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FON GAS AS A DILUENT FUEL IN ACETYLENE-AIR BASED ATOMIC ABSORPTION ESTIMATIONS OF TRACE METALS IN NATURAL WATERS

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Use is proposed for FON gas as a diluent fuel in the conventional acetylene/air based atomic absorption method. When applied to the estimation of trace metals in natural waters, the proposed method warrants an overall 50% economy in acetylene consumption with a positive gain in absorption sensitivity. The reliability of the method is ascertained quantitatively through the optimization of flow conditions both for the fuel and the oxidant (air). The experimental data are interpreted in terms of 95% confidence level for replicate measurements of the concentrations of sodium, potassium, zinc, magnesium, nickel, and strontium in various natural waters.

INTRODUCTION

Over the past few years, rapid advances in instrument design and structural flexibilities have opened a new era in spectrophotometric estimations of varied nature. This is specifically true about atomic absorption spectrophotometry wherein basic modification in circuit design, improvement in sensitivity scale, and the incorporation of new fuel systems have made possible the measurement of the relevant trace metals down to a few ng level.

These characteristics are directly related to the extent of absorption in the flame at defined conditions of operation. Consequently, both reliability and precision have gone up in trace metal analysis. Absorption sensitivity depends not only on the lamp, but on the whole instrumentation system employed, and factors such as burner efficiency, fuel mixture composition and beam geometry. It could be that the development on fuel systems has reached, in part, its limit, but the problem of instability at low concentrations still remains and leads to fluctuations of the order of $\pm 0.1\%$ [1]. Major stress today is on the search of fuel systems that can generate a fairly high temperature (2000-3000° K), to ensure that free atoms are produced, leading to a higher degree of absorption.

A low temperature (700-1500°) was first produced by the hydrogen-argon-air flame and it was found [2] that the flame is not capable of dissociating the compounds into free atoms. Later, fast acetylene-air flame was introduced which produced a temperature ranging from 2250 to 2350° depending on the fuel: oxidant ratio. A still better nitrous oxide-acetylene combination was tried that produced a temperature of about 2900° without any appreciable insta-

bility problems [3]. Subsequently, rapid introduction of various mixed fuel systems, improvement in burner geometry and introduction of high temperature furnaces [4] materialised following the earlier achievements. Although "flameless" spectrophotometry [5] has fast replaced the conventional method of estimation for certain trace metals that can be converted into vapour form, the latter method still remains in wide use because of the ease of operation [6] and the attainment of a reasonable detection limit [7].

In line with these objectives, an attempt has been made in the present investigation to check up the possibility of the use of FON gas as a diluent fuel in the conventional acetylene/air flame. A relevant experimental arrangement has been devised to ensure optimum absorption sensitivity as a function of diluted fuel flow rate as related to air flow rate. The proposed method is found to apply well on natural water samples for the estimation of sodium, potassium, zinc, magnesium, nickel and strontium. The data are reported at 95% confidence level for replicate measurements.

EXPERIMENTAL

Shown in Fig. 1. is the auxiliary arrangement used in conjunction with a Hitachi atomic absorption spectrophotometer (Model 170-10), equipped with a 0.5 x 100 mm single slot burner. The high vacuum, two-way quickfit stopcock (6 mm ID) facilitated a two-fold function to allow pure acetylene and FON gas-acetylene diluted fuel mixture to pass through the flame at desired preregulated flow rates. A commercially available FON gas cylinder,

fitted with an outlet gauge, was used as a source of compressed gas. The final flow rate of FON gas was regulated at 0.50 l/min through a rotameter (not shown in the Figure) while the volumetric flow rates for the diluted fuel and oxidant (air) were directly controlled onto the instrument panel, with their respective values ranging from 0.65 to 1.8 l/min and 5.7 to 6.3 l/min respectively for individual trace metals. Dust and oil free 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 on a Servogor potentiometric recorder. Standard solutions were prepared in bidistilled water in each case. Under the optimum flow conditions determined for each trace metal, the absorption sensitivity was obtained at the corresponding characteristic absorption wavelengths at a bandpass of 0.4 nm. The sensitivity was measured in terms of absorption peak heights (mm) in all the cases.

In order to optimize significant flow parameters the quantitative relationship between absorption sensitivity as related to the flow rate of the FON gas diluted and pure fuel, together with that of the air, was investigated, as shown in Fig. 2. A pt-Rh (10%) thermocouple (ISA, Type Sx) was used for the measurement of the flame temperatures for the diluted and pure fuel systems through the millivolt-°C calibration method using a sensitive millivolt meter at 0.6 ohm external resistance. The standard error for the measured temperatures was estimated at about $\pm 0.5\%$.

DISCUSSION

The estimated comparative concentrations of various trace metals under optimized flow conditions for both diluted and pure fuels, as related to that of air, are listed in Table 1. A close match between the two sets of concentration values for a given trace metal clearly indicates the

applicability of the proposed method at concentration levels given against each. The optimum diluted fuel flow rate is found to range between 0.65-1.8 l/min as compared with 2.5-2.8 l/min in the case of pure acetylene, thus warranting about 50% fuel economy by mixing a 9-10% proportion (calculated on the basis of their respective partial pressures) of FON gas with acetylene.

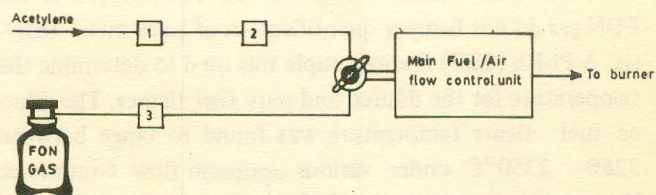


Fig. 1. Experimental set up: 1. pressure gauge; 2. pressure regulator; 3. low pressure regulator valve.

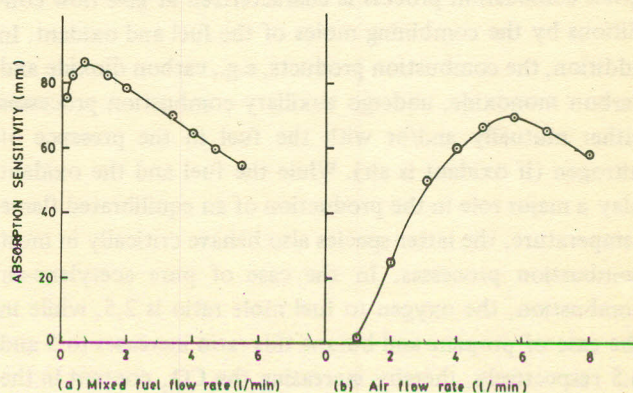


Fig. 2. Absorption variations for magnesium as function of (a) mixed fuel and (b) air flow rates.

The main constituents of FON gas are propane and butane which burn in air to produce a temperature of about 1900°. A typical percent composition of FON gas is as follows: propane, 60%; butane, 40%; and impurities as

Table 1. Estimated comparative concentrations of various trace metals under optimized flow conditions

Trace metal	Optimum flow rate (l/min)		Estimated concentration (ppm \pm 2S)	
	Dilute fuel/air	Acetylene/air	Diluted fuel	Pure acetylene
K	0.80/5.8	2.8/8.1	4.390 \pm 0.021	4.350 \pm 0.025
Na	0.65/5.6	2.8/8.0	10.300 \pm 0.020	10.210 \pm 0.026
Mg	0.75/5.7	2.6/8.0	8.42 \pm 0.027	8.41 \pm 0.023
Zn	1.2/6.2	2.5/8.7	0.194 \pm 0.003	0.200 \pm 0.004
Ni	1.5/6.0	2.5/8.7	0.113 \pm 0.002	0.115 \pm 0.001
Sr	1.8/6.3	2.7/7.9	0.491 \pm 0.10	0.500 \pm 0.009

traces only. The variation in this composition was checked on five different gas samples collected from local distributors. It turned out that the composition varied within $\pm 2\%$ for the C_3 component and $\pm 1\%$ for the C_4 component. Since the combustion is governed mainly by the C_3 and C_4 constituents the reason for consistency in observed absorption sensitivities with all of these samples was understandable. Hence, any minor changes in the composition of the FON gas do not hamper quantification of trace metal analysis. A Pt-Rh (10%) thermocouple was used to determine the temperature for the diluted and pure fuel flames. The diluted fuel flame temperature was found to range between 2280–2350°C under various optimum flow conditions. Hence, the temperature of flame is not a contributory factor towards the observed absorption sensitivity, as shown in Fig. 3. The flame temperature associated with a given combustion process is characterized at given flow conditions by the combining moles of the fuel and oxidant. In addition, the combustion products, e.g., carbon dioxide and carbon monoxide, undergo auxiliary combustion processes either mutually and/or with the fuel in the presence of nitrogen (if oxidant is air). While the fuel and the oxidant play a major role in the production of an equilibrated flame temperature, the latter species also behave critically in most combustion processes. In the case of pure acetylene-air combustion, the oxygen to fuel mole ratio is 2.5, while in the case of propane and butane this ratio increases to 5 and 6.5 respectively, thereby increasing the CO_2 content in the flame when FON gas is added as the diluent. Under the circumstances, the auxiliary combustion process whereby CO is produced via the utilization of carbon and oxygen atoms in the flame is also effectively operative within the flame zone. It is thermodynamically known that higher carbon dioxide to fuel ratio decreases the flame temperature while a contrary situation is met with in case of carbon monoxide combustion in the presence of nitrogen. Thus these two processes counterbalance any temperature differential in relation to both "pure" and "diluted" fuel cases. This explains why an almost non-variant temperature is obtained in the two modes.

The observed enhanced absorption sensitivity may now be conceived through its functional dependence on various processes the solution undergoes in the flame. Earlier studies on the process of flame atomization in relation to characteristic reactions within various combustion zones [8, 9] have revealed that the degree of atomization is a function of such processes as desolvation, vaporization, formation and dissociation. Although these processes may not necessarily reach completion within the flame zone, the mechanism and rates involved in these define the atomization efficiency

of the system. It is generally conceded that the metal oxide dissociation to the metal ($RO \rightleftharpoons R + O$) within the flame controls the degree of atomization, or, for that matter, the absorption sensitivity [10]. This dissociation reaction may

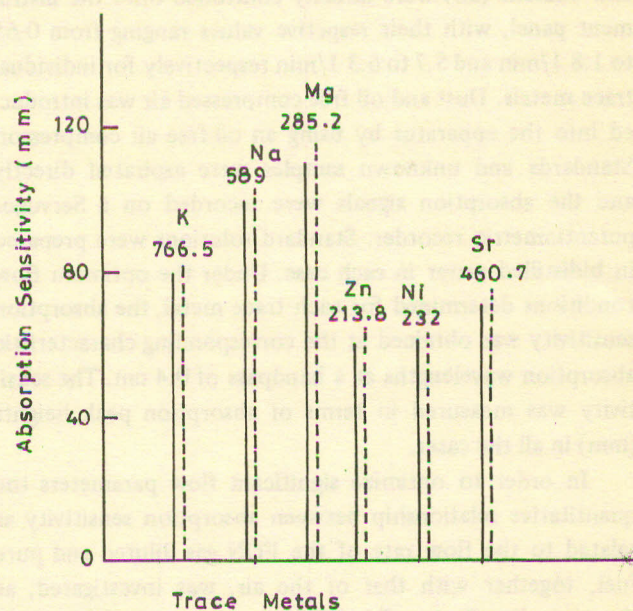


Fig. 3. Relative optimum absorption sensitivities for various traced metals by pure (—) & diluted (---) fuel systems.

be expediently promoted to the forward direction through the utilization of organic solvents and/or undertaking the combustion in a fuel-rich mode since the provision of carbon species within the flame produces a strong reducing environment [11] for obtaining elemental R^0 thereby increasing the number of ground state atoms in the flame.

A maximum relative error of 3% was encountered in the case of zinc estimation, whereas a minimum relative error of 0.12% was observed in the case, of magnesium, contrary to the fact that the determination of the latter is rather difficult as the magnesium line lies at the limit of UV region. The dispersion in estimated concentration values for the proposed method is, in general, less than that met in the case of pure acetylene fuel method. The data reveal that the spread around mean values is small even at 95% confidence level. The precision is better than 0.5% in any case of replicate measurements. The method affords flexibility of operation either in the "pure" or "diluted" mode, and has the potential of application to other related areas of trace metal estimation.

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The rate of oxidation of the carbonyl group in the polyethylene specimen was estimated by the method of [1]. The results are shown in Fig. 1. It is seen that the rate of oxidation increases with time and is higher in the case of the specimen which was irradiated with γ rays.

RESULTS

The carbonyl group in the polyethylene specimen was estimated by the method of [1]. The results are shown in Fig. 1. It is seen that the rate of oxidation increases with time and is higher in the case of the specimen which was irradiated with γ rays.

DISCUSSION

The above results clearly indicate that the rate of oxidation of the carbonyl group formation is much faster in comparison with open atmosphere. It may be due to the availability of active oxygen ($O_2^{\cdot -}$) in the water. In other

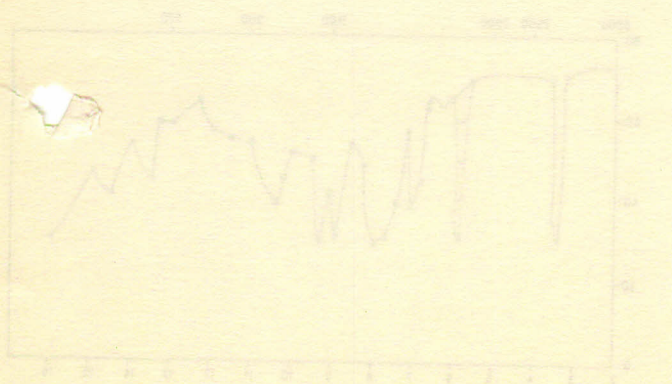


Fig. 1. Rate of oxidation of the carbonyl group in polyethylene specimen irradiated with γ rays and in open atmosphere.

The rate of oxidation of the carbonyl group in the polyethylene specimen was estimated by the method of [1]. The results are shown in Fig. 1. It is seen that the rate of oxidation increases with time and is higher in the case of the specimen which was irradiated with γ rays.

INTRODUCTION

The degradation of polymers due to radiation [1], oxygen and ultraviolet light [2, 3] is a complex phenomenon in polymers. Different types of carbonyl [4], ester [5], ketone [6, 7], aldehyde [8, 9], and hydroxyl [10] are formed. It is not possible to stop this reaction due to the autocatalytic nature of the reaction, the rate of oxidation increases as the amount of oxygen absorbed increases. It has been reported that some water-soluble [11] and some insoluble [12] antioxidants also retard the degradation of polymers. It has also been noted that climate-responsive antioxidants [13] retard the rate of degradation of polymers. The order of reactivity with the atmosphere of atmospheric polymers has been observed that oxidized polyethylene is more reactive than polyethylene oxide. It has also been reported that in accelerated outdoor exposure tests the extent of carbonyl group formation in polyethylene film depends greatly on test area [14].

EXPERIMENTAL

High-density polyethylene (HDPE) film of thickness 0.5 mm was irradiated with γ rays from a ^{60}Co source. The irradiation dose was 100 krad. The irradiated specimen was kept in open atmosphere for 100 hours.

RESULTS

The rate of oxidation of the carbonyl group in the polyethylene specimen was estimated by the method of [1]. The results are shown in Fig. 1. It is seen that the rate of oxidation increases with time and is higher in the case of the specimen which was irradiated with γ rays.