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A New Dispersion Medium for the Direct Slurry Atomization Electrothermal Atomic Absorption Spectrophotometric Determination of Magnesium in Carbon-black and Lampblack

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A new method has been developed for the formation of fine and stable slurry by mixing a few milligrams of carbon-black or lampblack samples with a mixture of xylene and 2- ethylhexanoic acid using ultrasonic vibration for a few minutes and the resulting slurry is dispensed directly into a graphite furnace to obtain the atomic vapours of the constituents of these samples. The developed method has been applied for the determination of magnesium at trace levels in these matrices by the construction of calibration graph using an organomagnesium (Mg 4-cyclohexylbutyrate) as a primary standard dissolved in the above-mentioned organic mixture. At optimum conditions a linear range up to 20 μg L^{-1} with absolute sensitivity of 0.21 pg, method detection limit of 1.2 pg and RSD within a linear range from 9.71 to 1.96 % are obtained. The recovery percentage is reported as from 84-106 %. The atomization mechanism of Mg in this medium is also investigated. The described method could be applicable to other trace metals in these matrices and in the meantime avoids interferences in case of aqueous calibrant (containing trace contaminants) are used instead.

Key Words: Magnesium, Carbon-black, Lampblack.

INTRODUCTION

Carbon-black and lampblack can be used as a filler for industrial plastics, rubber blend or in the manufacture of dry cell after extraction of inorganic compounds with HCl[1,2]. Carbon-black can be experienced to contamination during the stage of cooling of carbon with water containing a soluble salts of Ca, Mg, Na and of oxide of metals resulting from corrosion of the reactor surface[3] or to Ba and Sr salts added to the feedstock to increase the surface area of the finished carbon-black[4]. It is also used as interferent removal of F^- and PO_4^{3-} ions in Flame AAS determination of Al and Ti[5]. Furthermore, it is added to slurry solutions in direct ETA-AAS analysis of Al_2O_3 and Fe_2O_3, to enhance the absorbance of these oxides by about 1.5 times after addition of 0.5 % w/v carbon-black[6,7]. Consequently, metallic elements in carbon-black and lampblack to be of interest because of their effects on the industrial and analytical applications.

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A few techniques have been employed for trace elemental analysis in carbon-black and lampblack[8-11], but to our acknowledge there is no application of AAS determination of metals in these matrices.

The sample introduction techniques into the graphite atomizer are now considered to be one of the most prolific domains of research in atomic absorption and emission techniques to solve such dilemmas associated with conventional chemical procedures of digestion and dissolution of solid. Of these the slurry analysis in ETA-AAS is now well recognized as a sampling technique combines attractive features of both liquid and solid sampling atomization techniques[12].

This work describes a developed direct solid atomization for carbon-black and lampblack to determine magnesium by ETA-AAS using slurry of these matrices and magnesium 4-cyclohexylbutyrate as a primary standard and, according to the thermal behaviour of the last compound in the graphite furnace, an atomization mechanism has been devised for magnesium and found to be agreed with Sturgeon *et al.*[13] whom used the activation energy calculations to devise the atomization mechanism of some elements in aqueous solutions.

EXPERIMENTAL

A Shimadzu atomic absorption spectrometer model AA-670G equipped with an GFA-4A graphite furnace was used for all ETA-AAS measurements. The graphite furnace was fitted with commercially available tube coated with pyrolytic graphite (P/N 200-54525). Argon (99.999 %) was used as the atomizer purge gas. The graphite tube was cooled during operation by means of the cool flow CFT-33. The standard and sample solutions (10 μL) were dispensed with aid of an auto sample changer ASG-60G. The AA-signals for magnesium were measured at 285.2 nm, displayed with analytical conditions and data of measurements on the graphic printer PR-4. An ultrasonic bath type Branson 1200 model B 5200 E4 (Branson Ultrasonic Corporation, USA) was used for samples mixing.

A stock solution containing 100 mg L^{-1} magnesium was prepared by weighing out an appropriate amount of magnesium 4-cyclohexylbutyrate (BDH) (previously dried over P_2O_5 for 24 h) and equivalent to 5.00 mg of magnesium metal, then dissolved in 3 mL xylene (Fluka, puriss) and 5 mL 2-ethylhexanoic acid (Merck) with careful heating until it is completely dissolved. The content was transferred to a 50 mL volumetric flask and diluted to mark with xylene. This solution is stable for several weeks when stored in a well-sealed container.

The working standard solutions were freshly prepared by serial dilution of the stock solution with xylene. All glasswares were soaked in 10 % w/v nitric acid, washed 5 times with deionized water, then ethyl alcohol and finally with xylene prior to use.

Preparation of carbon-black and lampblack samples: About (1-3 mg) of sample (carbon-black or lampblack) was weighted in a clean 25 mL volumetric flask. A mixture of 3 mL of xylene and 5 mL of 2-ethylhexanoic acid was added.

The content of the flask was shaken vigorously for 1min, then immersed in an ultrasonic bath at 30 °C for 10 min until a fine slurry was obtained.

A 10 μL aliquot of this slurry was automatically injected into the graphite furnace and heating cycle is applied (Table-1).

TABLE-1
INSTRUMENTAL PARAMETERS AND OPTIMIZED FURNACE PROGRAMME FOR THE DETERMINATION OF MAGNESIUM IN CARBON-BLACK AND LAMPBLACK BY ETA-AAS USING SLURRY ATOMIZATION

Parameters	Setting
Wavelength (nm)	285.2
Slit bandpass (nm)	0.5
Lamp current (mA)	4.0
Mode	Peak area
Background correction	On
Expansion factor	1.0
Chart speed (mm/min)	10.0
Injected volume (μL)	10.0
Furnace programme:	
Dry (ºC/s)	70/30, ramp
Ash (ºC/s)	800/20, step
Atomize (ºC/s)	1900/5, step, gas flow (0.5 L min^{-1})
Clean (ºC/s)	2500/3, step
Cool down (ºC/s)	-/30

RESULTS AND DISCUSSION

Optimization of the heating programme: Table-1 shows the optimum experimental conditions for heating programme used for the determination of magnesium. As shown in Fig. 1, the loss of magnesium on ashing (peak height mode) starts at 800 °C, however with peak area mode, there is no magnesium loss until 1000 °C. It is shown (Fig. 1) that the peak area not only includes a higher thermal pretreatment, but also a shift in the appearance and in the atomization temperatures which was found to be 1480 °C compared with 1100 °C by peak height mode. It is also found (Fig. 2) that the optimum argon flow rate gives better sensitivity, was 0.5 L min^{-1}. Although the sensitivity of magnesium by peak height is better than that obtained by peak area, the latter was chosen because it gives better precision, high ashing temperature and expectedly more calibration graph for magnesium. In Fig. 3, at ashing temperature of 800 °C, the optimum ashing time was 45 s because it gives negligible background absorbance.

Precision of the procedure: To ensure the stability of the slurry in the organic matrix medium, the repeatability RSD % was measured after interval of the slurry preparation times. Two different liquid media were tried to test slurry of the sample. Firstly with a mixture of ethanol:ammonia:nitric acid and secondly with xylene:

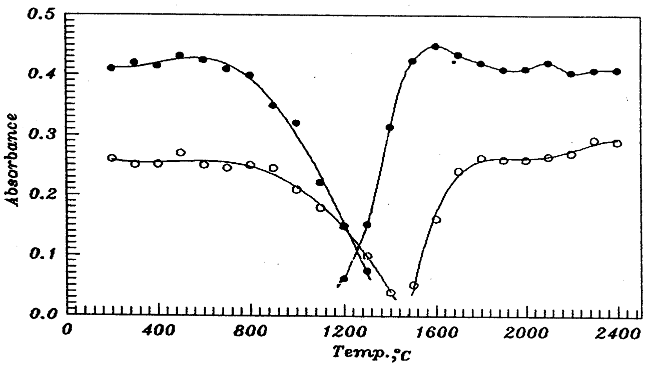


Fig. 1. Effect of ashing/atomization temperatures on (10 µL, 1 µg L^{-1}) magnesium signal using [O], peak area and [O], peak height measurements by ETA- AAS

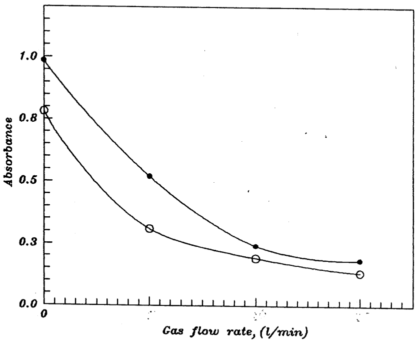


Fig. 2. Effect of gas flow on (10 µL, 1 µg L^{-1}) magnesium using [O], peak area and [O], peak height measurements by ETA- AAS

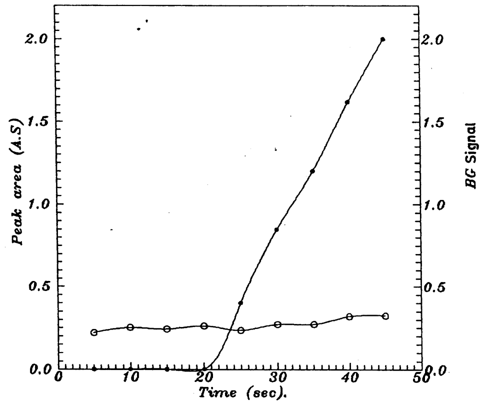


Fig. 3. Effect of ashing time (10 µg L^{-1}) magnesium signal under optimized conditions

2-ethylhexanoic-acid. The experiments showed that the later mixture kept the particles of different samples in suspension for a sufficient period and low background signal compared with the first mixture in which all samples have shown rapid sedimentation within 20 min and gives a high blank signal for magnesium.

Fig. 4 shows the magnesium repeatability test during 1 h of analysis for the two types of sample (carbon-black type SRF 760 and lampblack) suspended in the organic matrix medium and compared with RSD % of organic standard solution containing 6 µg L^{-1} magnesium. It is shown that the RSD % obtained for these 2 samples were acceptable within the limit of ETA-AAS measurement, Table-2 and Fig. 5 show the best RSD % achieved in the working range (2.5-20 µg L^{-1}) was found to be 9.97-1.96 %.

TABLE-2
STATISTICAL RESULTS OF ANALYSIS OF MAGNESIUM USING THE DEVELOPED SLURRY ETA-AAS TECHNIQUE

Linearity (mg L^{-1})	0-20
Characteristic mass (pg/ 1 % absorption)	0.21
Method detection limit (MDL) (pg)	1.2
RSD % at working concentration between 2.5 and 20 Mg L^{-1}	9.97- 1.96 %
Regression line	Y = 0.0115 + 0.0208X
Correlation coefficient (r)	0.9989

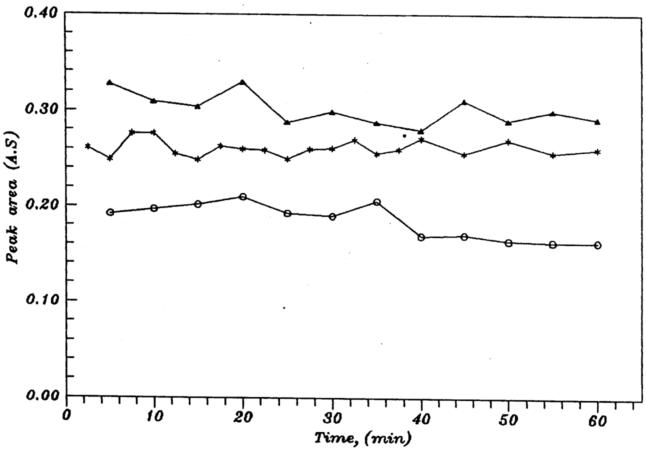


Fig. 4. Magnesium repeatability test for different slurry samples (10 µL). [*] organo-matrix standard (1 µg L^{-1}) $RSD_{n=20}$ = 3. i%, [O] carbon-black type SRF760, $RSD_{n=1}$ = 3.8%, [*] Lampblack $RSD_{n=12}$ = 5.1 %

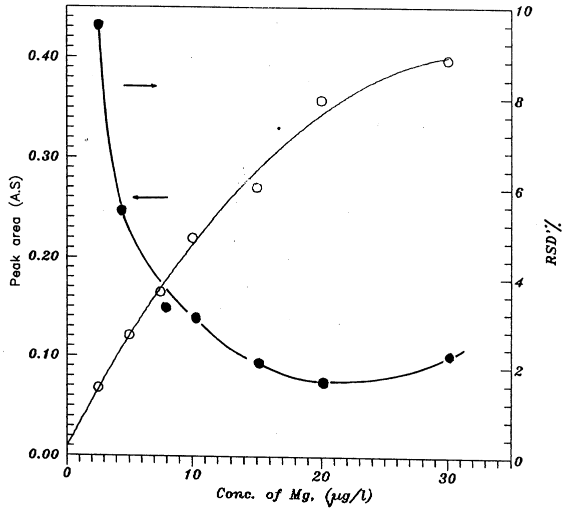


Fig. 5. Calibration graph and precision of magnesium by slurry ETA- AAS

Determination of magnesium in carbon-black and lampblack: Four different carbon-black sample have been analyzed, 2 of them locally produced (N-2-8 and N-3-8) and 1 lampblack (locally produced sample). Magnesium is determined in the slurred samples by direct and standard additions methods. The analytical results are given in Table-3. It can be seen from Figs. 5 and 6 that the slope ratios of the direct calibration and standard additions graphs for 3 different samples (GPF660, SRF760 and lampblack) are 1:1.25, 1:1.61 and 1:1.32, respectively, indicating that the interferences resulting from the sample matrices are almost significant and therefore standard additions has to be applied by treating equal volumes of sample with different volumes of magnesium organic standard solutions to give sample solution with 0, 2, 4 and 6 mg L^{-1} standard additions. Table-4 shows the average recovery percents of these additions and ranged between 84.5 and 106 %. The low recoveries may be due to the physical loss of magnesium due to the heterogeneity of the sample and or the presence of interfering elements such as Ca, Ba, Fe, Mn; while the high recoveries (above 100 %) may be caused by the presence of elements which enhance the magnesium signal.

TABLE-3
RESULTS OF ANALYSIS OF MAGNESIUM IN CARBON-BLACK AND LAMPBLACK BY ETA-AAS USING THE DEVELOPED SLURRY DIRECT SAMPLING

Sample type	Wt % of Mg (Direct calib).	Wt % of Mg (Std. Addn).
SRF 760	0.14	0.09
GPF 880	0.09	0.12
NF- 2-8	0.14	0.13
NF- 3-8	0.24	0.18
Lampblack	0.12	0.16

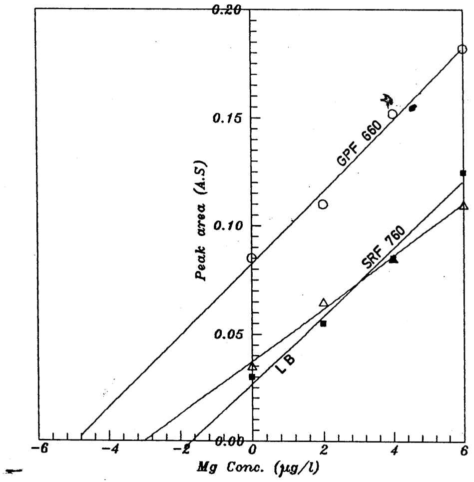


Fig. 6. Standard additions plot for magnesium in carbon-black and lampblack samples using the developed ETA-AAS slurry technique

TABLE-4
AVERAGE RECOVERY PERCENTAGES OF MAGNESIUM IN CARBON-BLACK AND LAMPBLACK SAMPLES USING THE SPIKED SLURRY ETA-AAS TECHNIQUE

Sample type	Mg in sample (mg L^{-1})	Mg added (mg L^{-1})	Mg found (mg L^{-1})	Recovery (%)
SRF_{760} (CB)	1.95	2	3.55	80.0
	1.95	4	5.41	86.5
	1.95	6	8.07	102.0
			Average	89.5 ± 9.2
GPF_{660} (CB)	4.84	2	6.92	104.0
	4.84	4	8.69	96.3
	4.84	6	10.31	91.2
			Average	97.2 ± 5.3
Lamp-black (LB)	3.51	2	5.11	80.0
	3.51	4	6.83	83.0
	3.51	6	8.84	90.5
			Average	84.5 ± 4.4
NF-3-8 (CB)	1.39	2	3.55	108.0
	1.39	6	7.47	101.0
	1.39	10	12.33	109.0
			Average	106 ± 2.0

Atomization mechanism for magnesium: To obtain a clear understanding of physico-chemical processes that occur in electrothermal atomizer during the application of heating cycle on magnesium-cyclohexylbutyrate, it is possible to explain that mechanism according to the empirical method[20] which is based on the insights into the physico-chemical data at molecules of metals which are expected to be formed during the heating cycle and compared with what would be produced during the application of heating cycle of the same element but as a hydrated ion. It can be concluded (Fig. 7) that the organomagnesium standard may decompose thermally before the appearance temperature (T_{app} = 1150 °C) in two stage leading to the formation of MgO(s) (m.p 2800 °C).

$$R(COO)_2Mg \xrightarrow{>300^{\circ}<500^{\circ}} MgC_2O_{4(s)} + 2R_{(g)}$$

$$Mg_2C_2O_4 \xrightarrow{>500^{\circ}} MgO_{(s)} + CO_{2(g)} + CO_{(g)}$$

It is also seen from Fig. 7 that a noticeable increase in absorbance observed at 500 °C may be due to the presence of Mg oxalate which may lead to this enhancement. The literatures indicate that MgO sublimes without decomposition at 2770 °C. If this occurred in graphite furnace, little if any atomic absorption signal of magnesium would be observed.

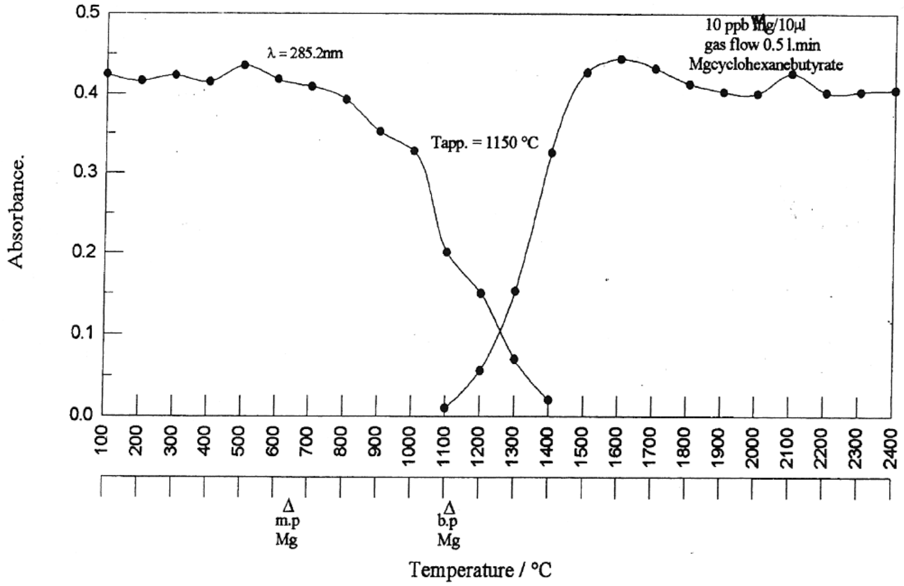
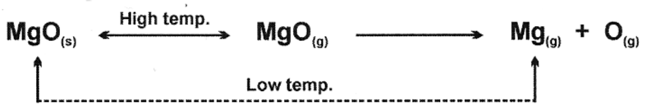


Fig. 7. Ash/atomize curves for Mg showing the thermal behaviour of Mg and Mg compounds

Fig. 7 shows that the highest absorption signal of organomagnesium can be obtained at 1600 °C. Since that MgO sublimes at 2270 °C and its formation in the graphite furnace will strongly reduce the Mg absorbance, but it was found experimentally that the highest absorbance could be occurred at 1550 °C[21]. This agrees well with present experiment data at 1600 °C (Fig. 7).

It was stated that carbon reduction for metal oxides becomes thermodynamically feasible if the value of ΔG° was negative. Sturgeon *et al.*[13] calculated the ΔG° for magnesium at 1237 °C and it was shown to be positive. Therefore, carbon reduction of MgO(s) is very unfavourable and must be ruled out. Consequently, the only pathway for the formation of gaseous magnesium atoms is due to the thermal decomposition of the oxide gas phase at high temperature.


$$\begin{tikzcd} \mathrm{MgO_{(s)}} \arrow[r, leftrightarrow, "\text{High temp.}"] & \mathrm{MgO_{(g)}} \arrow[r] & \mathrm{Mg_{(g)}} + \mathrm{O_{(g)}} \arrow[ll, dashed, bend left, "\text{Low temp.}"] \end{tikzcd}$$

It can be concluded that the formation of the intermediates resulting from the thermal decomposition of the organometallics can influence in the alteration of the appearance temperature of gaseous metal atoms before the atomization has occurred and these intermediates play a recognizable physicochemical role in the ashing and atomization processes compared with the same element in its aqueous solutions. By comparing the appearance temperatures (T_{app}) of magnesium in organomagnesium

(T_{app} = 1150 °C) and in aqueous solution (T_{app} = 1237 °C)[13], it is clear that the active carbon formed from the thermal decomposition of organomagnesium contributes effectively to accelerating the reduction of MgO.

Conclusion

New experimental conditions have been established for the direct slurry atomization of magnesium present in carbon-black and lampblack by ETA- AAS. The organic medium used (xylene:2-ethylhexanoic acid) has shown to be a powerful solution to get a good homogenized slurry of carbon-black and lampblack and found to be relatively free from magnesium and does not constitute a significant source of contamination. Standard additions method should be employed to eliminate interferences arising form sample matrix.

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