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Understanding microwave vessel contamination by chloride species

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ABSTRACT

Microwaves are widely used to assist digestion, general sample treatment and synthesis. The use of *aqua regia* is extensively adopted for the closed vessel mineralization of samples prior to trace element detection, leading to the contamination of microwave vessels by chlorine containing species. The latter are entrapped in the polymeric matrix of the vessels, leading to memory effects that are difficult to remove, among which the risk of silver incomplete recoveries by removal of the sparingly soluble chloride is the predominant one. In the present paper, we determined by mass spectrometry that hydrogen chloride is the species entrapped in the polymeric matrix and responsible for vessel contamination. Moreover, several decontamination treatments were considered to assess their efficiency, demonstrating that several cleaning cycles with water, nitric acid or silver nitrate in nitric acid were inefficient in removing chloride contamination (contamination reduction around 90%). Better results (≈ 95% decrease) were achieved by a single decontamination step in alkaline environment (sodium hydroxide or ammonia). Finally, a thermal treatment in a common laboratory oven (i.e. without vacuum and ventilation) was tested: a one hour heating at 150 °C leads to a 98.5% decontamination, a figure higher than the ones obtained by wet treatments which requires comparable time. The latter treatment is a major advancement with respect to existing treatments as it avoids the need of a vacuum oven for at least 17 h as presently proposed in the literature.

1. Introduction

Microwave assisted treatment in closed sample holders is a widely employed method in analytical chemistry [1–4] and for synthetic purposes [5–7]. Microwave assisted, sample dissolution for inorganic species determination has been widely adopted with several benefits, namely accelerated digestion time, reduced risk of environmental contamination and limitation in volatile analyte loss [8]. The procedure typically features the dissolution of the solid in a mixture of pure acids at high temperature in a closed sample holder usually referred to as "vessel". Fluoropolymers are largely employed as sample holder because of their excellent chemical stability: nevertheless, carryover effects have been evidenced due to the relatively high temperature (typically up to 240 °C) and pressure (up to 10 MPa with high pressure modules) reached during the digestion procedure. Permeation of gases into the polymeric matrix has been demonstrated and is proposed as the main mechanism responsible for carryover effects [9]: gases enter the voids in the polymeric matrix during microwave digestion (high temperature and pressure) and are trapped inside the polymer when it cools to room temperature. Any subsequent use releases the entrapped gases back into the digestion vessel, leading to contamination by gaseous species formed during the previous digestion. The interest is commonly focused on the release of chlorine containing species after digestion with *aqua regia* [9], although other gaseous species, namely nitrogen oxides from HNO_3 or *aqua regia* itself and sulphur species after H_2SO_4 use, may also be released. The chief interest in chlorine species is due to the deleterious effect they exert on the determination of silver and other elements (mainly mercury(I) and, to a lesser extent, lead) which form sparingly soluble chlorides. As an example, silver chloride is fairly soluble ≈ 30 mmol/L in concentrated hydrochloric acid [10] as the complexes $AgCl_n^{(n-1)-}$ are formed (n typically 2 and 3). Nevertheless, dilution of the solution resulting from MW digestion or removal of HCl is performed prior to analysis, because of the matrix effects exerted by HCl. This strong reduction in chloride concentration result in a dramatic decrease of AgCl solubility, down to values similar to the ones measured in water when HCl < 0.01 M [11]. As a general consideration, the release of any species from vessel walls may interfere with the planned activity, when the microwave system is used for different purposes like digestion under different pH conditions (acidic or alkaline), solvent extraction or synthetic purposes.

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Different strategies may be adopted to reduce chloride contamination caused by *aqua regia*. Extensive cleaning by repeated treatment with water or mixtures not including the contamination source, may be performed, although this procedure strongly affects the overall productivity of the microwave digestion. The employment of quartz cups inside the polymeric vessel [12] is a second choice, but it would probably be ineffective as the gaseous species released by the inner walls of the polymeric vessel may easily migrate into the digestion mixture (they are also unsuitable when hydrofluoric acid is needed and found limited application up to now). As an alternative option, a decontamination procedure was introduced in 2000 and features a treatment of the vessels at 140 °C under vacuum for more than 10 h [9], with treatment time depending on the contamination history of the vessels. This procedure is extremely efficient in removing chlorine species, although requires a specialized equipment and a prolonged time that strongly reduced sample throughput. In the same paper the authors suggested that probably the dominant chlorine species entrapped inside the polymer pore is NOCl.

Aim of the present paper is to directly identify for the first time the chloride species responsible for the contamination of the vessel inner surfaces and, based on this information, setup a faster and effective route to their removal.

2. Experimental

2.1. Solutions

Ultrapure water produced by a Millipore MilliQ A10 system was used throughout for rinsing and solution preparation (18.2 M Ω cm conductivity, 3 ppb TOC). Pure nitric acid (VWR, Ultrapure NORMATOM for trace metal analysis) and hydrochloric acid (Fluka, TraceSELECT® ultra) were employed.

Chloride standard solutions for the calibration of the ion chromatographic analysis were obtained by dilution of a concentrated chloride standard (1000 mg/L from Merck).

A 0.1 M silver nitrate solution was prepared by dissolving an adequate amount of silver nitrate (Fluka) in ultrapure water.

Hydrazine monohydrate (98%, Sigma Aldrich) was used as a source of hydrazine.

A 0.1 M solution of sodium sulfite was prepared by dissolving the adequate mass of solid Na_2SO_3 (Fluka) in ultrapure water.

A 0.1 M NaOH solution from Carlo Erba was used, whereas the 0.1 M ammonia solution was prepared by diluting concentrated ammonia (30% ammonia solution from Carlo Erba).

2.2. Apparatus

A Milestone 1200 Mega microwave digester was used for all the microwave treatments; standard, commercially available vessels made of polytetrafluoroethylene were used.

Chloride determinations were performed with a 761 Compact IC (Metrohm, Herisau, CH) connected to a sample exchanger (831 Compact Autosampler from Metrohm) on a Metrosep A Supp 5 250 mm column (Metrohm), employing a mixed sodium carbonate (3.2 mM)/sodium bicarbonate (1.0 mM) eluent; external calibration was used for quantification.

Polypropylene test tubes, used as sample containers in the sample exchanger, were cleaned by soaking for one day in a detergent bath (0.4% Nalgene L900 in ultrapure water) and successively rinsed several times with ultrapure water.

A customized vacuum oven was employed for the thermal treatment under vacuum, featuring a heated and sealed glass tube (i.d. 10 cm), which can be connected to a vacuum system. The atmospheric pressure oven was a standard, benchtop laboratory apparatus with no fan recirculation (PBI International, 1.4 kw power).

A home made apparatus was used for the detection of evolved species from the polymer of the vessel walls (this apparatus is usually employed to study evolved species under a defined temperature program like temperature programmed reductive decomposition, TPDR). Briefly, it features a temperature programmed heating furnace and a quadrupole mass spectrometer (VG Masstorr FX): the needed gas fluxes are regulated by computer controlled mass flow controllers [13,14].

2.3. Microwave (MW) digestion and cleaning procedures

The same digestion program was used for vessel contamination and decontamination. A ramping microwave power and thermalization steps were employed as follows: 250 W (1 min), 0 W (1 min), 250 W (2 min), 400 W (2 min), 500 W (5 min), 0 W (1 min), 600 W (5 min). Temperatures were measured with the T probe of the MW apparatus as follows (temperatures in degree Celsius): 42 (250 W, first step), 60 (250 W, second step), 85 (400 W), 130 (500 W) and 150 (600 W).

Vessels were contaminated by chloride species introducing 4 mL of *aqua regia* and applying the described MW program.

The procedure employed to evaluate decontamination efficiency was as follows. The contaminated vessels were allowed to cool to room temperature, opened and rinsed 5 times with ultrapure water. The initial contamination was assessed by introducing 5 mL of ultrapure water in each vessel, running the MW program and analysing the resulting solutions for their chloride content. The decontamination procedures reported in Table 1 were subsequently applied (the thermal treatment under vacuum is described in details in [9]). Decontamination under wet conditions was performed by transferring the reagents reported in Table 1 into the vessels and applying the mentioned MW program. The decontamination solutions were subsequently discarded and the vessels rinsed 5 times with ultrapure water to remove any trace of the decontamination reagents. Five mL of ultrapure water were transferred in each treated vessel and the MW program applied again (this procedure to test contamination is common to wet and thermal treatments). The resulting solution was analyzed by ion chromatography to determine the amount of chloride to test the effectiveness of the treatment and the residual chloride contamination. This procedure (rinsing, transfer of 5 mL of ultrapure water and application of the MW program) was repeated 1–4 times as reported in Table 1 to test the efficacy of subsequent treatments.

Table 1
Decontamination solutions, thermal treatment and tested decontamination steps.

Decontamination procedure	Tested decontamination steps
Solutions	
3 mL ultrapure water	3
3 mL HNO_3	6
3 mL HNO_3+1 mL $AgNO_3$ 0.1 M	2
3 mL ultrapure water+200 μL hydrazine monohydrate 98% (final conc. 1.3 M)	3
3 mL sodium sulfite solution 0.05 M	2
3 mL sodium sulfite solution 0.1 M	2
5 and10 mL NaOH 0.1 M	2
5 and 10 mL NH_3 0.1 M	2
Thermal treatments	
150 °C, 10^{-2} bar, 17 h	1
150 °C, 10^{-2} bar, 24 h	1
150 °C, 1 bar, 17 h	1
150 °C, 1 bar, 24 h	1