Determination of heavy metals in soil by inductively coupled plasma mass spectrometry (ICP-MS) with internal standard method

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Abstract: Soil, the carrier of agricultural production and an important part of the ecological environment, is heavily contaminated with hazards heavy metals. Therefore, it is a genuine obligation to research analytical techniques that can efficiently determine the total content of heavy metals in soil. The determination of heavy metals in soil was disturbed by matrix elements or spectral interferences. In this study, this problem was solved by the internal standard method. GBW07402, GBW07448, GBW07423, GBW07428, GBW074079 soil samples were chosen to be the Certified Reference Materials, soils were prepared by microwave digestion with mixed acid following analyzed for determination of the content (Cr, Cu, Pb, Ba, Ni, Mn) by Inductively coupled plasma mass spectrometric in 50ug/L internal standard concentration, the method was validated by compared with certified values, method contrast (standard addition method versus internal standard method) and recovery check. The results of internal standard method are in excellent agreement with the indicative values and the date obtained from standard addition method, respectively. Recoveries were adequate being in the acceptable range of 90-99% and RSD of <6.7 % for all the elements at three level of 5, 20 and 50mg/kg with quantified by standard addition method and internal standard method. Finally, The graph of quality control (n=100) were obtained to guide internal quality control in laboratory.

Key words: Soil; Heavy metal; Inductively coupled plasma mass spectrometry; Internal standard method

Introduction

With the rapid development of the global economy, the heavy metal pollution in soil is becoming a crucial environmental problem. Industrial, traffic and municipal wastes were the primary source of heavy metal for soil. These heavy metals were accumulated in waters and plant tissues, which will migrate into food chain finally. Studies have showed that heavy metals are pose hazardous risk to the health of humans when excess certain...
amount. Therefore, the emphasis has been given by many researchers to explore various techniques for analysis of heavy metals.

Up to present, different Analytical techniques for estimation of heavy metals in soil including atomic spectroscopy analysis and chemical method of analysis have been widely researched. Chemical method of analysis, based on the substance chemical reaction and characterized of high accuracy, applied to the samples which relative content more than 1%. For the trace component, the analytical techniques has great advantage, such as Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), Inductively Coupled Atomic emission Spectroscopy (ICP-AES), Inductively Coupled Mass Spectroscopy (ICP-MS), Atomic fluorescence spectrometry (AFS), Absorption Spectrometry (AAS)\textsuperscript{11-15}. All of the quantification techniques were have proved to be efficient with good detection limits. Despite the inductively coupled plasma mass spectrometry has been successfully applied to complicated matrices soil sample. The accuracy of the analysis results were inevitable disturbed by the spectral interference and non-spectral interference. Internal standardization as a correction for matrix effects and multiplicative effects in general is becoming the first choice in ICP-MS. Several workers has proved that internal standard undergo an equal relative matrix-induced signal intensity shift and achieve accuracy of the results\textsuperscript{16-17}.

This paper concentrate on developing a internal standard method for detecting the total amount of Mn, Cr, Pb, Cu, Ni, Ba in soil simultaneously by the means of ICP-MS. The method was validated according to the Certified Reference Materials, different method (internal standard method and standard addition method) and the percentage of recovery at three different spike levels.

1. Materials and methods

1.1 Reagents and materials

Standard stock solutions of Ni, Mn, Cr, Cu, Pb, Ge, In, Rh, Bi at the 1000ug/mL concentration were obtained from Guo biao (Beijing) Testing & Certification Co, Ltd. (GBTC, China). The commercially available nitric acid, hydrochloric acid, hydrofluoric acid and hydrogen peroxide were purchased from Baker-Instra analyzed (USA). Ultrapure water was prepared by a Milli-Q system from Millipore (USA). The Performance Solutions Kit were from Perkin Elmer (USA).

Mixed working solution (containing Ni, Mn, Cr, Cu, Pb, Ba) and internal standard solution (including Ge, In, Rh, Bi) in 2% nitric acid aqueous solution were prepared. Calibration standards were prepared by diluting mixed standard solution to reach the quantitative concentrations, which added internal standard solution to the concentration level of 50 ug/L.

2.2 Samples

Five candidate reference soil samples were acquired from Geophysics Prospecting Institute of Academy of Geological Science of China which containing GBW07402 (chestnut soil), GBW074079 (laterite soil), GBW07423 (lake sediment), GBW07428 (basin soil), GBW07448 (brown desert soil). Soil samples were collected from the main representative soil zones and different geological backgrounds or mineralized areas in China. The certified values for every heavy metal in each soil were analyzed and the expire time is 2020.

2.3 Sample preparation

Approximately 0.2g Soil samples (or spiked soil) were weighed into a PTFE beaker. 6 ml of nitric acid, 2 ml of hydrochloric acid and 2 ml of hydrofluoric in a combination have been used for the simultaneous extraction of a large
number of metals in soils. The solution was digested by the Microwave digestion instrument (CEM, MARS 6, USA) in the following procedure: heated to 120°C in 8 minutes and holding 3 min; raising the temperature to 150°C maintaining 5 min; increase the temperature to 190 °C keeping 35 min. After cooling, 2 ml of H₂O₂ was added to the digested mixture then taken to heating block in 140°C until the residue solution left about 1 mL. Finally, the solution was transported into 50 mL volumetric flasks, brought to volume with water and mixed fully. The determination of metals was performed by ICP-MS with internal standard method and standard addition method.

2.4 Instrumentation

The Inductively coupled plasma mass spectrometric (Perkin Elmer, NexION 300, American) was carried out to analyzed the contents of target elements in the standard mode. Operating conditions (parameters) are summarized in Table 1.

| operating conditions | Pb,Bi a | Cu,Ge a | Cr,Ge a | Mn,Ge a | Ba,In a | Ni,Ge a |
|----------------------|---------|---------|---------|---------|---------|---------|
| Nubulizer Gas Flow   | 0.88ml/min |         |         |         |         |         |
| Auxiliary Gas Flow   | 1.20ml/min |         |         |         |         |         |
| Plasma Gas Flow      | 18.00   |         |         |         |         |         |
| Deflector Voltage    | -11.00v |         |         |         |         |         |
| ICP RF Power         | 1250w   |         |         |         |         |         |
| Analyzer Vacuum      | 5.0×10⁻⁷|         |         |         |         |         |
| measured m/z         | 206,208 | 63,65   | 53      | 55      | 137,138 | 60      |
| calibration range    | 5-50    | 5-50    | 20-200  | 100-1000| 5-500   | 10-100  |
| internal concentration| std 50 | 50      | 50      | 50      | 50      | 50      |

Table 1 ICP-MS operating conditions and acquisition parameters

a used as an internal standard element

2.5. Measurement procedures

For the measurements of the elements, the digested solution were diluted to 1/10 with 2% nitric acid aqueous. Internal standard method: The sample were analyzed after adding 50ug/L mixed internal standard. Standard addition method: adding a serials of standard solution (the final solution is equal to the internal standard method calibration range for each element) into the same sample, then scan the standard solution. Draw standard curve which not pass zero point, from the calibration equation we can calculate the each heavy metal level 18-19. Sample and blank were analyzed in triplicate.

3. Results and Discussion

3.1 Evaluation of the method by Certified value and standard addition method

To verify the efficiency of the method, five quality control soil samples were digested and quantified by internal standard method and standard addition method. The results were tabulated in the table 2.

Table 2 Results for the total content analysis of 5 candidates reference materials compared to certified concentrations

| Element | Sample | The level of heavy metal (mg/kg) | certified value |
|---------|--------|----------------------------------|-----------------|
| 137Ba   | GBW07402| 924±37                           | 930±50          |

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| Isotope | Sample | $^{138}$Ba | $^{53}$Cr | $^{63}$Cu | $^{65}$Cu | $^{206}$Pb | $^{208}$Pb | $^{55}$Mn | $^{60}$Ni |
|---------|--------|------------|----------|---------|---------|---------|---------|---------|---------|
| GBW07407 | 178±9 | 175±6 | 180±27 |
| GBW07423 | 514±19 | 518±13 | 520±43 |
| GBW07428 | 603±9 | 611±7 | 608±13 |
| GBW07448 | 33.2±6.8 | 32.7±5.3 | 34±14 |
| GBW07402 | 928±31 | 932±24 | 930±50 |
| GBW07407 | 179±14 | 175±6 | 180±27 |
| GBW07423 | 531±26 | 518±13 | 520±43 |
| GBW07428 | 607±8 | 611±7 | 608±13 |
| GBW07448 | 33.2±4.9 | 32.7±5.3 | 34±14 |
| GBW07402 | 44.6±3.2 | 45.8±2.7 | 47±4 |
| GBW07407 | 403±14 | 409±8 | 410±23 |
| GBW07423 | 72.8±4.3 | 74.2±2.9 | 75±5 |
| GBW07428 | 68.5±2.6 | 69.0±1.8 | 70±3 |
| GBW07448 | 47.1±1.6 | 49.3±1.3 | 49±2 |
| GBW07402 | 15.6±0.68 | 16.2±0.57 | 16.3±0.9 |
| GBW07407 | 93.9±4.5 | 95.9±3.1 | 97±6 |
| GBW07423 | 23.7±1.1 | 24.7±1.6 | 25±3 |
| GBW07428 | 26.4±0.67 | 26.5±0.9 | 27.4±1.1 |
| GBW07448 | 16.2±0.29 | 16.0±0.48 | 16.0±0.5 |
| GBW07402 | 16.0±0.78 | 16.2±0.57 | 16.3±0.9 |
| GBW07407 | 94.7±4.2 | 95.9±3.1 | 97±6 |
| GBW07423 | 24.0±2.1 | 24.7±1.6 | 25±3 |
| GBW07428 | 28.3±0.89 | 26.5±0.9 | 27.4±1.1 |
| GBW07448 | 15.7±0.31 | 16.0±0.48 | 16.0±0.5 |
| GBW07402 | 18.9±2.4 | 21.4±2.7 | 20±3 |
| GBW07407 | 14.5±1.9 | 13.8±1.5 | 14±3 |
| GBW07423 | 24.0±1.6 | 23.8±2.0 | 25±3 |
| GBW07428 | 30.5±0.56 | 31.0±0.90 | 31±1 |
| GBW07448 | 18.0±0.78 | 19.1±0.51 | 18.7±0.9 |
| GBW07402 | 20.7±1.9 | 21.4±2.7 | 20±3 |
| GBW07407 | 15.0±1.4 | 13.8±1.5 | 14±3 |
| GBW07423 | 24.7±2.0 | 23.8±2.0 | 25±3 |
| GBW07428 | 30.4±0.68 | 31.0±0.90 | 31±1 |
| GBW07448 | 18.2±0.57 | 19.1±0.51 | 18.7±0.9 |
| GBW07402 | 500±13 | 507±10 | 510±16 |
| GBW07407 | 1729±90 | 1745±76 | 1780±113 |
| GBW07423 | 514±12 | 517±16 | 520±24 |
| GBW07428 | 679±14 | 690±12 | 688±15 |
| GBW07448 | 520±7 | 510±9 | 518±13 |
| GBW07402 | 19.0±0.79 | 18.9±1.1 | 19.4±1.3 |
| GBW07407 | 271±9 | 269±8 | 276±15 |
Asd stand for the date of standard addition method
Isd stand for the date of internal standard method
Certified value are taken from refs\textsuperscript{20}
Uncertainties are expressed as standard deviation (n=6)

As can be seen, determinations were carried out using the isotopes of $^{137}$Ba, $^{138}$Ba, $^{63}$Cu, $^{65}$Cu, $^{53}$Cr, $^{206}$Pb, $^{208}$Pb, $^{55}$Mn, $^{60}$Ni and the square of correlation coefficient $R^2$ was more than >0.9995. The internal standard method results are in the range of the certified values and excellent agreement with the standard addition method date.

### 3.1 Recovery Checks

To determine the accuracy of the methods used in the determination of the metals in the soil extracts, known-amounts of the elements studied were added to the soil. Recovery test was done at fortification levels of 5, 20, and 50 mg/kg with three replicates. The Mean recovery rate and RSD were listed in the table 3.

| Element | Sample | 5mg/kg | 20mg/kg | 50mg/kg |
|---------|--------|--------|---------|---------|
|         | Asd Mean(%) | Isd Mean(%) | Asd Mean(%) | Isd Mean(%) | Asd Mean(%) | Isd Mean(%) |
| $^{137}$Ba | GBW07402 91(3.7) | 92(4.2) | 97(1.0) | 96(0.9) | 94(1.0) | 95(1.3) |
|          | GBW07407 94(2.5) | 97(1.5) | 103(5) | 91(2.1) | 99(2.4) | 99(2.7) |
|          | GBW07423 90(1.0) | 90(3.0) | 97(4.6) | 92(5.7) | 98(3.1) | 97(1.5) |
|          | GBW07428 96(4.3) | 99(5.5) | 91(2.7) | 93(1.5) | 99(2.6) | 98(2.4) |
|          | GBW07448 95(2.8) | 98(0.9) | 94(5.4) | 99(3.2) | 93(0.9) | 94(3.8) |
| $^{138}$Ba | GBW07402 97(1.9) | 99(1.2) | 92(6.7) | 98(1.7) | 97(1.1) | 91(2.6) |
|          | GBW07407 93(1.4) | 94(1.8) | 98(1.7) | 99(4.2) | 95(1.4) | 97(1.1) |
|          | GBW07423 97(2.6) | 96(3.6) | 96(4.3) | 98(4.8) | 90(1.9) | 94(1.9) |
|          | GBW07428 99(1.5) | 95(1.4) | 97(1.2) | 98(3.4) | 99(2.7) | 92(3.7) |
|          | GBW07448 94(0.6) | 96(1.8) | 96(3.5) | 91(4.1) | 91(1.5) | 95(1.5) |
| $^{53}$Cr | GBW07402 98(4.8) | 98(2.6) | 97(2.3) | 94(0.9) | 98(3.8) | 93(1.7) |
|          | GBW07407 92(2.7) | 97(1.7) | 90(1.1) | 94(2.6) | 94(1.1) | 92(3.6) |
|          | GBW07423 97(5.8) | 98(2.4) | 92(2.4) | 94(3.8) | 95(2.4) | 94(2.4) |
|          | GBW07428 93(4.2) | 98(1.3) | 96(4.6) | 93(1.1) | 98(1.3) | 96(0.9) |
|          | GBW07448 97(3.1) | 99(3.2) | 93(1.3) | 97(2.2) | 91(2.8) | 91(3.0) |
| $^{63}$Cu | GBW07402 96(1.6) | 97(3.6) | 99(3.2) | 98(1.0) | 98(3.6) | 92(1.7) |
|          | GBW07407 90(5.3) | 98(1.7) | 91(4.6) | 96(0.9) | 94(1.9) | 96(2.8) |
|          | GBW07423 94(1.5) | 95(1.1) | 91(0.9) | 96(1.7) | 97(1.4) | 99(1.3) |
|          | GBW07428 93(3.6) | 96(3.5) | 97(1.7) | 98(4.4) | 94(3.6) | 92(1.7) |
|          | GBW07448 93(4.2) | 97(1.2) | 95(2.4) | 95(1.5) | 97(2.7) | 94(2.4) |
| $^{65}$Cu | GBW07402 96(5.3) | 95(0.8) | 90(4.2) | 96(3.8) | 98(1.9) | 94(3.1) |
A satisfied results were found for all the elements. The recovery percentage were more than 90% for each elements in fortification levels of 5, 20 and 50 mg/kg. The date of RSD ≤6.7% for all the chemicals.

3.3 The date of quality control graphy

Graphy of quality control based on the fact that the experimental data distribution is close to Gaussian distribution is one of effective measures to guarantee the analytical quality\(^{21-22}\). The chart is completed by horizontal lines derived from the normal distribution \(N(\mu, \sigma^2)\) that is taken to describe the random variations in the plotted values. \(\mu\), \(\mu \pm \sigma\), \(\mu \pm 2\sigma\), \(\mu \pm 3\sigma\) were selected to construct the chart, which were called centre line (CL), assistant line (AL), warning limit (WL) and control limit (CL). The chart is obtained values of concentration measured are plotted on a vertical axis against the run number on the horizontal axis. The results in the range of \(\mu \pm 2\sigma\) is satisfied; Attention should be paid if the measure values were located in the region from \(\mu \pm 2\sigma\) to \(\mu \pm 3\sigma\), however the values are acceptable; the experimental date were unbelievable if the date exceed the section of \(\mu \pm 3\sigma\), it regard as “out of control”. To Certified Reference soil from a system in statistical control over 100 runs for internal quality control in lab is shown in table 4.

| Element | Sample | The date of quality control(mg/kg) |
|---------|--------|----------------------------------|
| **206Pb** | GBW07402 | 99(3.2) 96(0.9) 97(2.7) 94(4.0) 99(0.8) 96(3.6) |
| | GBW07407 | 99(1.9) 99(5.3) 94(4.9) 97(2.5) 99(3.5) 96(2.4) |
| | GBW07423 | 93(4.7) 97(3.4) 98(5.6) 92(3.8) 90(2.9) 99(1.0) |
| | GBW07428 | 93(1.1) 91(2.6) 97(3.8) 97(1.3) 91(1.6) 96(1.3) |
| | GBW07448 | 95(3.5) 92(2.6) 92(4.5) 96(5.3) 95(3.4) 95(0.9) |
| **208Pb** | GBW07402 | 99(1.8) 91(3.7) 97(1.0) 97(0.9) 95(3.1) 90(2.6) |
| | GBW07407 | 94(2.6) 92(4.2) 90(2.7) 92(0.7) 98(1.2) 97(1.3) |
| | GBW07423 | 94(1.9) 91(2.7) 91(3.0) 99(4.5) 93(3.4) 93(2.7) |
| | GBW07428 | 96(0.9) 96(1.6) 98(1.7) 91(1.4) 99(1.1) 90(1.2) |
| | GBW07448 | 95(5.3) 95(1.0) 90(3.9) 99(1.1) 99(2.5) 98(2.6) |
| **55Mn** | GBW07402 | 90(1.2) 92(2.3) 96(2.7) 94(1.9) 91(2.3) 95(1.3) |
| | GBW07407 | 93(1.5) 95(2.7) 95(5.4) 95(4.6) 91(1.5) 96(3.5) |
| | GBW07423 | 91(4.3) 95(3.2) 97(1.3) 95(4.8) 93(3.7) 93(2.9) |
| | GBW07428 | 99(2.9) 99(1.9) 91(2.9) 98(4.7) 90(1.2) 97(1.0) |
| | GBW07448 | 95(3.6) 96(3.4) 99(1.2) 97(2.4) 91(2.5) 93(3.3) |
| **60Ni** | GBW07402 | 91(4.7) 99(3.2) 97(4.4) 92(3.8) 99(0.9) 94(2.8) |
| | GBW07407 | 95(1.6) 96(1.9) 98(5.8) 95(1.0) 97(2.6) 95(1.2) |
| | GBW07423 | 92(2.8) 98(2.5) 95(1.4) 97(1.9) 98(1.9) 92(2.7) |
| | GBW07428 | 90(1.3) 93(4.7) 97(1.6) 99(2.1) 93(3.4) 92(1.5) |
| | GBW07448 | 91(2.1) 91(0.8) 93(2.7) 96(5.3) 97(1.3) 98(2.4) |

Asd stand for the recovery date of standard addition method

Isd stand for the recovery date of internal standard method

Relative Standard deviation (RSD) were tabulated in the brackets

Table 4 The date of quality control(n=100)
|    | GBW07402 | GBW07407 | GBW07423 | GBW07428 | GBW07448 |
|----|----------|----------|----------|----------|----------|
| $^{137}$Ba | $\mu\pm\sigma$ | $\mu\pm2\sigma$ | $\mu\pm3\sigma$ |
| | | 926±34 | 926±64 | 926±102 |
| | | 925±39 | 925±78 | 925±117 |
| | | 925±6 | 925±12 | 925±18 |
| | | 925±10 | 925±20 | 925±30 |
| | | 32.8±5.9 | 32.8±11.8 | 32.8±17.7 |
| $^{138}$Ba | | GBW07407 | 175±6 | 175±12 | 175±18 |
| | | GBW07423 | 513±20 | 513±40 | 513±60 |
| | | GBW07428 | 599±10 | 599±20 | 599±30 |
| | | GBW07448 | 32.8±5.9 | 32.8±11.8 | 32.8±17.7 |
| | | GBW07407 | 175±17 | 175±34 | 175±51 |
| | | GBW07423 | 528±29 | 528±58 | 528±87 |
| | | GBW07428 | 598±11 | 598±22 | 598±33 |
| | | GBW07448 | 33.6±5.1 | 33.6±10.2 | 33.6±15.3 |
| $^{53}$Cr | | GBW07407 | 444±3.7 | 444±7.4 | 444±11.1 |
| | | GBW07423 | 71.8±4.9 | 71.8±9.8 | 71.8±14.7 |
| | | GBW07428 | 67.7±3.1 | 67.7±6.2 | 67.7±9.3 |
| | | GBW07448 | 46.8±2.0 | 46.8±4.0 | 46.8±6.0 |
| $^{63}$Cu | | GBW07407 | 444±3.7 | 444±7.4 | 444±11.1 |
| | | GBW07423 | 71.8±4.9 | 71.8±9.8 | 71.8±14.7 |
| | | GBW07428 | 67.7±3.1 | 67.7±6.2 | 67.7±9.3 |
| | | GBW07448 | 46.8±2.0 | 46.8±4.0 | 46.8±6.0 |
| $^{65}$Cu | | GBW07402 | 15.1±0.81 | 15.1±1.62 | 15.1±2.43 |
| | | GBW07407 | 92.9±4.5 | 92.9±9 | 92.9±13.5 |
| | | GBW07423 | 22.6±1.6 | 22.6±3.2 | 22.6±4.8 |
| | | GBW07428 | 26.0±0.78 | 26.0±1.56 | 26.0±2.34 |
| | | GBW07448 | 15.9±0.32 | 15.9±0.64 | 15.9±0.96 |
| $^{206}$Pb | | GBW07402 | 16.2±0.87 | 16.2±1.74 | 16.2±2.61 |
| | | GBW07407 | 94.1±4.7 | 94.1±9.4 | 94.1±14.1 |
| | | GBW07423 | 23.9±2.7 | 23.9±5.4 | 23.9±8.1 |
| | | GBW07428 | 27.8±0.90 | 27.8±1.8 | 27.8±2.7 |
| | | GBW07448 | 15.9±0.53 | 15.9±1.06 | 15.9±1.59 |
| $^{208}$Pb | | GBW07402 | 18.5±2.3 | 18.5±4.6 | 18.5±6.9 |
| | | GBW07407 | 14.7±2.0 | 14.7±4.0 | 14.7±6.0 |
| | | GBW07423 | 23.7±1.4 | 23.7±2.8 | 23.7±4.2 |
| | | GBW07428 | 31±0.76 | 31±1.52 | 31±2.28 |
| | | GBW07448 | 17.9±0.86 | 17.9±1.72 | 17.9±2.58 |
| $^{55}$Mn | | GBW07402 | 18.5±2.3 | 18.5±4.6 | 18.5±6.9 |
| | | GBW07407 | 14.7±2.0 | 14.7±4.0 | 14.7±6.0 |
| | | GBW07423 | 23.7±1.4 | 23.7±2.8 | 23.7±4.2 |
| | | GBW07428 | 31±0.76 | 31±1.52 | 31±2.28 |
| | | GBW07448 | 17.9±0.86 | 17.9±1.72 | 17.9±2.58 |
Conclusion

The work verify an efficient ICP-MS-based internal standard method to quantify the presence of Cr, Cu, Pb, Ba, Ni, Mn in soils. In this study, Certified Reference analysis, different method contrast and recovery experiment has been carried out. Overall results indicate that the presented method has satisfactory reproducibility, recovery, and accuracy for Cr, Cu, Pb, Ba, Ni, Mn analysis in five categories soils. Thus, the proposed method can be used successfully to monitor above six heavy metal in soil.

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| 60Ni | GBW07402 | 18.7±0.56 | 18.7±1.12 | 18.7±1.68 |
|------|----------|----------|----------|----------|
| GBW07407 | 267±11 | 267±22 | 267±33 |
| GBW07423 | 30.2±2.5 | 30.2±5 | 30.2±7.5 |
| GBW07428 | 31.9±0.86 | 31.9±1.72 | 31.9±2.58 |
| GBW07448 | 18.7±0.98 | 18.7±1.96 | 18.7±2.94 |

μ is population mean
σ is population standard deviation
n is run number
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