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## (54) Isotopic reference material

(57) This application relates to a reference material for the calibration of a mass spectrometer for isotopic analysis, the reference material including

a filament comprising one or more metals (X) selected from W, Re, Rh, Ir, Pd and Pt and alloys thereof having melting points greater than approximately 1800°C and vapour pressures lower than approximately $10^{-6}$ Torr at 2000°C,

the filament having a coating on at least a portion thereof of an intermetallic compound comprising one or more metals (Y) selected from W, Re, Rh, Ir, Pd and Pt and alloys thereof having melting points greater than approximately 1800°C and vapour pressures lower than $10^{-6}$ Torr at approximately 2000°C and one or more metals (Z) selected from the lanthanides and the actinides.

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## Description

**[0001]** The present invention relates to isotopic reference materials and a process for the production thereof. In particular, the present invention relates to isotopic reference materials for use in thermal ionisation mass-spectrometers.

**[0002]** Thermal ionisation mass-spectrometers (TIMS) are widely used for the accurate determination of isotope ratios. The measurements may be used for the tracking of material, known as "fingerprinting"; for determining particular processes which alter isotope abundances, such as nuclear, chemical, and geochemical processes; or for the amount determination of elements by applying a well-characterised isotopic spike material (a spike material is a reference material certified for the amount of a particular isotope). By addition of a known amount of a spike and determining the ratio of the spike isotope to the main isotope of the element to be analysed in the sample, the amount of this element is measured. This process is known as Isotope Dilution Mass-Spectrometry (IDMS). These methods are particularly widespread for the determination of the amounts of nuclear material, for example uranium or plutonium, where the amounts of specific isotopes are often the crucial parameters to be measured.

**[0003]** Extremely high accuracies are required in these measurements, of the order of 0.1% or lower, and at these levels the instrument or measurement bias has to be compensated for. This can only be done by the measurement of Isotopic Reference Materials (IRMs), where the isotope amounts and their uncertainties are certified.

**[0004]** Typically, therefore, a sequence of measurements will be carried out on samples. IRMs are then deposited and prepared on filaments so that the IRM measurements can be used to determine the instrument response. This can then be applied to the sample measurement results to compensate for the instrument or measurement bias.

**[0005]** The filaments consist typically of rhenium ribbons approximately 2 mm to approximately 3 mm wide and up to approximately 2 cm long. Other metals such as platinum or tungsten may be used as the filament under certain circumstances but rhenium is widely used on account of its favourable physical properties such as its high melting point, its very low vapour pressure and its high work function. The sample of IRM may be deposited as a very small spot on the filament by, for example, dropping a drop (approximately 1 $\mu$l) of a solution on the filament. The material to be deposited must be highly pure and is generally in a 1 M nitric acid solution, for example. Alternatively, the sample of IRM may be deposited by electro-deposition, although this requires a specially constructed apparatus.

**[0006]** After deposition and drying in air, the filament subsequently undergoes a baking treatment which yields the material in the required form, usually as an oxide. In the mass-spectrometer, under ultra-vacuum, the atoms of the element being measured are emitted on heating the filament. At this point, small amounts of impurities of other elements or changes in the deposition procedure can effect the production of the atoms and subsequent ionisation for measurement by mass-spectrometry. Slight differences can lead to subtle differences in the measured isotope amount ratios leading to inaccurate results. The filaments produced are prepared and used directly, the success of the filament so prepared is dependent on factors at the time of preparation and the results cannot be guaranteed nor certified.

**[0007]** Presently, IRMs are produced for many elements in solution form ready for deposition on filaments for mass-spectrometry. Some examples of "tailor-made" IRMs are described in a paper presented by the Institute for Reference Materials and Measurements at the *International Atomic Energy Agency Symposium on International Safeguards* (Vienna, Austria, 14-18 March 1994). These are used by customers typically in the same preparation procedure as used for the samples and the results in turn used to characterise the mass-spectrometer measurements of the samples. This method is valid but suffers from the possible effects of the deposition method in the measurement step chain which is carried out by the customer. The possibility of contamination is high and the preparation parameters are difficult to control and reproduce. A major source of error arises when the element exists on the filament in more than one chemical form. The chemical form and interaction with the filament substrate induces isotope fractionation effects on the measurements.

**[0008]** Accordingly, the present invention provides a reference material for the calibration of a mass spectrometer for isotopic analysis, the reference material including a filament comprising one or more metals (X) selected from W, Re, Rh, Ir, Pd, and Pt and alloys thereof having melting points greater than approximately 1800°C and vapour pressures lower than approximately $10^{-6}$ Torr at 2000°C, the filament having a coating on at least a portion thereof of an intermetallic compound comprising one or more metals (Y) selected from W, Re, Rh, Ir, Pd, and Pt and alloys thereof having melting points greater than approximately 1800°C and vapour pressures lower than approximately $10^{-6}$ Torr at 2000°C and one or more metals (Z) selected from the lanthanides and the actinides.

**[0009]** The reference to alloys in the preceding paragraph is intended to include both alloys formed from a combination of one or more of the metals identified above and also alloys formed from a combination of one or more of the metals identified above with one or more other metals.

**[0010]** In many cases the metals X and Y will be the same element, but it will be appreciated that X and Y may be different.

**[0011]** The intermetallic compound will typically

have the general formula $Y_YZ$, wherein y is in the range of from 1 to 5 and need not necessarily be an integer. Preferably, the intermetallic compound has the formula $Y_5Z$.

**[0012]** Preferably, the metals X and Y are selected from Pt, W and Re. More preferably, the metal used for X and/or Y is Re on account of its favourable physical properties.

**[0013]** Preferably, the metal Z is U and/or Pu because of the importance of the measurement of these elements and their isotopic amounts for safeguards and international agreements, and because of the very high demands placed upon the measurements, especially on the accuracies required.

**[0014]** Preferably the reference material comprises a filament of Re coated on at least a portion thereof with an intermetallic compound comprising or consisting essentially of $Re_5U$. It has previously been found that $Re_5U$ is highly stable, resistant to oxygen and moisture and, furthermore, remains so quasi-permanently.

**[0015]** Preferably the reference material described above may comprise a further coating on at least a portion thereof of a metal selected from W, Re, Rh, Ir, Pd and Pt. Preferably the metal used is Pt. Preferably said coating is of a thickness of not more than approximately 1000 nm and, more preferably, not more than approximately 5 nm.

**[0016]** Coatings of this sort interact with the intermetallic compound on the filament and potentially can improve the yield of atoms from the surface as well as ensure pure atomic emission by breaking up possible molecular clusters.

**[0017]** The metal filaments formed for different mass spectrometers will typically have different sizes and construction. Preferably, the filament is formed from a sample of a metal which is in the form of a ribbon from approximately 2 mm to approximately 5 mm wide and up to approximately 3 cm long. More preferably, the filament is formed from a sample of metal which is in the form of a ribbon from approximately 2 mm to approximately 3 mm wide and up to approximately 2 cm long.

**[0018]** A second aspect of the present invention pertains to the use of a reference material as herein described as an isotopic reference material (IRM). In particular to the use of such a reference material as an isotopic reference material in a thermal ionisation mass spectrometer.

**[0019]** The use of such a reference material is advantageous because it is homogeneous and highly stable, being resistant to attack from the air, especially by oxygen and moisture, and should remain so quasi-permanently. If properly stored such reference materials exhibit permanent stability. These characteristics make the IRM easy to handle and transport.

**[0020]** A further advantage of this aspect of the present invention is the removal of the deposition step which is necessary when providing IRMs in the form of certified solutions of the reference materials which are subsequently handled, and possibly contaminated, by customers.

**[0021]** A third aspect of the present invention pertains to a process for forming a reference material as herein described wherein X and Y are one and the same element, the process comprising the steps of:

(i) providing a filament comprising one or more metals (X) selected from W, Re, Rh, Ir, Pd, and Pt and alloys thereof having melting points greater than approximately 1800°C and vapour pressures lower than approximately $10^{-6}$ Torr at 2000°C;

(ii) contacting at least a portion of a surface of the filament from step (i) with a solution comprising a compound of one or more metals (Z) selected from the lanthanides and the actinides;

(iii) heating the filament from step (ii) under conditions suitable for forming an oxide of the metal (Z); and

(iv) exposing the filament from step (iii) to a reducing atmosphere under conditions suitable for forming an intermetallic compound comprising X and Z on at least a portion of the surface of the metal filament.

**[0022]** Preferably, the filament comprising one or more metals (X), which is used in step (i), is in the form of a ribbon from approximately 2 mm to 5 mm wide and up to approximately 3 cm long, more preferably from approximately 2 mm to 3 mm wide and up to approximately 2 cm long.

**[0023]** Preferably, step (ii) comprises depositing a droplet of said solution on the filament.

**[0024]** Preferably, step (iii) comprises heating the filament at approximately 70°C to evaporate substantially all of the solvent from said solution, then progressively heating in air to a temperature of approximately 1000°C. Typically, the progressive heating occurs over a period of approximately 30 minutes.

**[0025]** Step (iii) results in decomposition of the metal (Z) compound into a metal (Z) oxide.

**[0026]** The compound of metal (Z) in solution may be, for example, a metal nitrate, such as uranyl nitrate. A preferred solution consists of a quantity of uranyl nitrate sufficient to provide approximately 1 mg of uranium ions in 1 ml of a 5 M $HNO_3$ solution. This is then diluted with distilled high purity water (Milli-Q) to provide a solution with a uranium concentration of approximately 1 $\mu gl^{-1}$. It will be appreciated by a person skilled in the art that the concentration of the metal (Z) in solution and the concentration of the nitric acid may vary.

**[0027]** Preferably the reducing atmosphere in step (iv) is provided by hydrogen gas optionally mixed with a group VIII noble gas. Most preferably the hydrogen gas used for reducing atmosphere is pre-purified by reaction

with liquid sodium. When hydrogen gas is used, the chemical changes occurring in step (iv) may be represented by the equation below:

$$Z_zO_y(s) + yH_2(g) + xX(s) \rightarrow Z_zX_x(s) + yH_2O(g)$$

**[0028]** Typically, conditions suitable for forming an intermetallic compound in step (iv) comprise heating at a temperature up to approximately 1000°C.

**[0029]** A fourth aspect of the present invention pertains to an alternative process for forming a reference material as herein described wherein X and Y may be the same or different, the process comprising the steps of:

(i) providing a filament comprising one or more metals (X) selected from W, Re, Rh, Ir, Pd, and Pt and alloys thereof having melting points greater than approximately 1800°C and vapour pressures lower than approximately $10^{-6}$ Torr at 2000°C;

(ii) providing a sample of an intermetallic compound comprising one or more metals (Y) selected from W, Re, Rh, Ir, Pd, and Pt and alloys thereof having melting points greater than approximately 1800°C and vapour pressures lower than approximately $10^{-6}$ Torr at 2000°C and one or more metals (Z) selected from the lanthanides and the actinides; and

(iii) contacting the intermetallic compound with the filament and effecting a join therebetween by a heat treatment to result in an intermetallic compound comprising Y and Z on at least a portion of a surface of the metal filament.

**[0030]** Preferably, the heat treatment of step (iii) comprises heating the intermetallic compound up to its melting point so that it melts onto the filament.

**[0031]** Preferably the processes described above in the third and fourth aspects may comprise a further step wherein the reference material is coated on at least a portion thereof with a metal selected from W, Re, Rh, Ir, Pd and Pt. Said coating may be deposited by evaporation from a heated filament of said metal so that a thin layer of said metal, preferably of a thickness of not more than approximately 1000 nm and more preferably not more than approximately 5 nm, is deposited on the reference material. Alternatively said coating may be deposited by sputtering from a target of said metal using an ionised atomic beam so that a thin layer of said metal, preferably of a thickness of not more than approximately 5 nm, is deposited on the reference material. Preferably the metal selected is Pt.

**[0032]** Apparatus for performing the process described in the third aspect above suitably comprises a vacuum chamber connected to a pumping system for controlling the gas pressure, a rare gas inlet, a hydrogen gas inlet, means for mounting the filament and means for varying the temperature. Preferably the apparatus has a pumping system which is adapted to provide a vacuum of approximately $10^{-7}$ Torr or lower.

**[0033]** The present invention aims to address the problems associated with the prior art by the provision of IRMs which are certified for isotope amount ratios and which are substantially stable over an unlimited time period if properly stored. This would be a fundamental difference from certifying materials in solution form which are then handled, and possibly contaminated, by the customer before measurement.

## Claims

1. A reference material for the calibration of a mass spectrometer for isotopic analysis, the reference material including

   a filament comprising one or more metals (X) selected from W, Re, Rh, Ir, Pd and Pt and alloys thereof having melting points greater than approximately 1800°C and vapour pressures lower than approximately $10^{-6}$ Torr at 2000°C,

   the filament having a coating on at least a portion thereof of an intermetallic compound comprising one or more metals (Y) selected from W, Re, Rh, Ir, Pd and Pt and alloys thereof having melting points greater than approximately 1800°C and vapour pressures lower than approximately $10^{-6}$ Torr at 2000°C and one or more metals (Z) selected from the lanthanides and the actinides.

2. A reference material as claimed in claim 1, wherein the intermetallic compound has the general formula $Y_yZ$, wherein y is in the range of from 1 to 5.

3. A reference material as claimed in claim 1 or claim 2, wherein the metals (X) and (Y) are both Re.

4. A reference material as claimed in any one of the preceding claims, wherein the metal (Z) is U and/or Pu.

5. A reference material as claimed in any one of the preceding claims, wherein the intermetallic compound comprises or consists of $Re_5U$.

6. A reference material as claimed in any one of the preceding claims, wherein the filament of the one or more metals (X) is in the form of a ribbon from 2 mm to 5 mm wide and up to 3 cm long, preferably from 2 mm to 3 mm wide and up to 2 cm long.

7. A reference material as claimed in any one of the

preceding claims, comprising a further coating on at least a portion thereof of one or more metals selected from W, Re, Rh, Ir, Pd and Pt.

**8.** A reference material as claimed in claim 7, wherein said coating is not more than approximately 1000 nm thick.

**9.** Use of a reference material in accordance with any one of claims 1 to 8 as an isotopic reference material, preferably as an isotopic reference material in a thermal ionisation mass spectrometer.

**10.** A process for forming a reference material in accordance with any one of claims 1 to 8, the process comprising the steps of:

(i) providing a filament comprising one or more metals (X) selected from W, Re, Rh, Ir, Pd and Pt and alloys thereof having melting points greater than approximately 1800°C and vapour pressures lower than approximately $10^{-6}$ Torr at 2000°C;

(ii) contacting at least a portion of a surface of the filament from step (i) with a solution comprising a compound of one or more metals (Z) selected from the lanthanides and the actinides;

(iii) heating the filament from step (ii) under conditions suitable for forming an oxide of the metal (Z); and

(iv) exposing the filament from step (iii) to a reducing atmosphere under conditions suitable for forming an intermetallic compound comprising X and Z on at least a portion of the surface of the metal filament.

**11.** A process as claimed in claim 10, wherein the filament provided in step (i) is in the form of a ribbon from 2 mm to 5 mm wide and up to 3 cm long.

**12.** A process as claimed in claims 10 or 11, wherein step (iii) comprises heating the filament at a temperature of up to approximately 70°C to evaporate substantially all of the solvent of said solution, then progressively heating in air over a period of up to approximately 30 minutes to a temperature of up to approximately 1000°C.

**13.** A process as claimed in any one of claims 10 to 12, wherein the reducing atmosphere of step (iv) is provided by hydrogen gas optionally mixed with a Group VIII noble gas, and wherein the hydrogen gas is preferably pre-purified by reaction with liquid sodium.

**14.** A process as claimed in claim 13, wherein the conditions suitable for forming an intermetallic compound in step (iv) comprise heating at a temperature up to approximately 1000°C.

**15.** A process for forming a reference material as defined in any one of claims 1 to 8, the process comprising the steps of:

(i) providing a filament comprising one or more metals (X) selected from W, Re, Rh, Ir, Pd and Pt and alloys thereof having melting points greater than approximately 1800°C and vapour pressures lower than approximately $10^{-6}$ Torr at 2000°C;

(ii) providing a sample of an intermetallic compound comprising one or more metals (Y) selected from W, Re, Rh, Ir, Pd and Pt and alloys thereof having melting points greater than approximately 1800°C and vapour pressures lower than approximately $10^{-6}$ Torr at 2000°C and one or more metals (Z) selected from the lanthanides and the actinides; and

(iii) contacting the intermetallic compound with the filament and effecting a join therebetween by a heat treatment to result in an intermetallic compound comprising Y and Z on at least a portion of the surface of the metal filament.

**16.** A process as claimed in any one of claims 10 to 15, which comprises the further step of coating said reference material on at least a portion thereof with one or more metals selected from W, Re, Rh, Ir, Pd and Pt.

**17.** A process as claimed in claim 16, wherein the coating is deposited by either:

evaporation from a heated filament of said metal so that a layer of said metal is deposited on the reference material, or

sputtering from a target of said metal using an ionised atomic beam so that a layer of said metal is deposited on the reference material.

**18.** A process as claimed in claim 16 or claim 17, wherein said coating is of a thickness of not more than approximately 1000 nm.

**19.** A mass spectrometer, particularly a thermal ionisation mass-spectrometer, containing a reference material in accordance with any one of claims 1 to 8.