

Development of two Explosive Candidate Reference Materials: Certification of Metallic Impurities in LLM-105 and FOX-7

Rong Guo¹, Ru-Qin Liu^{1,2}, Yong Zhang², Zhi-Rong Suo^{1,*}, Jia-Jin Xia¹, Shuang Chen¹, Xiao-Lu Yao¹

¹School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, P. R. China

²Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang 621900, P. R. China

* Corresponding author: suozhirong@163.com

Abstract: Explosive reference materials are significant to traceability analysis, quality control and measurement of energetic materials applied in modern weapon system. In the field of engineering-oriented application, LLM-105 and FOX-7 were proved that they had a promising prospect in used extensively as insensitive high energetic ingredients in munitions. Certification of metallic impurities in LLM-105 and FOX-7 was achieved by the microwave digestion-assistant inductively coupled plasma-mass spectrometry method. The contents of metallic impurities, including Na, K, Ca, Cr, Ni, Fe, Mg, Al, Co, Cu and Zn, in several LLM-105 and FOX-7 samples were accurately detected under the optimal conditions. And the detected results suggested that recrystallization was an effective method for high-purity explosive reference materials. This study could be helpful for the development of LLM-105 and FOX-7 candidate reference materials.

1. Introduction

In the modern national defence industry, explosive reference materials, which are characterized by a metrological procedure [1], play a unique role in traceability analysis, quality control and measurement for energetic materials applied in weapon system. 2,6-Diamino-3,5-dinitropyrazine-1-oxide (LLM-105), seen in Fig.1, is a six-membered *N*-heterocyclic compound showing low sensitivity and high thermal stability (DSC decomposition point of 342 °C) [2], while 1,1-diamino-2,2-dinitroethylene (FOX-7) is of the high energy materials with a lower impact sensitivity than 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX, also called as *the king of explosives*) [3]. They are well suited for being used extensively as insensitive high energetic ingredients in explosive formulations. However, owing to the absence of its relative certified reference materials, rigorous quality evaluation and diagnosis of explosive charge derived from raw materials or products might be unfeasible in term of engineering-oriented application for LLM-105 and FOX-7. Thus, it's believed that the development of those two explosive reference materials could be beneficial to the accurate chemical analysis and quality inspection of munitions, the technology enhancement of insensitive high energetic explosives manufacture process and the establishment of detection method for LLM-105 and FOX-7.



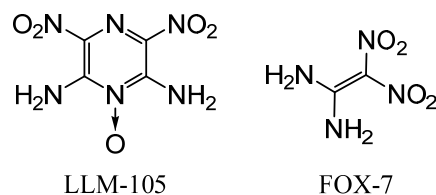


Fig. 1 Chemical structures of two explosives

Certification of impurities in explosives belongs to the key part of developing candidate reference materials. Impurities might alter material properties and stability, and be serviced to forensic identification [4]. Among various impurities, metallic elements have an influence on the thermal performance and crystallization of explosives obviously. Zhang et al [5] reported that the sublimation rate of pentaerythritol tetranitrate (PETN) was decreased but its sublimation temperature was increased by adding zinc ion. Xu et al [6] claimed that disperse crystallization was observed because the metallic ions (e.g. Fe^{3+} , Zn^{2+} , Ca^{2+} and Na^{+}) changed nucleation and growth of HMX crystals. And the quality of HMX crystals was also changed due to the growth-step hindered effect of metallic ions. The certified contents of target metallic impurities in explosive candidate reference materials could be fast examined by the inductively coupled plasma-mass spectrometry (ICP-MS) technique [7-9]. Therefore, in the present work, metallic impurities in LLM-105 and FOX-7 were certified by the ICP-MS for the development of those two explosive candidate reference materials. And an accurate and repeatable IPC-MS method was also developed for detecting trace metallic components in LLM-105 and FOX-7.

2. Experimental

2.1. Chemicals and apparatus

Explosive candidate reference materials (LLM-105 and FOX-7) were provided by Institute of Chemical Materials, China Academy of Engineering Physics. Their purities were both more than 98% by HPLC. AR grade nitric acid and AR grade DMSO were purchased from Chengdu Kelong Chemical Reagent Factory (China) and used without further purification. Deionized water was prepared by the Merck-Millipore Milli-Q Deionized Water Maker. Detection of metallic impurities was performed on the Agilent 7700x ICP-MS. Other apparatus mainly include the Milestone ETHOS ONE Microwave Digestion System and the Mettler Toledo AG135 Electronic Balance.

2.2. Metallic impurities analysis

2.2.1. Preparation of samples

Approximately 0.1 g of the pulverized explosives (LLM-105 and FOX-7) were accurately weighted and then poured into the polytetrafluoroethylene-made digested tanks of 50 mL, respectively. Samples were digested with concentrated HNO_3 (65%) of 8 mL under the specified procedure (Microwave power of 1000 W). Total time of digestion program was 65 min. Digested temperature was gradually rose to 180 °C from 0 to 10 min. System was kept at 180 °C during 10 min to 30 min, and then digested temperature was gradually dropped to room temperature from 30 min to 65 min. After ending digestion program, the digested residues were collected and transferred into a 25 mL of plastic volumetric flask. Then deionized water was added into the flask for dilution. After finishing constant volume, those solution samples were used for IPC-MS analysis.

2.2.2. IPC-MS work conditions

IPC-MS work conditions were as follows: the radio-frequency generator power of 1350 W, a peristaltic pump speed of $0.1 \text{ r} \cdot \text{s}^{-1}$, the spray chamber temperature of 2 °C, a carrier gas flow rate of 1.0

$\text{L}\cdot\text{min}^{-1}$, an assistant gas flow rate of $1.0\text{ L}\cdot\text{min}^{-1}$, a plasma gas flow rate of $15.0\text{ L}\cdot\text{min}^{-1}$. ^6Li , ^{89}Y and ^{209}Bi were used as the internal standards.

3. Results and discussion

3.1. Sample treatment

Heating digestion and microwave digestion were investigated for the optimization of sample treatment method, respectively. Common heating digestion is a simple operation method, but it consumes more nitric acid results in a significant impact on the detection of trace inorganic components. Therefore microwave digestion method was used in the pre-treatment process.

3.2. Method validation

The validation results of methodological study, comprising the precision tests, the repeatability experiments and the retrieving tests, were shown in Tab. 1. The relative standard deviation (RSD) was utilized as a measure for precision and repeatability. This detection method was accurate and repeatable. The recovery ratios of all detected elements were in the range of 96.9% to 99.0%.

Tab. 1 Investigation of detecting methodology for the trace inorganic impurities (n=6)

	Na	K	Ca	Cr	Ni	Fe	Mg	Al	Co	Cu	Zn
Accuracy	1.7%	1.6%	1.7%	2.1%	1.9%	1.9%	1.8%	1.7%	1.9%	1.6%	1.7%
Repeatability	2.1%	1.9%	2.0%	2.1%	2.3%	2.1%	2.0%	2.0%	2.4%	2.1%	2.3%
Recovery ratio	97.6%	98.1%	99.0%	96.9%	97.2%	98.1%	98.7%	98.6%	97.7%	98.5%	97.9%

3.3. Metallic impurities detected in two explosives by ICP-MS

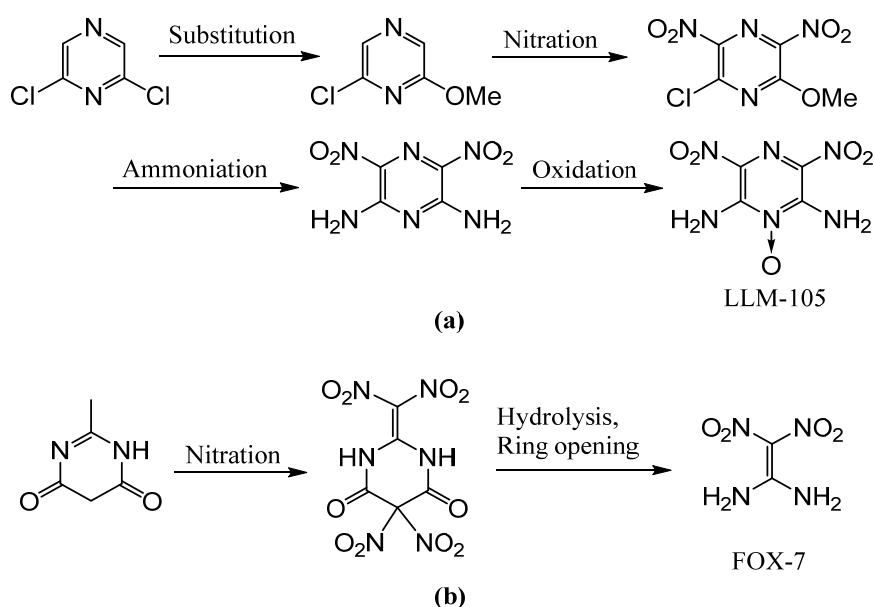
Several LLM-105 and FOX-7 samples were detected by ICP-MS under the optimal operations. The contents of metallic impurities in various samples were shown in Tab. 2. Raw samples of LLM-105 and FOX-7 were synthesized via the following chemical reaction routes (Scheme 1). Refining processes of raw samples were finished by the solvent crystallization method. In general, metallic impurities in explosives mainly stem from the tap water used in industrial manufacturing process of explosives [10]. The total contents and species of inorganic impurities in FOX-7 were both higher than those of LLM-105 due to the different and complicated synthesis technologies. The results of refining experiments indicated that the contents of metallic impurities in two explosives could be reduced obviously via recrystallization in DMSO.

Tab. 2 Detecting results for samples ($\mu\text{g}\cdot\text{g}^{-1}$)

Sample Name	Na	K	Ca	Cr	Ni	Fe	Mg	Al	Co	Cu	Zn
LLM-105 (1) ^a	-	0.65	13.69	1.84	0.83	5.77	9.22	0.04	0.01	0.14	-
LLM-105 (2) ^a	-	0.66	13.89	1.87	0.84	5.85	9.35	0.04	0.01	0.14	-
LLM-105 #1(1) ^b	-	0.29	6.23	0.84	0.38	2.62	4.19	0.02	-	0.06	-
LLM-105 #1(2) ^b	-	0.28	5.98	0.80	0.36	2.52	4.03	0.02	-	0.06	-
LLM-105 #2(1) ^b	-	0.21	4.50	0.60	0.27	1.89	3.03	0.01	-	0.05	-

LLM-105 #2(2) ^b	-	0.22	4.65	0.62	0.28	1.96	3.13	0.01	-	0.05	-
FOX-7 (1) ^a	36.49	20.46	70.89	7.01	3.27	52.64	42.88	2.09	0.07	-	13.35
FOX-7 (2) ^a	37.02	20.75	71.92	7.11	3.32	53.40	43.50	2.12	0.07	-	13.54
FOX-7 #1(1) ^b	16.60	9.31	32.25	3.19	1.49	23.94	19.51	0.95	0.03	-	6.07
FOX-7 #1(2) ^b	15.94	8.94	30.97	3.06	1.43	22.99	18.73	0.91	0.03	-	5.83
FOX-7 #2(1) ^b	11.99	6.72	23.29	2.30	1.07	17.29	14.09	0.69	0.02	-	4.39
FOX-7 #2(2) ^b	12.38	6.94	24.06	2.38	1.11	17.86	14.55	0.71	0.02	-	4.53

a. Raw samples; b. Samples after recrystallization treatment in DMSO



Scheme 1 Synthetic routes of LLM-105 (a) and FOX-7 (b)

4. Conclusions

An accurate and repeatable microwave digestion-assistant ICP-MS method has been proposed to certification of metallic impurities in explosive candidate reference materials. The contents of metallic impurities, including Na, K, Ca, Cr, Ni, Fe, Mg, Al, Co, Cu and Zn, in several LLM-105 and FOX-7 samples were detected by ICP-MS under the optimal conditions. Recrystallization in DMSO is an effective path to refining LLM-105 and FOX-7 for attaining its candidate reference materials conveniently.

Acknowledgments

This work was supported by Technology-Fundamental Research Project of *State Administration of Science, Technology and Industry for National Defence* of China (JSJL2015212A001); National Training Program of Innovation and Entrepreneurship for Undergraduates (201610619019).

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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