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Article

Evaluation of the Mixtures Ammonium Phosphate/Magnesium Nitrate and Palladium Nitrate/Magnesium Nitrate as Modifiers for Simultaneous Determination of Cd, Cr, Ni and Pb in Mineral Water by GFAAS

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Um método é descrito para a determinação simultânea de Cd, Cr, Ni e Pb em amostras de água mineral por espectrometria de absorção atômica em forno de grafite com um atomizador de grafite aquecido transversalmente (THGA) e um sistema de corretor de fundo por efeito Zeeman longitudinal. O comportamento eletrotérmico dos analitos durante as etapas de pirólise e atomização foi estudado sem modificador, na presença de 5 µg Pd e 3 µg $Mg(NO_3)_2$ e na presença de 50 µg $NH_4H_2PO_4$ e 3 µg $Mg(NO_3)_2$. Um volume de 20 µL de uma solução 0,028 mol L^{-1} HNO_3 contendo 50 µg L^{-1} Ni e Pb, 10 µg L^{-1} Cr e 5 µg L^{-1} Cd foi dispensado dentro do tubo de grafite a 20 °C. A mistura paládio/magnésio foi selecionada como o melhor modificador. As temperaturas de pirólise e atomização foram fixadas em 1000 °C e 2300 °C, respectivamente. As massas características calculadas foram 2,2 pg Cd, 10 pg Cr, 42 pg Ni e 66 pg Pb, e o tempo de vida do tubo de grafite foi cerca de 600 queimas. Os limites de detecção, baseados na absorbância integrada, foram 0,02 µg L^{-1} Cd, 0,94 µg L^{-1} Cr, 0,45 µg L^{-1} Ni e 0,75 µg L^{-1} Pb, que excederam os valores requeridos pela Legislação Brasileira, o qual estabelece um nível máximo permitido para Cd, Cr, Ni e Pb de 3 µg L^{-1}, 50 µg L^{-1}, 20 µg L^{-1} e 10 µg L^{-1}, respectivamente. As recuperações de Cd, Cr, Ni e Pb adicionados a amostras de água mineral variaram dentro dos intervalos de 93-108%, 96-104%, 87-101% e 98-108%, respectivamente. Resultados de análises de materiais de referência padrão (National Institute of Standards and Technology: 1640-Trace Elements in Natural Water; 1643d-Trace Elements in Water) foram concordantes com seus valores certificados a um nível de confiança de 95%.

A method is described for the simultaneous determination of Cd, Cr, Ni and Pb in mineral water samples by graphite furnace atomic absorption spectrometry with a transversely heated graphite atomizer (THGA) and a longitudinal Zeeman-effect background correction system. The electrothermal behavior of analytes during pyrolysis and atomization steps was studied without modifier, in presence of 5 µg Pd and 3 µg $Mg(NO_3)_2$ and in presence of 50 µg $NH_4H_2PO_4$ and 3 µg $Mg(NO_3)_2$. A volume of 20 µL of a 0.028 mol L^{-1} HNO_3 solution containing 50 µg L^{-1} Ni and Pb, 10 µg L^{-1} Cr and 5 µg L^{-1} Cd was dispensed into the graphite tube at 20 °C. The mixture palladium/magnesium was selected as the optimum modifier. The pyrolysis and atomization temperatures were fixed at 1000 °C and 2300 °C, respectively. The characteristic masses were calculated as 2.2 pg Cd, 10 pg Cr, 42 pg Ni and 66 pg Pb and the lifetime of the graphite tube was around 600 firings. Limits of detection based on integrated absorbance were 0.02 µg L^{-1} Cd, 0.94 µg L^{-1} Cr, 0.45 µg L^{-1} Ni and 0.75 µg L^{-1} Pb, which exceeded the requirements of Brazilian Food Regulation that establish the maximum permissible level for Cd, Cr, Ni and Pb at 3 µg L^{-1}, 50 µg L^{-1}, 20 µg L^{-1} and 10 µg L^{-1}, respectively. The recoveries of Cd, Cr, Ni and Pb added to mineral water samples varied within the 93-108%, 96-104%, 87-101% and 98-108% ranges, respectively. Results of analysis of standard reference materials (National Institute of Standards and Technology: 1640-Trace Elements in Natural Water; 1643d-Trace Elements in Water) were in agreement with certified values at the 95% confidence level.

Keywords: GFAAS, simultaneous determination, mineral water, inorganic trace elements

Introduction

Graphite furnace atomic absorption spectrometry (GFAAS) is a suitable and widely used technique to determine elements at trace levels.[1] Besides main characteristics of GFAAS (e.g. high selectivity and sensitivity, low detection limits and sample consumption, capability for direct analysis with minimal sample preparation, solid sampling, easy to operate or handling) the applicability of the technique has been further extended

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with the development of simultaneous multielement spectrometers.[2-4]

Graphite furnace simultaneous atomic absorption spectrometry technique (GFSIMAAS) has been used to analyze different matrices such as urine,[5] blood,[6] hair,[7] seawater,[8] edible oils,[9] waters,[10] ultrapure acids,[11] cigarette smoke,[12] rock,[13] beverages and vegetables materials,[14] certificated materials,[15] orange juice,[16] soils and sediments,[17] animal tissues[18] and metal oxides.[19]

The accurate determination of cadmium, chromium, nickel and lead in most environmental and food samples is of importance because of the toxicity of these elements and their compounds.[20] Drinking water is one of the main sources of exposure to inorganic trace contaminants because of the large volume consumed.[21] The development of simple, fast and reliable analytical methods are very attractive for laboratories that routinely analyze mineral waters in large-scale. Because Cd, Cr, Ni and Pb are usually present at low concentrations in most mineral waters, the GFSIMAAS can be properly used for this quality control.

The determination of Cd, Cr, Ni and Pb in water samples using single detection by GFAAS has already been found in the literature[22-28] and several modifiers are proposed. Ascorbic acid,[22] phosphoric acid,[23] ammonium phosphate[24] and lanthanum[25] have been used for lead. The mixture lanthanum-nitric acid has also been applied as modifier for the determination of cadmium in water[26] although ammonium phosphate/magnesium nitrate is the most used.[27] For Cr determinations, magnesium nitrate is recommended.[29] On the other hand, no modifier is needed for Ni determinations.[29]

In 1992, Welz and co-workers proposed the mixture $Pd(NO_3)_2$ + $Mg(NO_3)_2$ as an "universal modifier" for 21 elements, including lead and cadmium.[30] For simultaneous multielement determinations, this mixture has been largely used.[11,18,21,31-39] Indeed, in GFSIMAAS the modifier and heating program of atomizer is common for all analytes. So, the optimum conditions should be selected as a compromise between required sensibility and precision.

The multielement determination of Cd, Cr, Cu, Ni and Pb in potable and surface waters was proposed by Feuerstein and Schlemmer in 1999.[32] In this work the authors used THGA tubes with end caps and Pd/Mg as modifier, and the characteristic masses were 1.5 pg Cd, 4.1 pg Cr, 14.7 pg Cu, 16.6 pg Ni and 34 pg Pb, the limits of determination were below 1 µg L^{-1} for Cr, Ni, and Pb and 0.1 µg L^{-1} for Pb, respectively and the analytical cycle for each replicate takes 123 s.

The Brazilian Food Regulation (Decree # 310 – ANVS from Health Department) establishes the maximum allowed level for Cd, Cr, Ni and Pb (and others 7 elements) in mineral waters at 3 µg L^{-1}, 50 µg L^{-1}, 20 µg L^{-1} and 10 µg L^{-1}, respectively.[40]

After taking into consideration the limits above, the aim of this work is to study the electrothermal behaviour of Cd, Cr, Ni and Pb in mineral water without and in presence of $Pd(NO_3)_2 + Mg(NO_3)_2$, or $NH_4H_2PO_4 + Mg(NO_3)_2$ as modifiers for the direct multielement determination of all analytes.

Experimental

Instruments and apparatus

A Perkin Elmer (Shelton, CT USA) SIMAA™ 6000 simultaneous multielement atomic absorption spectrometer with longitudinal Zeeman-effect background correction, a transversely heated graphite tube atomizer (THGA) and an AS-72 autosampler were used.[41] The whole system was controlled by means of AA Winlab™ control software running under Microsoft Windows™. The instrumental conditions are given in Table 1. Standard pyrolitic graphite-coated electrographite THGA tubes with integrated platforms (Perkin Elmer Part B050-4033) were used. Perkin-Elmer Lumina™ electrodeless discharge lamps (EDL) were used for the determination of Cd (P/N N305-0615) and Pb (P/N N305-0657) at the analytical wavelengths and lamp currents recommended by the manufacturer. Perkin-Elmer Lumina™ hollow cathode lamps (HCL) were used for the determination of Cr (P/N N305-0119) and Ni (P/N N305-0152) at the analytical

Table 1. SIMAA 6000 spectrometer and atomizer conditions

Specific parameters	Cd	Cr	Ni	Pb
Light source	EDL	HCL	HCL	EDL
Current/mA	180	25	25	450
Wavelenght/nm	228.8	357.9	232.0	283.3
Slit/nm	0.7	0.7	0.7	0.7

Instrument-specific parameters	
Background correction	Longitudinal Zeeman
Measurement mode	Integrated absorbance
Sample volume	20 µL
Chemical modifier volume	5 µL Pd + 3 µL $Mg(NO_3)_2$

THGA program[a]

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Gas flow rate (mL min^{-1})
1	110	1	20	250
2	150	5	30	250
3	1000	5	10	250
4	2300	0	5	0
5	2450	1	3	250

[a] Analytical cycle = 80s.

wavelengths and currents recommended by the manufacturer. High-purity argon (99.999%, White Martins, Brazil) was used as the purge gas. The experiments were carried out under STPF conditions.[42] The heating program of atomizer used for the simultaneous determination of Cd, Cr, Ni and Pb is shown in Table 1.

Standards and reagents

All samples and standards were acidified to 0.028 mol L^{-1} HNO_3 (ultrapure grade, Merck, Darmstadt, Germany) and high-purity deionized water using a Milli-Q™ water purification system (Millipore). Five µL of a solution containing 1.00 g L^{-1} $Pd(NO_3)_2$ and 3 µL of a solution containing 1.00 g L^{-1} $Mg(NO_3)_2$ were used as chemical modifiers. All 1.00 g L^{-1} Pd and Mg nitrate solutions were prepared by appropriate dilution from individual 10.0 g L^{-1} stock solutions in water. For the study involving phosphate/magnesium, 50 µL of 1.00 g L^{-1} $NH_4H_2PO_4$ solution and 3 µL of 1.00 g L^{-1} $Mg(NO_3)_2$ solution were used as modifiers. The 1.00 g L^{-1} $NH_4H_2PO_4$ solution was also prepared by appropriate dilution from individual 10.0 g L^{-1} stock solution in water. Analytes stock solutions (1.00 g L^{-1}) were prepared by appropriate dilution from standard atomic absorption solutions (*Carlo Erba*, Normex®). For calibration, five reference solutions (5.00, 10.0, 20.0, 40.0 and 50.0 µg L^{-1} Cr, Ni, Pb and 0.50, 1.00, 2.00, 4.00 and 6.00 µg L^{-1} Cd) were daily prepared in 0.028 mol L^{-1} HNO_3 by appropriate dilution of the stock solution. The autosampler washing solution was 0.028 mol L^{-1} HNO_3 and high purity argon (99.999%, White Martins, Brazil) was employed as the purge gas.

Two standard reference materials (SRM) from National Institute of Standards and Technology National Institute of Standards and Technology, Gaithersburg, MD (1640 – Trace Elements in Natural Water; 1643 d – Trace Elements in Water) were used for checking the accuracy of the method.

Procedure

For each measurement, 20 µL of the sample or of the analytical solution and 5 µL of 1.00 g L^{-1} $Pd(NO_3)_2$ solution or 50 µL of 1.00 g L^{-1} $NH_4H_2PO_4$ solution and 3 µL of 1.00 g L^{-1} $Mg(NO_3)_2$ solution were injected into the graphite tube at 20 °C.

Pyrolysis and atomization curves were established without chemical modifier and in the presence of $Pd(NO_3)_2$ + $Mg(NO_3)_2$ and $NH_4H_2PO_4$ + $Mg(NO_3)_2$. These studies were made with the following solutions: *Solution a*. 5.00 µg L^{-1} Cd, 10.0 µg L^{-1} Cr, 50.0 µg L^{-1} Ni and 50.0 µg L^{-1} Pb in 0.028 mol L^{-1} HNO_3; *Solution b*. mineral water (1:1 in 0.028 mol L^{-1} HNO_3) spiked with 5.00 µg L^{-1} Cd, 10.0 µg L^{-1} Cr, 50.0 µg L^{-1} Ni and 50.0 µg L^{-1} Pb.

Brazilian mineral water samples were purchased at a local super market. The water samples were used without previous treatment. They were directly transferred from the original bottles to the autosampler cup and the 0.056 mol L^{-1} nitric acid solution was added automatically by the autosampler, thus eliminating the need for manual dilutions. Addition/recovery tests were carried out using water samples (1:1 in 0.028 mol L^{-1} HNO_3) spiked with 3.00 µg L^{-1} Cd, 25.0 µg L^{-1} Cr, 25.0 µg L^{-1} Ni and 25.0 µg L^{-1} Pb.

The SRMs with certified values for Cd, Cr, Ni and Pb were diluted (1:1, v/v) with deionized water before analysis. The SRM 1640 was also diluted (1:5, v/v) for accurate Cd determination. All measurements of integrated absorbance were made with at least three replicates.

Results and Discussion

Graphite furnace AAS is an efficient technique for single-element determination of Cd, Cr, Ni and Pb in natural water with a minimum sample preparation.[26] The recommended single-element THGA conditions for the above elements revealed some differences in the electrothermal behaviors and chemical modifiers,[29] which may appear rather large and preclude successful multielement analyses. Initially, the selection of the atomization temperature at 2300 °C (for Cr and Ni having the highest atomization temperature) appears to indicate the use of non-optimum atomization conditions for the other elements. However, the thermal stability of THGA may minimize those differences.[21]

The electrothermal behavior of Cd, Cr Ni and Pb in diluted nitric acid (0.028 mol L^{-1} HNO_3) and mineral water without and in presence of the mixtures $Pd(NO_3)_2/Mg(NO_3)_2$ or $NH_4H_2PO_4/Mg(NO_3)_2$ was evaluated. The modifier volume (5 µL $Pd(NO_3)_2$ and 3 µL $Mg(NO_3)_2$ or 50 µL $NH_4H_2PO_4$ and 3 µL $Mg(NO_3)_2$) was added to a 20 µL volume of sample. Pyrolysis and atomization curves were employed to determine the optimal pyrolysis and atomization temperatures with and without modifiers. For this study, 0.028 mol L^{-1} HNO_3 solutions and diluted mineral water were spiked with 5.00 µg L^{-1} Cd, 10.0 µg L^{-1} Cr, 50.0 µg L^{-1} Ni and 50.0 µg L^{-1} Pb. All results were based on peak area measurements.

First experiments were carried out without modifier. The selected pyrolysis temperature was 350 °C because it was limited by cadmium, the most volatile element from the group. The atomization temperature was fixed at 2300 °C. The calculated characteristic mass values (m_0, in pg/0.0044A

s) for Cd, Cr, Ni and Pb (in 0.028 mol L^{-1} HNO_3 or samples) were 2.2 pg, 7.0 pg, 26 pg and 33 pg, respectively. Using the heating program of Table 1 (pyrolysis and atomization temperatures fixed at 350°C and 2300 °C) and 20 μL of sample dispensed into the graphite tube in triplicate, calibration curves in the 0.500 – 6.00 μg L^{-1} Cd, 5.00 – 50.0 μg L^{-1} Cr, Ni and Pb ranges were established with good linearity (R^2= 0.98948, 0.99927, 0.99918, and 0.99966 for Cd, Cr, Ni and Pb, respectively). Typical r.s.d. values (n = 12) were < 25.3% for Cd, < 4.4% for Cr, < 12.5% for Ni and < 2.4% for Pb. Accuracy was checked analyzing two SRMs from NIST (1640 - Trace Elements in Natural Water; 1643d - Trace Elements in Water). Without modifier, results for Cd and Pb were not acceptable. The determination of the analytes were carried out with mineral water samples spiked with 3.00 μg L^{-1} Cd and 25.0 μg L^{-1} Cr, Ni and Pb containing 0.028 mol L^{-1} HNO_3. The results from analyte addition tests revealed that recoveries for Cd and Pb were not acceptable.

Regarding studies involving the mixture phosphate/magnesium as modifier, the common pyrolysis temperature was 1100 °C (limited by Cd). It should be pointed out that absorbance for cadmium abruptically drops for temperatures slight greater than 1200 °C. The selected pyrolysis temperature may be lower than 1200 °C in order to avoid Cd loses when small variations in the pyrolysis temperature occurs. Hence, 1100 °C was the pyrolysis temperature selected for further experiments. Regarding the influence of variation of atomization temperature, similar absorbance signals were obtained for measurements of integrated absorbance from analytical solutions prepared either in 0.028 mol L^{-1} nitric acid or samples. The atomization temperature was fixed at 2400 °C because this temperature promoted better peak profile and repeatability of measurements. With 50 μL PO_4 + 3 μL Mg as modifiers, and 20 μL of sample, analytical curves with good linearity (R^2= 0.99378, 0.99699, 0.99887 and 0.99655 for Cd, Cr, Ni and Pb, respectively) were consistently obtained. Typical r.s.d values (n = 12) were < 7.3% for Cd, < 7.0% for Cr, < 5.4% for Ni and < 11.9% for Pb. The characteristic mass values were 2.5 pg Cd, 12 pg Cr, 31 pg Ni and 38 pg Pb. The determination of the analytes were carried out with mineral water samples spiked with 3.00 μg L^{-1} Cd and 25.0 μg L^{-1} Cr, Ni and Pb containing 0.028 mol L^{-1} HNO_3. Recoveries were within the range: 98-108% (Cd), 85-102% (Cr), 96-109% (Ni) and 63 - 81% (Pb). Results show that recoveries for Pb were not acceptable. On the other hand, the modifier can be applied for accurate simultaneous determination of Cd, Cr and Ni in mineral water. Accuracy was also checked analyzing two SRMs from NIST. A paired *t-test* showed that results for Cd, Cr and Ni were in agreement at 95% confidence level with certified values of SRMs.

With regards to studies involving the use of palladium/magnesium as modifier, the common pyrolysis temperature was 1000 °C (also limited by Cd). The atomization temperature was selected as 2300 °C because this temperature promoted better peak profile and repeatability of measurements. Using this pair of temperatures, the calculated characteristic mass values for Cd, Cr, Ni and Pb were 2.2 pg, 10 pg, 42 pg and 66 pg, respectively. It is interesting to point out that different characteristic mass values (1.5 pg Cd, 4.1 pg Cr, 14.7 pg Cu, 16.6 pg Ni and 34 pg Pb) were obtained by Feuerstein and Schlemmer.[32] However, these authors used end-cap THGA tubes which usually give better sensitivity.

With 5 μg Pd + 3 μg $Mg(NO_3)_2$ as the modifiers, pyrolysis temperature at 1000 °C and atomization temperature at 2300 °C, a volume of 20 μL of analytical solution or sample were dispensed into the graphite tube in triplicate, analytical curves in the 0.500 – 6.00 μg L^{-1} Cd, 5.00 – 50.0 μg L^{-1} Cr, Ni and Pb ranges with good linearity (R^2= 0.99706, 0.99943, 0.99967 and 0.99815 for Cd, Cr, Ni and Pb, respectively) were consistently obtained. Shown in Figure 1 are typical absorbance and background signals for Cd, Cr, Ni and Pb in water samples. The r.s.d. values (n = 12) were typically < 0.1% for Cd, < 5.0% for Cr, < 2.0% for Ni and < 6.7% for Pb. The determination of the analytes in spiked mineral water samples resulted in acceptable recoveries for all analytes: 93-108% (Cd), 96-104% (Cr), 87-101% (Ni) and 98-108% (Pb). Accuracy was also checked for cadmium, cromium, nickel and lead determination in two water SRMs and 10 mineral water samples. A paired *t-test* showed that results were in agreement at 95% confidence level with certified values

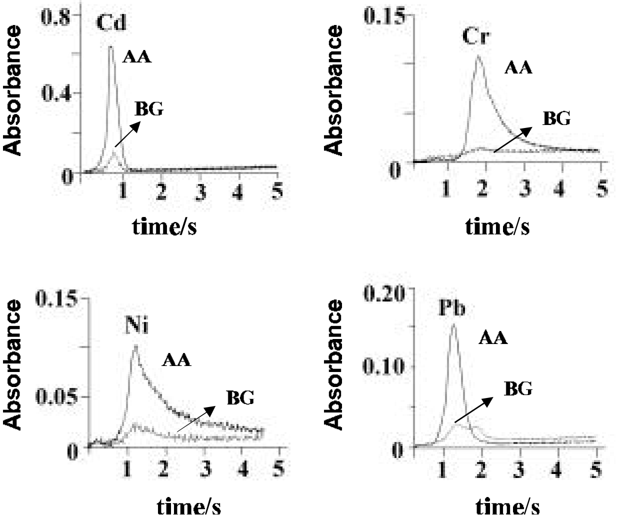

Figure 1. Atomic absorption profiles for 0.1 ng Cd, 0.2 ng Cr, 1 ng Ni and 1 ng Pb (AA) and background (BG) in mineral water sample containing 0.028 mol L^{-1} HNO_3 and using 5 mg Pd + 3 mg $Mg(NO_3)_2$ as chemical modifiers.

Table 2. Results in µg L^{-1} for Cd, Cr, Ni and Pb (n=3) in mineral water samples and standard reference materials (SRM1: 1640 - Trace Elements in Natural Water; SRM2: 1643d - Trace Elements in Water) using the proposed method and Pd/Mg$(NO_3)_2$ as modifier

Sample number	Cd	Cr	Ni	Pb
1	< 0.02	< 0.94	< 0.45	< 0.75
2	< 0.02	< 0.94	0.6 ± 0.1	< 0.75
3	< 0.02	< 0.94	< 0.45	< 0.75
4	< 0.02	3.0 ± 0.1	1.4 ± 0.1	< 0.75
5	< 0.02	< 0.94	< 0.45	< 0.75
6	< 0.02	< 0.94	< 0.45	< 0.75
7	< 0.02	8.4 ± 0.2	< 0.45	< 0.75
8	< 0.02	< 0.94	< 0.45	< 0.75
9	< 0.02	< 0.94	< 0.45	< 0.75
10	< 0.02	< 0.94	< 0.45	< 0.75
SRM1[a]	21.30±0.11	35.2 ± 0.3	27.9 ± 1.6	28.89 ± 0.29
SRM2 [b]	7.42 ± 0.06	16.40±0.22	55.6 ± 0.8	18.23 ± 1.10

[a] Certified values: 22.79 ± 0.96 (Cd); 38.6 ± 1.6 (Cr); 27.4 ± 0.8 (Ni); 27.89 ± 0.14 (Pb); [b] Certified values: 6.47 ± 0.30 (Cd); 18.53 ± 0.20 (Cr); 58.1 ± 2.7 (Ni); 18.53 ± 0.20 (Pb).

of standard reference materials (Table 2). The limits of detection (LOD) based on integrated absorbance (0.02 µg L^{-1} Cd, 0.94 µg L^{-1} Cr, 0.45 µg L^{-1} Ni and 0.75 µg L^{-1} Pb) exceeded the requirements of Brazilian Food Regulations (decree # 310-ANVS from Health Department).[40] The lifetime of the graphite tube using the mixture Pd/Mg$(NO_3)_2$ as modifier was around 600 firings.

Conclusions

This work presents a simple, fast and accurate method for multielement determination of Cd, Cr, Ni and Pb in drinking water samples by graphite furnace atomic absorption spectrometry. The results from spiked water samples and standard reference materials indicated that direct determination of selected analytes without sample preparation is possible by means of automatically addition of nitric acid by the autosampler thus eliminating the need for manual dilutions. The limits of quantification obtained (0.1 µg L^{-1} Cd, 4.7 µg L^{-1} Cr, 2.3 µg L^{-1} Ni and 3.8 µg L^{-1} Pb) exceeded the requirements of Brazilian Food Regulations (decree # 310-ANVS from Health Department), which establish the maximum permissible level for Cd, Cr, Ni and Pb at 3 µg L^{-1}, 50 µg L^{-1}, 20 µg L^{-1} and 10 µg L^{-1}, respectively.

It was possible to find compromise THGA conditions for elements with significative differences in thermal properties in order to produce reliable analytical data.

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