock (6mm 1D) facilitated a two-fold function to allow pure acetylene and natural gas-acetylene mixture to pass through the flame at preregulated flow rates. Natural gas, directly taken from the lab supply, was first made devoid of any moisture content by passing it through the drying unit packed loosely with 5-10 mesh silica gel and Merck grade wool. The flow rate of the natural gas was regulated at 0.50 l/min through a rotameter, not shown in the figure. The volumetric flow rates for the mixed fuel and oxidant (air) were directly controlled onto the instrument panel, with their respective values ranging from 0.5 to

1.3 l/min and 5.3 to 6.3 l/min for the individual metals. Compressed air was introduced into the apparatus by using an oil-free air compressor. Standards and unknown samples were aspirated directly and the absorption signals were recorded onto a Servogor XY strip recorder. Standard solutions were prepared in bidistilled water using research grade Merck chemicals. Under the optimum flow conditions determined for each trace metal, the absorption sensitivity was obtained in each case at a bandpass of 0.4 nm. The sensitivity was measured in terms of absorption peak height (mm).

In order to optimise flow parameters the quantitative relationship between absorption sensitivity and the flow rate of the mixed and pure fuel gases, together with that of the air, was investigated, as shown in Figure 2. A platinum-platinum + 10 percent rhodium thermocouple (ISA, Type SX) was used for the measurement of the flame temperatures for the mixed and pure fuel systems by the millivolt-C^o calibration method using a sensitive millivoltmeter at 0.6 ohm external resistance. The standard error for the measured temperatures was estimated at about ± 0.5 percent.

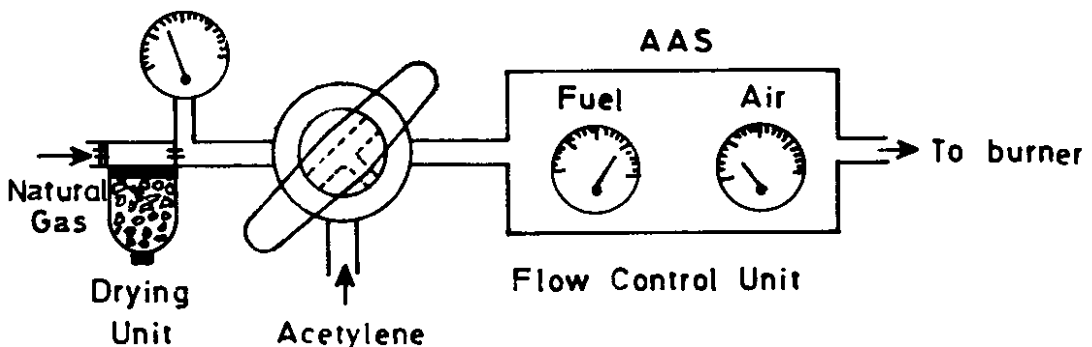


Fig.1: Schematic of the arrangement for natural gas-acetylene mixed fuel system.

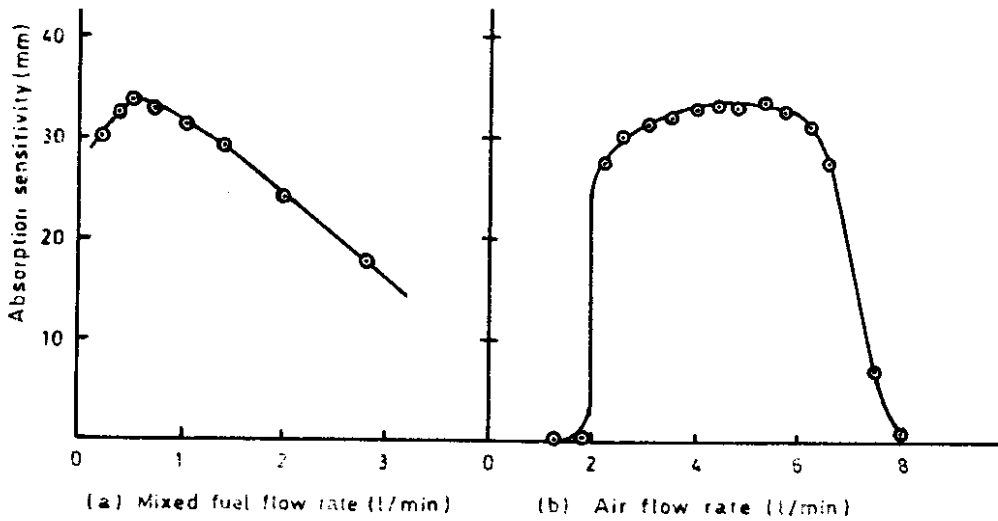


Fig.2: Absorption variations for sodium as function of (a) mixed fuel and (b) air air flow rates.

Table-1: Optimum flow conditions and comparative measured trace metal concentrations through mixed and pure fuel systems

Trace Metal	Optimum flow rate (l/min)		Estimated Concentration (ppm \pm 2S)		Lower detection limit (ppb)	
	Mixed fuel/air	Acetylene/air	Mixed fuel	Pure acetylene	Mixed fuel	Pure acetylene
Na	0.51/5.3	2.7/8.0	9.700 \pm 0.021	9.69 \pm 0.05	0.5	1.0
K	0.58/5.6	2.8/8.1	2.89 \pm 0.024	2.940 \pm 0.043	2.5	0.5
Zn	0.91/6.3	2.5/8.8	0.259 \pm 0.005	0.264 \pm 0.007	0.4	0.6
Ni	1.10/5.9	2.5/8.7	0.192 \pm 0.002	0.187 \pm 0.003	1.3	2.0
Co	1.23/5.8	2.9/8.5	0.071 \pm 0.002	0.073 \pm 0.004	1.5	2.0
Sr	0.98/6.2	2.7/7.9	0.500 \pm 0.010	0.492 \pm 0.02	1.8	3.0
Mg	0.52/5.4	2.6/8.0	9.70 \pm 0.025	9.56 \pm 0.06	0.02	0.05

Discussion

The optimum operating conditions established for the mixed fuel system are listed in Table 1 for each estimated trace metal. A comparison between the two sets of values for a particular trace metal demonstrates high reliability in favour of the proposed method. Best absorptions were recorded when the mixed-fuel flow rate ranged from

0.51 to 1.23 l/min as against 2.5 to 2.9 l/min for pure acetylene in the conventional method, thus saving more than 50 percent acetylene. Air consumption for the proposed method is also much less than that required for the conventional method. The present investigation reveals that the absorption sensitivity is a critical function of flow rates of fuel and air in addition to burner height. Also, it is found

that properly controlled gas supply and stabilized pressure are the major prerequisites for the attainment of a high sensitivity.

Table 1 also provides a comparative statement of the estimated concentrations of various trace metals in different drinking water samples by the two methods. The two sets of measured concentrations are in excellent agreement within a minimum relative error of 0.10 percent in case of sodium, and a maximum relative error of 2.73 percent in case of cobalt. The data indicate a favourably lower spreading around the mean in case of the mixed-fuel system.

Under optimum conditions, the estimated temperature of the natural gas-acetylene/air flame was found to be 2450°C as against 2350°C for the pure acetylene/air flame. The attainment of a higher absorption sensitivity, and hence a lower detection limit, in the proposed method may thus be attributed in part to the increase in flame temperature. Methane is the principal component (87 volume percent) of the natural gas. Small amounts of minor components such as ethane (about 7 volume percent), propane (1.5 volume percent), butane (0.5 volume percent), pentane (0.2 volume percent), carbon dioxide (2.3 volume percent) and nitrogen (1-1.5 volume percent) are also present. Methane can burn in oxidizing flames in a variety of chemical modes in the presence of carbon dioxide, nitrogen, carbonmonoxide and combustible fuels such as acetylene, methane, propane, etc. The study of the mechanisms

and rates of these combustion reactions, and the routes they follow to finish up with a finally equilibrated temperature, is rather too complex.

Although the determination of magnesium is rather restricted since its spectral line lies at the limit of UV region, yet the detection limit determined for this element is very satisfactory. The method has the potential of application to other trace metal estimations in waters of varied nature.

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