

Evaluation of four sample treatments for determination of platinum in automotive catalytic converters by graphite furnace atomic absorption spectrometry

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Received 31 May 2006; accepted 2 October 2006

Available online 7 November 2006

Abstract

Conventional and microwave assisted digestion, both using aqua regia, alkaline fusion with lithium metaborate and aqueous slurries were evaluated as sample treatments for determination of Pt in automotive catalytic converters by Graphite Furnace Atomic Absorption Spectrometry (GF-AAS). Determination of platinum by GF-AAS in samples of the catalytic converter's substrates, prepared by the four methods described, indicates that the highest platinum concentration i.e. maximum Pt extraction in the range of 748 ± 15 – $998 \pm 10 \mu\text{g mL}^{-1}$, is obtained for samples dissolved by alkaline fusion, closely followed by analysis of aqueous plus Triton X-100 slurries 708 ± 14 – $958 \pm 10 \mu\text{g mL}^{-1}$, while neither one of the acid digestion procedures achieved total dissolution of the samples. Slurry analysis is thus shown to be a viable alternative and is recommended, based on its speed and ease of implementation. Aqueous standards calibration curves and the standard addition methods were also compared. The results showed that no appreciable matrix effects are present, regardless of the sample preparation procedure used. Precision of the measurements, expressed as percentage relative standard deviation, ranged between 2.5 to 4.9%. Accuracy of the results was assessed by recovery tests which rendered values between 98.9 and 100.9%.

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Keywords: Slurry sampling; Graphite Furnace Atomic Absorption; Platinum determination; Automotive catalytic converters

1. Introduction

Due to the high levels of atmospheric contamination in most USA large cities, the Federal Government issued a law in 1970 which imposes a 90% reduction of contaminants in automobile exhaust fumes [1]. Among other measures, the incorporation of catalytic converters (CCs), on each car exhaust system was proposed and became used worldwide since the 1990s [1]. The use of such converters has become one of the most important applications of heterogeneous catalysis [2].

A catalytic converter generally consists of a combination of catalytically active metals, such as Pd, Pt, and Rh, deposited on a large surface area substrate, such as alumina or cordierite, which are inert and thermally stable [3]. The substrate plus catalytically active metals are contained in a metallic case which is coupled to the car's exhaust pipe. According to their geom-

etry, CCs can be of two types, pellet or monolith, the latter also known as "honeycomb" converters [3]. The first commercially available CCs were developed for oxidation of hydrocarbons to carbon dioxide and water. The "three way" converters were later developed to oxidize carbon monoxide and hydrocarbons to carbon dioxide and water and to reduce nitrogen oxides to molecular nitrogen. This type of CC contains Pd, Pt and Rh as active elements, usually comes in the honeycomb shape and is the most widely used in recently built automobiles.

According to the USA Bureau of Mines Information Circular 9302 [4], in 1989 the USA automotive industry consumed around 32,094 kg of Platinum group elements (PEG), mainly Pd, Pt and Rh, in the production of three way CCs, that is, approximately 32.7% of the national consumption. Only 6594 kg of that amount of (PEGs) were recycled. During the same year, approximately 37% of the world's demand for Pt was assigned to the automotive industry [4]. Although natural reserves of Pd, Pt and Rh in South Africa, the ex-Soviet Union and Canada have been estimated to cover the actual demand

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for over 400 years, the huge investment needed for extracting, separating and refining these metals makes them highly expensive [5]. A less expensive alternative for obtaining Pd, Pt and Rh could be their recovery from the substrates of old, no longer in use, automotive catalytic converters. It has been shown that Pt, the noble metal found in the highest concentration in CCs, could be recovered with up to 99% efficiency [6]. To estimate the efficiency and have an idea of profitability of a given extraction procedure of noble metals from catalytic converter's substrates, it will be necessary to have a way of knowing with enough certainty their concentration in the original sample. Graphite Furnace Atomic Absorption Spectrometry (GF-AAS) has been widely used for determination of PGEs in samples originated from the use of catalytic converters after convenient sample treatment [7–12]. In this paper we propose four different sample treatment procedures conventional acid digestion, microwave assisted acid digestion, alkaline fusion and slurry sampling to render catalytic converter's substrates amenable for the determination of their Pt content by GF-AAS. Slurry sampling is shown to be the most convenient sample treatment in regards to speed, ease and accuracy of the results obtained.

2. Experimental

2.1. Instrumentation

All absorbance measurements, peak areas, were performed using a model 2380 Perkin–Elmer atomic absorption spectrometer (Norwalk, CT, USA) with continuum source (deuterium lamp) background correction, equipped with a HGA-400 graphite furnace. A hollow cathode lamp (Varian, Australia) for Pt was used as a line source. Pyrolytic graphite-coated tubes (Perkin–Elmer) with totally pyrolytic graphite platforms (Perkin–Elmer) were used for atomization. Samples and standards were manually injected using 10 μ l micropipettes with disposable plastic tips. All results are the average of at least three replicate measurements.

A model MDS 2000 CEM (Indian Trails, NC, USA) microwave oven with pressure and power control for heating twelve 100 ml PTFE reaction vessels was used for microwave assisted digestions. A mechanical model RX-24 Tyler Industrial Products Sieve was used to select the finest particles obtained after manual grinding, using agate mortar and pestle, of the substrate plus analyte samples. Alkaline fusion of the ground samples was carried out in graphite crucibles heated in a model 629 Weilberg/Lahn Herbert Arnold muffle oven with 1100 °C maximum temperature and a ± 1 °C resolution. Weighing was accomplished using a model AJ 180 L Mettler (Mettler, Switzerland) balance with 160 g maximum load and 0.1 mg resolution.

2.2. Reagents and samples

All reagents were of analytical reagent grade. Purified water from a Millipore distilling–deionizing system (Millipore, Bedford, MA, USA) with 18 M Ω cm resistivity, was used

throughout. Platinum working solutions were prepared daily by convenient dilution of a 1000 μ g/ml Titrisol (Merck, Darmstadt, Germany) stock solution, keeping a 0.1% (v/v) final nitric acid concentration.

Samples selected for this work were taken from three different monolith, or “honeycomb”, catalytic converters which will be referred to as CC1, CC2 and CC3. The converter's cases were open and the substrate containing the analyte was manually ground using an agate mortar and pestle until a talc texture powder was obtained. After grinding, each sample was sieved for about 30 min and aliquots of the finest particle fractions were taken to prepare slurries in water with 0.4% (m/v) Triton X-100 surfactant or submitted to conventional acid digestion, microwave assisted acid digestion and alkaline fusion procedures to bring them into solution.

3. Results and discussion

3.1. Instrumental conditions

GF-AAS working conditions are grouped in Table 1. Since the catalytic converters contained sufficient concentration of the analytes as for easy determination by GF-AAS, no attempt was made for optimization of instrumental conditions or determination of detection limits. In spite of the fact that Pt is a rather refractory element for which the “platform effect” should not be highly significant, we decided to keep the graphite platform for all the measurements carried out in order to perform the evaluation under atomization conditions normally used in our laboratory. Hence, working parameters were those recommended by the manufacturers.

3.2. Sample preparation

3.2.1. Conventional acid digestion

Aqua regia, HCl:HNO₃ in a 3:1 ratio, was chosen for acid digestion of the finest particle size portions of the powdered CCs substrates. Preliminary tests showed that 5 ml aqua regia were sufficient to dissolve approximately 0.1 g of the substrates. The Pt concentration in these solutions produced easily detectable absorbance signals. This preliminary information was taken as a basis for more exhaustive tests which produced the information presented in Table 2. In the tests, three 0.1 g aliquots of the samples of each CC were heated and stirred for

Table 1
Instrumental conditions for Pt determination in solutions and by slurry sampling GF-AAS

Parameters	Value
Wavelength, nm	266.0
Slit width, nm	0.7
Lamp current, mA	25
Drying temperature, °C	130
Drying time, s	20
Ashing temperature, °C	1300
Ashing time, s	20
Atomization temperature, °C	2650
Atomization time, s	5

Table 2

Influence of heating time during conventional digestion on Pt extraction from automobile catalytic converters

Sample	Pt, $\mu\text{g mL}^{-1} \pm s, n=3$			
	30 min	60 min	90 min	120 min
CC 1	643 \pm 13	688 \pm 7	740 \pm 15	742 \pm 22
CC 2	413 \pm 12	498 \pm 20	539 \pm 11	543 \pm 16
CC 3	404 \pm 12	473 \pm 24	525 \pm 10	530 \pm 16

several periods of time, avoiding strong boiling and dryness. According to the data shown in Table 2, a heating time of 120 min was enough to extract most of the Pt in the samples, but not for total dissolution of the sample. Heating for longer periods of time improved Pt extraction only marginally and did not seem to improve sample dissolution.

3.2.2. Microwave assisted acid digestion

The same aqua regia sample ratio described above was used for the microwave assisted acid dissolution tests performed under the following heating conditions. Four heating steps at increasing pressure 50, 100, 150 and 180 psi; a ramp time of 15 min between steps; 15 min at each step after reaching pressure and 100% magnetron power. Pt content in the solutions obtained after microwave heating is shown in Table 3. It is clear from these results that microwave assisted dissolution, as expected, is more efficient for extraction of Pt from this type of sample than conventional digestion. It is important to notice that for these tests the microwave oven was operated at its maximum power for a rather long irradiation time. In spite of these harsh conditions, not one of the samples was totally dissolved.

3.2.3. Alkaline fusion

Addition of HF to the acid mixture used for the two digestion procedures previously mentioned could result in total dissolution of the samples. However, the excess HF remaining in solution would require for addition of boric acid to neutralize it, if the solutions were to be analyzed by inductively coupled plasma optical emission (ICP-AES), as was planned for other objectives of this study. This would make the procedure a bit more laborious and time consuming. Hence, rather than adding HF, investigating the possibility of taking the samples into solution by means of alkaline fusion was preferred.

For alkaline fusion, approximately 0.1 g of the powdered sample was directly weighed in a previously heated high purity graphite crucible. Approximately 0.6 g of lithium metaborate were added on top of the sample and the crucible was heated in a muffle oven to 1150 °C for 30 min. The crucible was then removed, with due precaution, from the muffle and swirled to loosen the liquid melt from the crucible walls and bottom. Once cold, the melt was transferred to a beaker containing 10 ml of a 3% (v/v) nitric acid solution and dissolved. The resultant solution was then quantitatively taken to a 100 ml volumetric flask and made to volume with distilled/deionized water. Results obtained after analysis of the fused samples are listed in Table 3. Since there is no sample residue present after alkaline fusion dissolution, the Pt content determined in these samples could be considered as the best representative value of

Table 3

GF-AAS determination of determination of Pt (\pm standard deviation, s) in automobile catalytic converters after different sample treatments

Sample	Pt, $\mu\text{g mL}^{-1} \pm s, n=3$		
Conventional acid digestion	742 \pm 22 (-25)	543 \pm 17 (-28)	530 \pm 16 (-16)
Microwave acid digestion	898 \pm 18 (-10)	669 \pm 20 (-15)	658 \pm 13 (-12)
Slurry	958 \pm 10 (-4)	715 \pm 14 (-5)	708 \pm 14 (-5)
Alkaline fusion	998 \pm 10 (0)	752 \pm 8 (0)	748 \pm 15 (0)

the real content of the analyte in the converter's sample taken for analysis.

3.2.4. Slurries

As described, alkaline fusion is a powerful method for sample dissolution. Unfortunately, the procedure entails the use of costly high purity graphite crucibles, long heating and cooling times and practically constant operator's attention. In search for a faster and simpler sample preparation method, analysis of aqueous slurries of the powdered substrates was evaluated.

It is well known that success of slurry sampling is heavily dependent on the sample particle size due to the fact that stability and homogeneity are highest for the smallest particle slurries [7,8]. The whole substrate of each converter was taken out of its metallic case and manually ground by batches. The different portions obtained after this first grinding were thoroughly mixed together and aliquots of the mixture were further ground for 30 min. Slurries were prepared by direct weighing, in a 10 ml flask, of approximately 10 mg of the smallest particle powder which was achievable under manual grinding for 30 min., that is, the sample portion which passed the 200 mesh sieve and was retained in the 400 mesh sieve, which roughly corresponds to a 75 μm particle diameter. Increasing amounts of Triton X-100 were added to the aqueous slurries to check stability. A concentration of 0.4% (v/v) Triton X-100 was the minimum concentration of the surfactant that permitted certain slurry stability. Manual shaking of the slurries and visual observation indicated that these were stable for at least 1 min. This was enough time to aspirate 10 μl of the slurry for injection in the graphite furnace. Therefore, in order to ensure homogeneity of the samples injected, each sample injection was performed immediately after manually shaking the slurries. As can be seen from Table 3 analysis of slurries could be a valid alternative. The numbers in parenthesis in Table 3 indicate the difference between the results, taking alkaline fusion as reference values. It shows that results obtained using slurries are closer to those obtained by alkaline fusion than the corresponding results obtained by the two acid

Table 4

Recovery test for Pt determination from automobile catalytic converters

Sample	% Recovery \pm R.S.D			
	Conventional acid digestion	Microwave acid digestion	Alkaline fusion	Slurry sampling
CC 1	93.8 \pm 3.6	97.6 \pm 4.3	99.3 \pm 3.8	100.5 \pm 3.6
CC 2	94.1 \pm 3.8	96.2 \pm 3.7	98.7 \pm 2.5	98.9 \pm 4.9
CC 3	92.7 \pm 4.4	95.4 \pm 4.8	100.9 \pm 3.9	99.7 \pm 3.9

digestion procedures previously described. The higher precision for Pt determination using slurries as compared to those obtained after acid digestion, is somehow unexpected since analysis of dissolved samples should generally be more precise than analysis of slurries. However, in this particular case, the irreproducibility in measuring the platinum content of the solutions could be a consequence of the irreproducibility of platinum extraction from each aliquot of each converter being tested. Due to the impossibility of dissolving the whole sample aliquots, each attempt for dissolution could extract a different amount of platinum thus leading to a large variability of results when the three aliquots are individually analyzed and the corresponding results are grouped together for averaging the Pt content in each converter. This is not so for determination of Pt in samples dissolved by alkaline fusion or by analysis of slurries since, in the first case, all the platinum in the three aliquots of each CC is extracted and, in the second case, each slurry was shaken immediately before injection to ensure homogeneity.

3.2.5. Matrix effects

Standard addition curves for samples prepared by conventional and microwave assisted dissolution, alkaline fusion and aqueous slurries were compared with a calibration curve obtained using aqueous, matrix free, Pt standards. No significant visual difference was observed between the corresponding slopes, thus indicating the absence of appreciable matrix interference.

4. Accuracy of the results

4.1. Percentage recovery

Due to lack of suitable standard reference materials in our laboratory, we resorted to recovery tests in order to have an estimate of the accuracy of the results obtained. Table 4 contains the results of the different tests. Recovery ranged between 92.7 for conventional acid digested samples and 100.9% alkaline fused samples, which attests for analyte responses practically free from matrix interference.

5. Conclusions

Conventional or microwave assisted acid digestion, using aqua regia, or alkaline fusion may be used for dissolution of the substrates of automotive catalytic converters for determination of their Pt content. However, acid digestion procedures besides being laborious and time-consuming do not provide total dissolution of the catalytic converter substrates. Alkaline fusion results in clear solutions with no solid residues but it is a slow procedure, requires costly graphite crucibles and demands practically continuous operator's attention. Aqueous slurries of finely powdered CCs substrates using Triton X-100 could be a

valid alternative for determination of the Pt content of automotive catalytic converters with acceptable accuracy and precision. Additionally, slurry sampling has the added advantages of being a less time-consuming and less laborious procedure than the other sample treatments evaluated in this work.

Acknowledgments

This work was supported by the Consejo Nacional de Investigaciones Científicas y Tecnología, CONICIT, ahora FONACIT de la República Bolivariana de Venezuela. The authors express their gratitude to Lic. Ivelin Morales for revision of the manuscript.

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