**Journal of Radiation Researches, vol.6, №1, 2019, Baku**
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**pp. 29-33**

**PACS: 71.23An**

# MICROWAVE DECOMPOSITION OF SOIL SAMPLES FOR ANALYSIS OF THE HEAVY METALS AND RADIONUCLIDES

**M.M. Ahmadov, F.Y. Humbatov, V.S. Balayev, S.Sh. Mammadzada, N.A. Ibadov, N.Sh. Karimova**

*Institute of Radiation Problems of ANAS*
hfamil@mail.ru

***Abstract:*** Sample preparation of soil samples (reference material) in a microwave oven using the EPA - 3051 methods showed that, with microwave decomposition, the extraction coefficient of metals from the soil improved and sample preparation time is drastically reduced.

***Key Words:*** AAS, heavy metals, Uranium, Thorium, microwave decomposition.

## 1. Introduction

The development of the use of microwave energy as a source of heating made it possible to use this method for determining trace and ultra-trace amounts of elements in the environment, in chemical, biological and other objects. For the analysis of objects of this type, an atomic absorption (emission) spectrometer (AAS or AES), AES with inductively coupled plasma (ICP), AAS with an electrothermal atomizer (GTA), ICP with a spectrometer, etc. are used.

Atomic absorption spectrometry is a very simple high-performance analysis method and the most common selective method for determining heavy metals used in modern analytical practice. Depending on the composition of the object under study, the methods of dry (hardening) or wet mineralization, which are often laborious and long-lasting, have so far been used. A particular disadvantage of these methods is the loss of volatile elements, especially during ashing. Therefore, nowadays microwave ovens are widely used for the decomposition of various samples [1-3]. Processing of the sample with acids in a microwave oven has several advantages: duration of the process and consumption of acids are significantly reduced, reaction volume is clean and closed, computer-programmed control allows you to get a recoverable result.

The purpose of this study is to apply microwave decomposition to soil analysis (reference material GTMO44MS) with subsequent instrumental analysis of solutions using the AAS and AAS with GTA and compare these data with the result obtained by decomposition of the same sample in the traditional way.

## 2. Experimental

**Solutions and reagents.** HNO3, HCl, HF (ultra clean) acids are used. The initial solutions of metal salts (in 1g / l in terms of metal) bought from the "Merck" company. PdNO3 solutions 500 mg / l, 2% citric acid solution were used as modifiers for the determination of As, Cd and Pb using GTA. Working solutions of metals were prepared in an environment of 0.2% HNO3.

**Equipment**

The analysis was carried out in AAS SpektrAA 220FS and AAS with an electrothermal atomizer GTA 110 (Varian). The instrumental measurement conditions are given in Table 1. Note

that the software of the SpektrAA 220FS instrument allows simultaneous multi-element analysis with the flame atomizer. This feature of the instrument leads to a reduction in the measurement time in a significant way. Flame generated with a propane-air mixture. The electrothermal atomizer has a PSD type auto-dose and thanks to that, analysis of the sample was performed automatically under the control of the computer. Pyro-coated graphite tube used for the atomization of the sample. An inert atmosphere was created with argon (purity 99.99%). Hollow cathode lamps of the same company are used as light sources. Background absorption was taken into account with the deuterium background corrector.

**Table 1:** Instrumental measurement conditions

| | Absorption wavelength (nm) | Lamp Current (mA) | The spectral width of the slit (nm) | Type of atomizer |
|---|---|---|---|---|
| As | 193,7 | 10 | 0,5 | GTA |
| Cd | 228,8 | 4 | 0,5 | GTA |
| Cr | 357,9 | 7 | 0,5 R | GTA |
| Cu | 324,8 | 4 | 0,5 | Flame |
| Ni | 232 | 4 | 0,2 | Flame |
| Pb | 283,3 | 10 | 0,5 | GTA |
| Zn | 213,9 | 5 | 1,0 | Flame |

Acid decomposition of the sample was carried out in a microwave oven ("Ethos plus" from Milestone) and in a 250 ml flask in a traditional way.

1) Acid decomposition in a microwave oven: A portion of 0.5 g was carried to an autoclave, 8 ml of HNO3, 5 ml of HCl and 1.5 ml of HF were added, closed with a lid, sealed and placed in a microwave oven. The analytical program for the microwave decomposition is shown in Table 2 below.

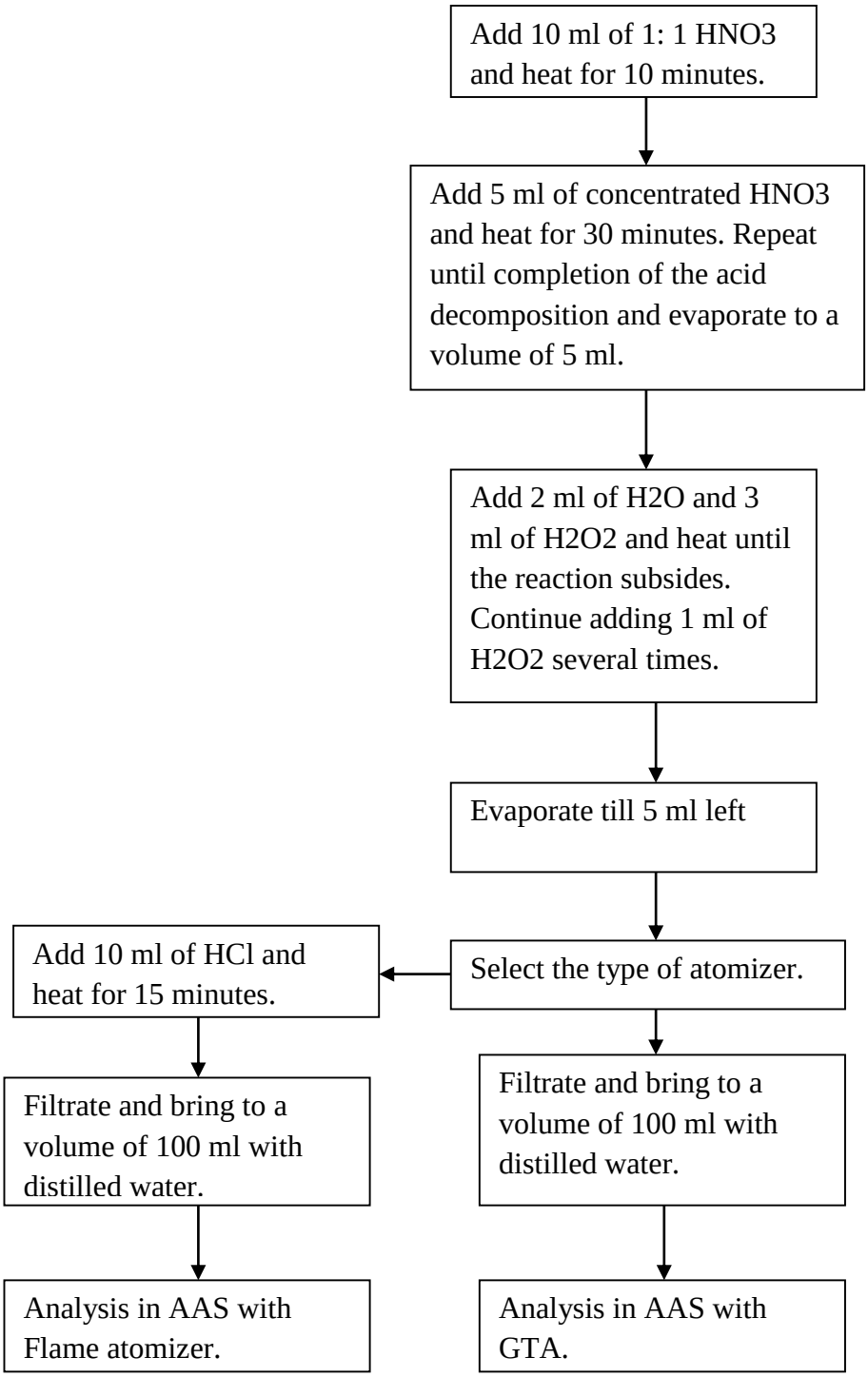
**Table 2.** Analytical program of microwave decomposition

| Step | Time | Temperature | Microwave generator power |
|---|---|---|---|
| 1 | 6 minute | 160 $^0$C | till 1000 W |
| 2 | 4 minute | 210 $^0$C | till 1000 W |
| 3 | 20 minute | 210 $^0$C | till 1000 W |

After cooling, autoclaves were opened and filtered with adding distilled water till 50ml.

2) The traditional way; In this case, the acid decomposition carried out by the method of EPA-3051/4 /. A sample of 1-2 g was carried into a round-bottomed 250 ml flask, and further preparation process was carried out according to the scheme given below.

Block diagram sequence of procedure




The measurement results are shown in Table 3. As can be seen from the table with the microwave decomposition of samples determined coefficient of extraction of the elements improves. It is known that microwave decomposition of samples provides clean, closed and controlled reaction environment. The high temperature achieved by microwave decomposition gives relatively high kinetic advantages than the heater, which is described by the Arrhenius equation:

$$\frac{d\ln k}{dT} = \frac{E_a}{RT^2}$$

Integrating this equation we get

$$\ln \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

In this expression $k_1$ and $k_2$ are reaction rate constants at temperatures $T_1$ and $T_2$, respectively, Ea is the activation energy and R is an ideal gas constant. This equation shows that the reaction rate exponentially increases with increasing temperature. Therefore, the time required for acid decomposition of the sample at a temperature of 210°C will be sharply reduced in comparison with decomposition at 95°C, which is carried out in the method EPA-3051. The high temperature of microwave heating improves the decomposition process and prevents the loss of volatile elements from the closed reaction environment. These facts are the main reasons for the improvement of the extraction coefficient for microwave decomposition of soil samples.

**Table 3:** Comparison of the results of the analysis of reference soil samples acid decomposition, in a microwave oven and heating in a hot plate. Concentration value in mg/kg.

| Defined element | Heating with hot plate | Microwave heating | Reference value |
|---|---|---|---|
| As | 24.28 | 25.89 | 27 |
| Cd | 1.98 | 2.26 | 2,4 |
| Cr | 68.7 | 78.95 | 77 |
| Cu | 85.62 | 89.84 | 90 |
| Ni | 32.5 | 36.8 | 37 |
| Pb | 138.7 | 151.12 | 154 |
| Zn | 465.8 | 502.4 | 494 |
| U | 0.527 | 0.641 | 0.498 |
| Th | 0.276 | 0.309 | 0.263 |

## 3. Conclusion

Using microwave decomposition on soil analysis (reference material GTMO44MS) with subsequent instrumental analysis of solution using the AAS and AAS with GTA methods and comparing these data with the result obtained by decomposition of the same sample in the traditional way, showed that:

1) The time required for acid decomposition of samples at a temperature of 210°C in a microwave oven of the "Ethos plus" manufactured by Milestone drastically reduced in comparison with the decomposition at 95°C, which is carried out according to the EPA-3051 method;

2) The high temperature exerted by microwave heating improves the decomposition process and the closed reaction volume prevents the loss of volatile elements.

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## МИКРОВОЛНОВОЕ РАЗЛОЖЕНИЕ ОБРАЗЦОВ ПОЧВЫ ДЛЯ АНАЛИЗА ТЯЖЕЛЫХ МЕТАЛЛОВ И РАДИОНУКЛИДОВ.

**М.М. Ахмедов, Ф.Ю. Гумбатов, В.С. Балаев, С.Ш. Мамедзаде, Н.А. Ибадов, Н.Ш. Каримова**

***Резюме:*** Проведением пробоподготовки проб почв (референсный материал) в микроволновом печи и по методом EPA – 3051 показано что, при микроволновом разложения коэффициент извлечения металлов из почв улучшается и время пробоподготовка резко сокращается.

***Ключевые слова:*** ААС, тяжелые металлы, уран, торий, микроволновое разложение.

## AĞIR METALLARIN VƏ RADİONİKLİDƏRİN ANALİZİ ÜÇÜN TORPAQ NÜMUNƏLƏRİNİN MİKRODALĞALI PARÇALANMASI

**M.M. Əhmədov, F.Y. Hümbətov, V.S. Balayev, S.Ş. Məmmədzadə, N.Ə. İbadov, N.Ş. Kərimova**

***Xülasə:*** Torpaq nümunələrinin (referens materialın) Mikrodalğalı sobada EPA-3051 metodu ilə nümunə hazırlığı aparılıb və mikrodalğalı ekstrasiya ilə torpaqdan metalların ekstraksiya əmsallarının yaxşılaşdığı və nümunə hazırlama müddətinin kəskin şəkildə azaldığı göstərilmişdir.

***Açar sözlər:*** AAS, ağır metallar, Uran, Torium, mikrodalğalı parçalanma.