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Short communication

Atmospheric pressure vapour phase decomposition: A proof of principle

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ABSTRACT

In the present work we demonstrated that the digestion of difficult matrices (high boiling petrochemical fractions and distillation bottoms) can be achieved by oxidation with nitric acid vapours at atmospheric pressure employing simple laboratory glassware. The application of this procedure as a digestion method prior to Total Reflection X-Ray Fluorescence (TXRF) is presented, although the employment of other detection techniques may be foreseen. The method ensured a fast, less than half an hour, treatment time and detection limits in the range 20–100 μg/kg for As, Bi, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr, Zn, whereas higher values were obtained for Ba, Ca, K, P, Rh, Ti and V (0.3–3 mg/kg). The potentialities and limitations of this procedure were discussed: the application to a broad range of matrices may be foreseen.

1. Introduction

Trace element determination in high boiling petrochemicals and their derivatives is a challenging task. Sample treatment is clearly the main issue to be addressed if reliable results are to be obtained as it should make the heavy matrix compatible with the detection method ensuring at the same time no analyte loss and independence from elemental speciation. Several procedures have been investigated, involving both sample dilution with solvents and matrix decomposition by dry ashing or wet procedures (see e.g. [1] for a review on the detection of wear metals in oils). Direct introduction by laser sampling should also be mentioned as a promising tool in this field [2]. A number of standard procedures has also been established, the two methods described in ASTM D5708 being representative of both procedures: solvent dilution (test method A) and wet sulphate ashing (test method B, see [3]). Solvent dilution is a fast, straightforward method but it strongly dilute the sample and may easily lead to inconsistent results, due to the segregation of suspended phases and/or incomplete atomisation when atomic techniques are involved for the detection step (Inductively Coupled Plasma-Optical Emission Spectroscopy, ICP-OES, or Atomic Absorption Spectroscopy, AAS). Conversely, the decomposition of the matrix usually avoids issues related to element physical and chemical speciation at the expenses of time consumption and, generally, detection capabilities (see e.g. microwave assisted decomposition [4]). Better digestion procedures are actively sought. In this regard, vapour phase decomposition seems an attractive method as it does not lead to any contamination from the reagents, results in no dilution of the sample and it is fast (around one hour sample treatment time), although it has never been applied to the digestion of petrochemical products. In this procedure (introduced by Matusiewicz and co-workers [5]), a sample holder is hanged into the microwave vessel and the attack mixture is place at the bottom of the bomb: during the microwave digestion, the sample is in contact only with the oxidising vapours and not directly with the liquid mixture. Thanks to these advantages, it has been recently used as a pretreatment method for TXRF [6].

Aim of the present work is to demonstrate that vapour phase decomposition can be also achieved at atmospheric pressure by an efficient, fast and inexpensive procedure. This possibility is demonstrated by digesting traditionally time and work consuming samples like high boiling point petrochemical products (see [7] for low to medium boiling point samples).

2. Material and methods

2.1. Analytical instrumentation

The TXRF measurements were performed using an Ital Structures TX2000 Total Reflection X-ray spectrometer (now GNR TX2000). The instrument is equipped with a sample holder for the automatic analysis of up to twelve samples. Monochromatic (obtained by a W/C multilayer reflector) Mo Kα ($Z \leq 26$) or W Lα ($Z > 26$) excitations from a long fine focus tube with Mo/W anode were used as X-ray sources. The fluorescent X-ray derived from

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the sample was detected using a solid-state lithium-drifted silicon detector Si(Li) of 20 mm^2 active area with an 8 μm thick beryllium window (Röntec, Germany). The measured energy resolution (full width at half maximum, FWHM) of the detector was 137 eV for Mn Kα. Data elaboration (intensity measurement and quantification) was carried out by the software packages provided by the manufacturer. A 1000 s acquisition time was used for all of the experiments. The limits of detection were calculated according to IUPAC recommendations (see [8])

A simultaneous ICP-OES Jarrell Ash IRIS from Thermo was employed for all comparative measurements. The instrument is equipped with a cyclonic spray chamber and a standard Meinhard nebuliser: instrumental parameters were set as suggested by the manufacturer.

An Environmental Scanning Electron Microscope (ESEM) model XL-30 from FEI Company equipped with an X-ray energy dispersive detector was used to study the morphology of the residue after the digestion procedure. The X-ray fluorescence spectrum was registered at 20 keV with an acquisition time of 600 s.

2.2. Digestion procedure

The digestion chamber was composed by two glass crystallisers (Shott Duran, 95 and 25 mm diameter) and a watch glass cover (100 mm diameter). The digestion procedure was conducted as follows. The larger crystalliser was placed on a hot plate and the smaller one at its centre. Four millilitres of nitric acid (reagent grade Carlo Erba, 65%) were added to the latter and six, 30 mm diameter reflectors placed around it. Reflectors were previously siliconised by depositing 10 μl of a silicone solution in isopropanol (Serva, cod. 35130) and drying at room temperature. 5 g of each sample were accurately mixed with 100 mg of the gallium internal standard solution (gallium 2,4-pentanedionate in N-methyl pyrrolidone, 300 μg/g, see [7]). 8 μl of each sample, amended with the internal standard, were deposited onto the 6 reflectors. The crystalliser was subsequently covered with the watch glass and the hot plate heated to 100 °C. After 30 min of digestion, only a slight deposit was visible with the naked eye. A larger crystalliser (140 mm diameter) may be used to allocate up to 10 reflectors.

Three different samples were treated: a distillation bottom from oxo alcohol production (Safol Heavis, Sasol, mixture of heavy ethers, esters and alcohols in a paraffin matrix), a distillation bottom from linear alkyl benzene production (Alchisor DE, Sasol) and used mineral hydraulic oil. All of these materials are a mixture of petrochemicals with carbon numbers higher than 24, which are not distilled under vacuum at 250 °C. The same samples were treated according to the standard procedure described in ASTM D5708 – method B for comparison purposes. Briefly, 5 g of each sample were ashed with 5 mL of sulphuric acid (ultrapure Fluka, 98% m/m) in a quartz vessel on a hot plate. The carbonaceous residue was burned in a muffle at 550 °C, the ashes dissolved in diluted nitric acid and analysed by ICP-OES using external calibration. This digestion procedure typically requires an entire day.

3. Results and discussion

3.1. Effectiveness of the digestion procedure

Liquid samples cannot be directly analysed with TXRF as the total reflection conditions are not fulfilled even if only a few microlitres of sample are deposited on the sample holder (see [9] for the definition of critical mass and thickness: recently, the deposition of picoliter volumes was proposed to circumvent this issue [10]). Accordingly, liquid matrices have to be removed. The effect of the proposed procedure on a used oil sample is shown in Fig. 1 (30 min, 100 °C). A seven to twenty four-fold increase in the signal to noise ratio (S/N) was observed, with calcium, chromium, zinc and the internal standard gallium lower than LOD in the untreated sample. The removal of the matrix enabled the deposition of a much higher sample mass with respect to the untreated sample which had to be diluted not to exceed the critical film thickness (20-fold dilution in xylene which was subsequently removed by evaporation).

A morphological investigation by SEM revealed that the residue of the sample is composed by isolated structures similar to the one reported in Fig. 2. The X-ray fluorescence spectrum (also reported in Fig. 2) confirmed that the residues contained the elements present in the deposited solution, whereas the surrounding reflector surface was free from relevant fluorescence signals. The thickness of several of these residues was approximately determined by SEM and found in all of the cases lower than 10 μm, which is comparable with the critical thickness needed to obtain total reflection for organic materials [9].

3.2. Figures of merit

As a first step, a multielement standard in oil (CONOSTAN® S21 from Conoco) was diluted to 3 mg/L and treated according to the new procedure. As a result, a mean 96% recovery was

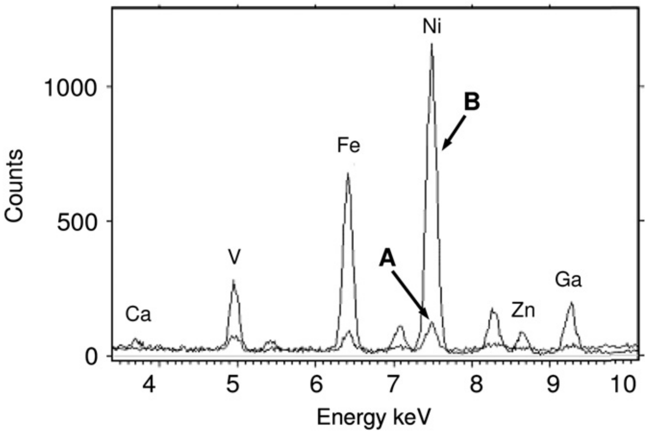

Fig. 1. Comparison of the X-ray fluorescence spectra of a used oil sample. (A) 8 μL untreated sample diluted 1:20 in xylene (solvent was removed by evaporation before measurement); (B) 8 μL sample treated by the atmospheric pressure vapour phase decomposition.

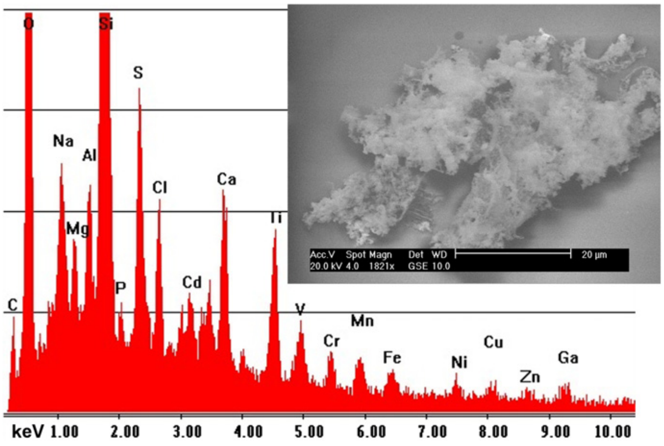

Fig. 2. Scanning Electron Microscopy image of a 8 μL CONOSTAN S-12 standard (10 μg/g) treated according to the atmospheric pressure vapour phase decomposition.

Table 1
Trace element concentrations and LOD obtained with the new procedure.

Element	Safol heavis		Alchisor DE		Used hydraulic oil		LOD
	Concentration (mg/kg)	Standard deviation	Concentration (mg/kg)	Standard deviation	Concentration (mg/kg)	Standard deviation	
As	< 0.03		na				0.03
Ba	na		na		28	6.4	1.3
Bi	na		na		0.50	0.02	0.05
Ca	na		1.3	0.78	234	17	3.2
Co	< 0.02		0.05	0.02	0.05	0.01	0.02
Cr	0.55	0.07	< 0.15		0.4	0.17	0.15
Cu	0.6	0.1	0.04	0.01	23	0.51	0.03
Fe	4.4	0.5	0.5	0.36	36.7	1.8	0.02
K	na		na		5	1.6	0.9
Mn	0.06	0.02	< 0.04		0.86	0.09	0.04
Ni	1.9	0.1	0.03	0.013	0.50	0.06	0.03
P	< 3		na		na		3.0
Pb	na		0.02	0.01	1.9	0.015	0.01
Rh	< 1		na		na		1.0
Sr	na		na		0.37	0.01	0.03
Ti	na		na		1	0.85	0.6
V	na		na		< 0.3		0.3
Zn	0.3	0.1	0.04	0.02	233	2.0	0.02

calculated, with a 14% standard deviation (13 elements, Ba, Ca, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sn, Ti, V, Zn, RSD% between 7 and 34, three replicates), evidencing no systematic deviations from the expected values.

The accuracy of the proposed procedure on real samples was assessed by comparison with the standard method ASTM D5708 – method B based on sulphate ashing: data are reported in Table 1 along with their standard deviations and the limits of detection. The results obtained by the new procedure and the standard method are in good agreement: the linear regression of the ICP-OES vs TXRF data had a slope of 0.94 ± 0.066 (value ± one standard deviation), an intercept not significantly different from zero and a regression coefficient of 0.92 ($n = 17$, only data below 2.5 mg/kg were considered). The precision of the proposed procedure, as estimated by the standard deviation of the data obtained from three independent digestions, is also not significantly different from the one measured with the standard method. Relative percentage standard deviations are in most cases below 20%, although higher values are also obtained: the highest values were nevertheless obtained for concentration values close to the limit of detection. The latter are also reported in Table 1 and ranged between 20 and 100 μg/kg for As, Bi, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sr and Zn. Higher values were calculated for Ba, Ca, K, P, Rh, Ti and V (0.3–3 mg/kg), as expected from the detection capabilities of TXRF (low and high atomic numbers). These values are on average comparable with the ones previously obtained for medium boiling products where the matrix was completely removed by evaporation (see [7] for comparison). This feature is an indirect indication that the matrix was completely decomposed. LoD may be lowered by on site enrichment [7].

4. Conclusion

Vapour phase decomposition was shown to be feasible at atmospheric pressure with ordinary laboratory glassware and reagents (reagent grade nitric acid). As a result, a simple and fast (half an hour) digestion of traditionally difficult matrices like heavy petrochemical products was possible. This sample treatment is even more efficient when coupled with TXRF detection as no further sample manipulation (dilution, reagent addition, use of sample bottles) is required. As a result, the *S*/*N* ratio increased by approximately one order of magnitude with respect to the untreated sample.

More efficient conditions may also be devised, with particular regard to the digestion temperature and the digestion cell geometry, although the results achieved during this work were satisfactory with a very easy configuration.

The application of the atmospheric pressure vapour decomposition coupled with TXRF detection to other matrices may be foreseen, although a careful validation would be required, especially when solid samples are involved; the use of different digestion acids and/or mixtures should moreover be considered. As an example, the digestion of organic matrices (chemicals, food, pharmaceutical and cosmetics, vegetal and animal tissues, biological fluids) and inorganic samples (geological, environmental, material science) could be tested. The employment of different acids could require the use of different material for the glassware and the reflectors (e.g. fluoro polymers if HF is needed).

It is interesting noting that some restrictions to the elements that can be analysed may be foreseen. Halogenides and sulphides may be lost during the digestion step due to volatilisation of the corresponding acids. As a general feature, volatile species (e.g. elemental mercury and organophosphorous additives) may be lost as no oxidiser is added to the sample: volatilisation could take place before oxidant vapours decompose the sample.

As a final remark, the proposed analytical protocol is also expected to play a major role when microsamples have to be analysed, as is generally true for TXRF thanks to the very limited amounts of specimen required. The possibility to digest biological microsamples is under test.

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