



Determination of iodine in polyamide by inductively-coupled plasma/mass spectrometry

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ABSTRACT

A method was developed for the determination of iodine in polyamide (PA). This method is needed as PA containing iodine (such as CuI/KX (X = I or Br) heat stabilizing agent), may represent a risk of corrosion for electronic parts in the automotive industry. The method involved a microwave assisted digestion method using nitric acid followed by inductively coupled plasma mass spectrometry (ICP-MS) analysis. A dilution in 0.5% NH₃ was needed prior to ICP-MS analysis to suppress memory effect. The limit of quantification was estimated to be 0.9 mg kg⁻¹ which allows the control of very low iodine content PA used for applications in sensitive electronic parts. Spiking with iodide at 50 mg kg⁻¹ gave recovery factors of 100 ± 0.8%. The acid digestion method was compared with microwave assisted extraction of PA with 5% NH₃ solution. Alkaline extraction gave slightly lower results (10% below). Finally, the acid digestion method was applied to the analysis of raw materials PA pellets and molded parts (used or not). Obtained iodine contents were ranged from < 0.9–1000 mg kg⁻¹ with relative standard deviation (RSD) on samples in the range 2.2–4.5%.

1. Introduction

Polyamides are widely used materials and, in particular in the automotive industry because of their low cost as regard to their mechanical strength, their recyclability and their thermal and chemical resistance [1]. For instance, these polymers are used for housing electronic devices acting as pressure and/or temperature sensors in the exhaust gas, as well as in the gas intake for motors. In order to limit thermo-oxidative degradation of the polyamide during the molding of the part or its use, thermal stabilizers are added to the polymer. Many stabilizers are used such as phenolic compounds, amines but also metal derivatives such as mixtures of copper (I) iodide and potassium iodide or bromide [2]. The mixture CuI/KX (X = I or Br) is one of the most used.

However, in recent years, some studies [3,4] have shown that the use of thermal stabilizers containing CuI/KX could present a risk of corrosion for electronic devices, and this, even without direct physical contact. Verdingovas *et al.* [4] have thus shown corrosion of aluminum-gold wire used in microcircuits in the presence of polyamide comprising a CuI/KI thermal stabilizer. This was observed, either by direct contact in a humid environment, probably by solubilization of the iodide species, but more surprisingly, also with no direct contact. The latter phenomenon was assumed to be due to an emission of I₂(g) from PA.

Under dry conditions I₂ could react directly with Al, under humid conditions, I₂(g) could react with water, leading to hypoiodous acid and hydrogen iodide that will react as well with Al. Emission of I₂(g) is in agreement with the proposed mechanism of thermal stabilization of polyamides in the case of the use of a CuI/KI (or CuI/KBr) mixture [5,6]. This potential corrosion risk associated with the use of polyamides with iodide-based thermal stabilizers is to be taken into account in the case of direct or non-direct contact with electronic devices. Thus, in recent years, new halogen-free PA formulations have emerged specifically for sensitive automotive electronics with < 1 mg kg⁻¹ halogen content. It is therefore necessary to have a method for the evaluation of the iodide content in polyamide materials.

However, to our knowledge, at present there are no sufficiently sensitive methods for the evaluation of the iodine content at such a low level in polyamides. Although the determination of iodine in matrices such as biological samples, food and water has been quite well studied [7,8], polymer materials has been little addressed unlike with bromine and chlorine. Krzyzaniak *et al.* [9] used microwave-induced combustion (MIC) for the determination of I, Cl, Br and S in high purity polyimide. In this article, MIC was performed and combustion gases were trapped with an NH₄OH absorbing solution in the combustion reactor. The resulting solution was analyzed by either ion chromatography (IC) or inductively coupled plasma mass spectrometry (ICP-MS).

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The same strategy was used for Br and Cl determination in nitrile-butadiene rubber, styrene-butadiene rubber, and ethylene-propylene diene monomer elastomers [10]. The determination of the Br or Cl content in the polymers can also be carried out by direct measurements using WDXRF [11]. Other methods include pyrolysis of the polymer and trapping the combustion gases with an absorbent solution [12]. This solution is then analyzed by potentiometric titration or ion chromatography. These methods have been used, for example, for the Cl and Br certification of ERM®-EC680k and ERM®-EC681k polyethylene reference materials [11] in the 1000–100 mg kg⁻¹ range. These techniques may be used as well for the determination of iodine, but overall, methods using ICP-MS or ICP-OES appear to be one of the most sensitive and have been extensively used for iodine determination for instance, in food or biological samples [13–16].

Thus, the purpose of this study was to develop a method for the determination of iodine in polyamide samples stabilized with CuI/KI. The microwave-assisted digestion method was chosen as it is largely encountered in laboratories. This analysis is challenging because conventional methods of digestion of PA are in an acidic medium [17], and can lead to the formation of I₂ and thereby cause loss by volatilization and significant memory effect during ICP analysis similar to problems observed in food analysis [18,19]. In this article, we compared different microwave-assisted extraction/digestion methods for PA. The optimized method was applied to the evaluation of iodine content of various polyamide samples on the market.

2. Materials and methods

2.1. Instrumentation

ICP-OES measurements were performed on an ICAP 6300 series instrument (Thermo-Fisher Scientific) using the axial view. The quantification of iodine was performed at 178.276 nm and using the 183.038 nm line for confirmation. Copper was quantified at 327.395 nm and 324.754 nm and potassium at 769.896 nm. ICP-MS measurements were performed on an ICAP RQ ICP-MS instrument (Thermo-Fisher Scientific) equipped with a collision cell and a 4DX Autosampler (Elemental Scientific, Omaha, NE) with a FAST valve system. Autosampler and tubes were rinsed with 0.5% NH₃ solution. Two different analytical modes were used in this study (standard mode (STD) and kinetic energy discrimination mode (KED)). When the STD mode was used no He gas was introduced in the collision cell whereas He gas was injected in the collision cell in the KED mode. Solutions were diluted online with an internal standard solution of Tellurium at 100 µg L⁻¹ (mixture sample: internal standard solution; 2:1 (v:v)), optimized conditions for the plasma and nebulizer for ICP-OES and ICP-MS are given in Table 1. ¹²⁷I and ¹²⁵Te were used for quantification. The optimized conditions for the plasma and nebulizer for ICP-OES and

Table 1
Instruments operating conditions.

	ICAP 6300 ICP-OES	ICAP RQ ICP-MS
Radio Frequency power (W)	1050	1550
Plasma gas flow rate (L min ⁻¹)	14	14
Auxiliary argon flow rate (L min ⁻¹)	1.0	0.8
Nebulizer gas flow rate (L min ⁻¹)	0.5	1.0
Peristaltic Pump rate (rpm)	50	15
Sample uptake delay (s)	30	30
Replicates	3	3
Rinse time (s)	30	30
Sampler	ASX520-CETAC	SC-2DX (with fast valve system)
Chamber	Cyclonic	Cyclonic
Nebulizer type	concentric	concentric

ICP-MS are given in Table 1.

Grinding of the PA pellets samples was performed using a A10 Basic Mill (IKA®) and particles were sieved to reach < 500 µm particle size. Cryogenic grinding was performed on PA pellet samples using an SPEX® Sample prep 6770 Freezer Mill (Horiba scientific) cooled with liquid nitrogen.

Digestion and extraction of samples, were performed with a microwave oven (Milestone ETHOS 1) equipped with a temperature sensor. TFM reactors were used with a maximum pressure of 100 bar.

An Energy Dispersive X-Ray Fluorescence spectrum (EDXRF) was obtained using a portable NITON XI3t EDXRF spectrometer with a main range filter and a 30 s acquisition time.

Potentiometric titration of ammonia was performed on a DL50 Rondolino instrument (Mettler Toledo) using HCl (0.1 mol L⁻¹) as the titrant solution. The same potentiometric titrator was used for the acidic titration using a titrant solution of 1 mol L⁻¹ NaOH.

2.2. Reagents and chemicals

All solutions were prepared with 18 MΩ cm Milli-Q water (Millipore, Bedford, MA, USA). An aqueous standard stock solution of iodine at 1000 mg L⁻¹ was prepared from potassium iodide in Milli-Q water. Tellurium standard solution at 1000 mg L⁻¹ in 10% HNO₃ was obtained from Sigma Aldrich (TraceCERT®). Working standard solutions were prepared daily from these stock solutions by dilution with 0.5% NH₃. All glassware was cleaned with 10% HNO₃ solution followed by deionized water. Ammonia (20–22%, optima grade) and nitric acid (67–69%, optima grade) were obtained from Fisher Scientific. All other reagents used were p.a. grade. PA66 sample 1, containing CuI/KI as the heat stabilizing agent with a total iodine content close to 1000 mg kg⁻¹ (considering the amount of iodine added during formulation of the polymer) was obtained from a polymer producer. It was used as the reference sample, as no certified PA sample for iodine determination is available. PA 66 sample free halogen grade (Sample 3) was obtained from the same polymer producer, this sample was used for recovery determination.

2.3. Sample treatments

2.3.1. Nitric acid digestion

200 mg of polyamide sample (cut in small parts (< 0.5 mm) for molded parts) was weighed in the TFM digestion vessels. 5 mL of nitric acid (68%) were added. The sealed container was placed in the microwave oven. Sample was heated at 150 °C and maintained 30 min, and then cooled to 20–25 °C. The solution was then transferred quantitatively into a 50 mL polypropylene flask and diluted with Milli-Q water and analyzed by ICP-OES for copper and potassium determination. For iodine determination, 1 mL of the diluted acidic solution was diluted 25 times with 0.5% NH₃ solution prior ICP-MS analysis with online addition of Tellurium as the internal standard.

2.3.2. Ammonia or TMAH extraction

Polyamide pellets were ground and then sieved at 500 µm. Subsample of 200 mg was weighted in the TFM digestion vessels. The alkaline extraction solution was added (see tested composition in Table 2). The closed container was placed in the microwave oven. Samples were heated at 150 °C or 50 °C for 30 min and then cooled to 20–25 °C. The resulting solutions were then transferred quantitatively into 50 mL polypropylene flask and diluted with Milli-Q water. Particles were removed by centrifugation (4000 rpm, 10 min) and an aliquot of the supernatant solution was filtered over 0.47 µm filter (Nylon) and diluted 50 times with 0.5% NH₃ solution before ICP-MS analysis for iodine determination.

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