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(54) **X-RAY FLUORESCENCE ANALYSIS METHOD, X-RAY FLUORESCENCE ANALYSIS PROGRAM, AND X-RAY FLUORESCENCE SPECTROMETER**

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(57) **ABSTRACT**

An X-ray fluorescence analysis method according to an FP method uses a predefined theoretical intensity formula in a standard sample theoretical intensity calculation step for obtaining a sensitivity constant and in an unknown sample theoretical intensity calculation step during iterative calculation. In the formula, only in an absorption term relating to absorption of X-rays, a mass fraction of each component is normalized so that a sum of the mass fractions of all components becomes 1.

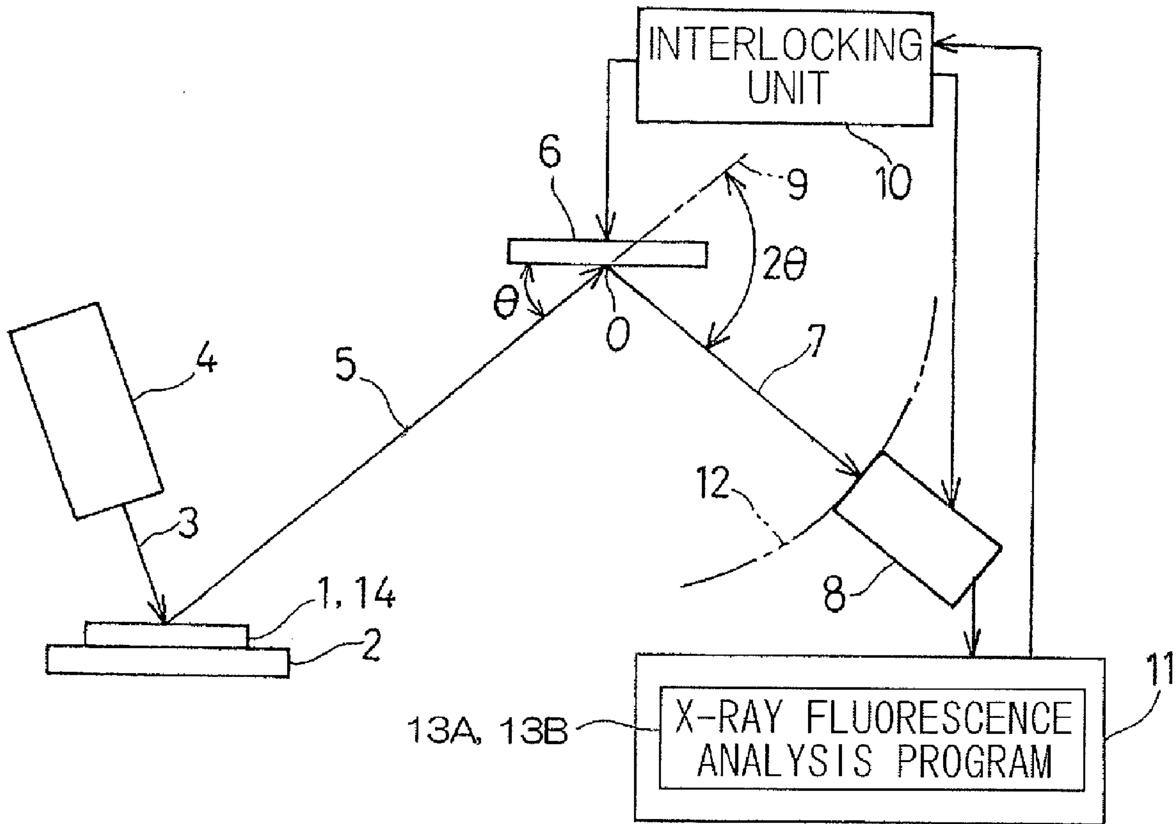


Fig. 1

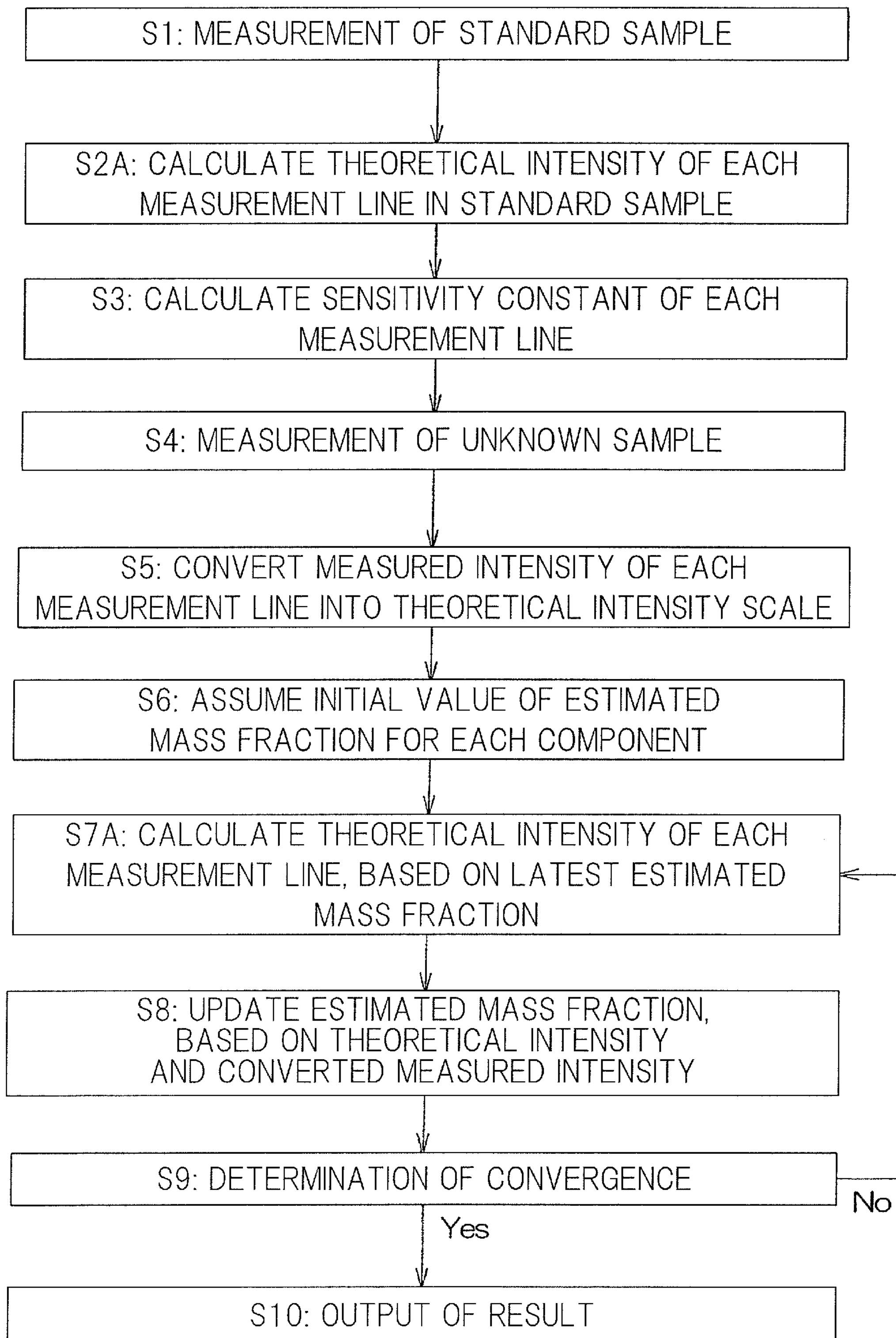


Fig. 2

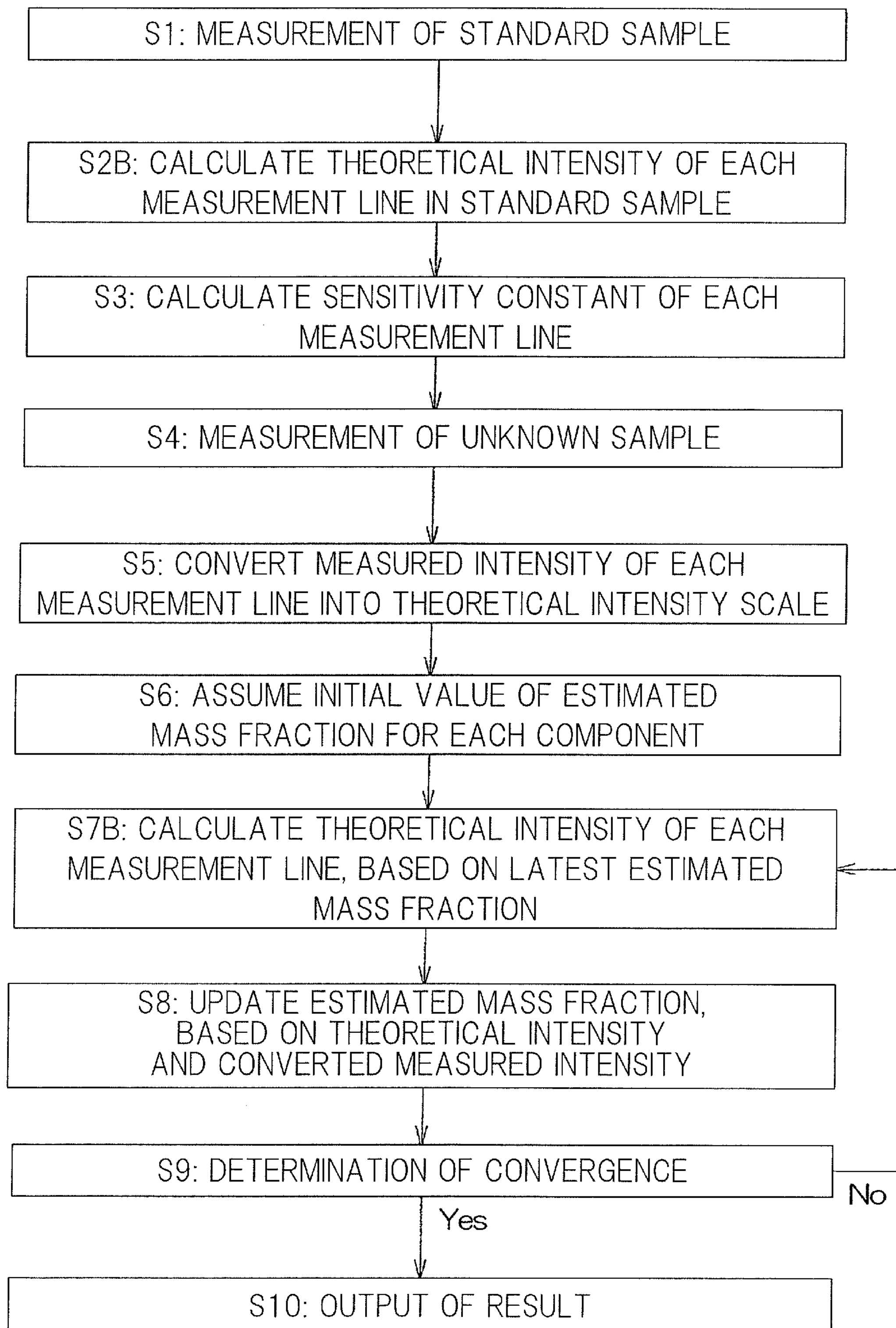
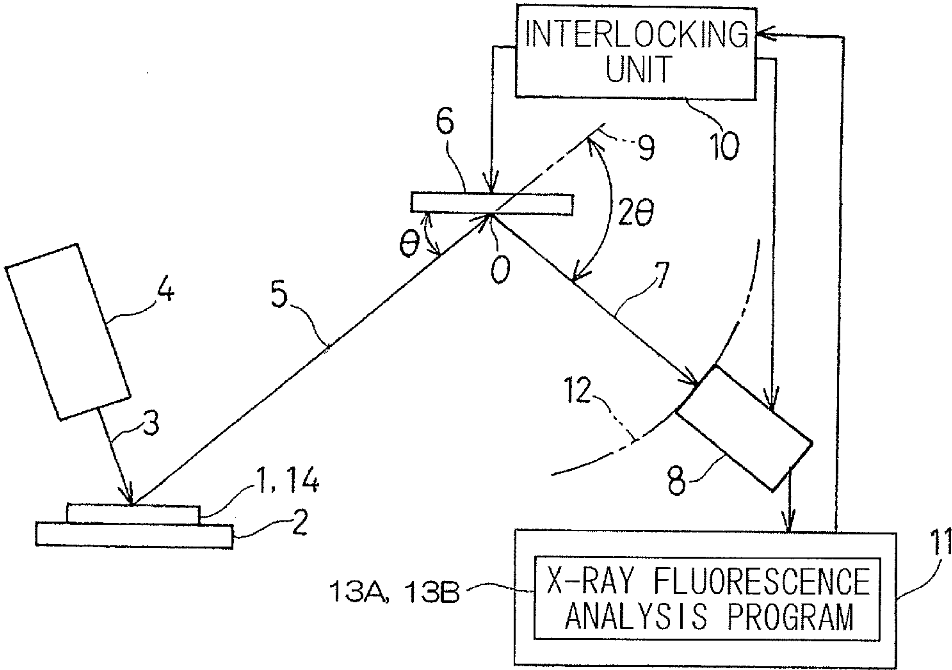


Fig. 3



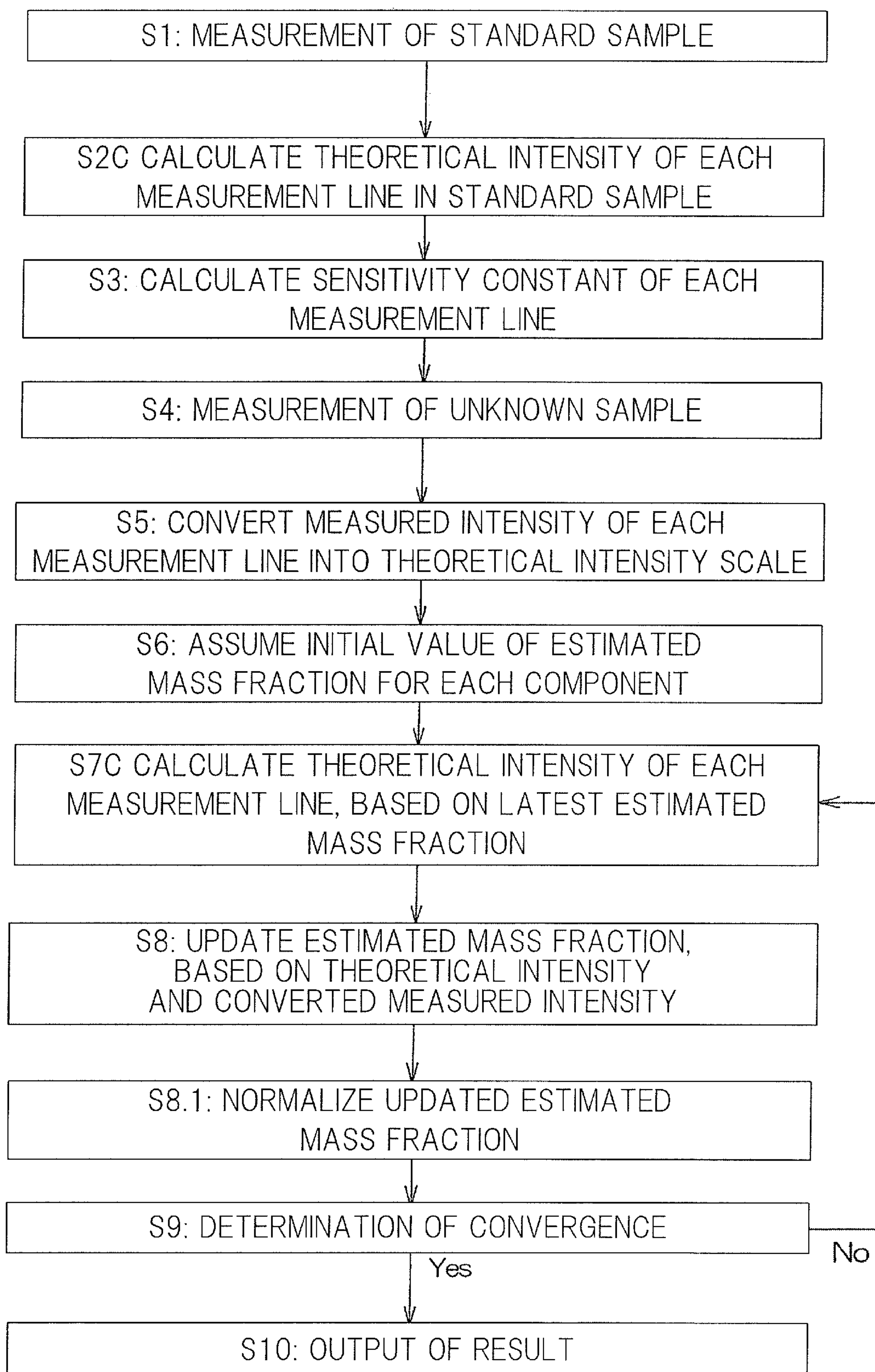


Fig. 4
S1: MEASUREMENT OF STANDARD SAMPLE
S2C CALCULATE THEORETICAL INTENSITY OF EACH MEASUREMENT LINE IN STANDARD SAMPLE
S3: CALCULATE SENSITIVITY CONSTANT OF EACH MEASUREMENT LINE
S4: MEASUREMENT OF UNKNOWN SAMPLE
S5: CONVERT MEASURED INTENSITY OF EACH MEASUREMENT LINE INTO THEORETICAL INTENSITY SCALE
S6: ASSUME INITIAL VALUE OF ESTIMATED MASS FRACTION FOR EACH COMPONENT
S7C CALCULATE THEORETICAL INTENSITY OF EACH MEASUREMENT LINE, BASED ON LATEST ESTIMATED MASS FRACTION
S8: UPDATE ESTIMATED MASS FRACTION, BASED ON THEORETICAL INTENSITY AND CONVERTED MEASURED INTENSITY
S8.1: NORMALIZE UPDATED ESTIMATED MASS FRACTION
S9: DETERMINATION OF CONVERGENCE
No
Yes
S10: OUTPUT OF RESULT

X-RAY FLUORESCENCE ANALYSIS METHOD, X-RAY FLUORESCENCE ANALYSIS PROGRAM, AND X-RAY FLUORESCENCE SPECTROMETER

CROSS REFERENCE TO THE RELATED APPLICATION

[0001] This application is a continuation application, under 35 U.S.C. § 111(a), of international application No. PCT/JP2018/010004, filed Mar. 14, 2018, which claims priority to Japanese patent application No. 2017-049447, filed Mar. 15, 2017, the entire disclosure of which is herein incorporated by reference as a part of this application.

BACKGROUND OF THE INVENTION

Field of the Invention

[0002] The present invention relates to an X-ray fluorescence analysis method, an X-ray fluorescence analysis program, and an X-ray fluorescence spectrometer according to a fundamental parameter method.

Description of Related Art

[0003] Conventionally, a fundamental parameter method (FP method) has been known as an X-ray fluorescence analysis method including: irradiating a sample with primary X-rays; measuring intensities of secondary X-rays such as fluorescent X-rays generated from the sample; and performing qualitative analysis of, for example, the mass fractions (sometimes represented by contents) of components (elements or compounds) in the sample based on the measured intensities (refer to Non-Patent Literature 1). In the FP method, as shown in the flowchart of FIG. **4**, a sensitivity constant for correcting apparatus sensitivity is obtained in advance based on the measured intensity and a theoretical intensity of a standard sample (steps **S1** to **S3**). Then, as for an unknown sample, mass fractions of the components thereof are obtained (step **S10**) based on an initial value of each mass fraction appropriately estimated based on the measured intensity and the sensitivity constant (steps **S4** to **S6**) through iterative calculation using a theoretical intensity (steps **S7**C to **S9**).

[0004] In the conventional FP method, it is assumed that a standard sample in which a sum of the mass fractions of all components is 1 is used. In a normalization step **S8.1** in the iterative calculation, an estimated mass fraction of each component, which has been updated in an update step **S8**, is divided by a sum of estimated mass fractions of all the components, thereby normalizing the estimated mass fraction of each component so that the sum of the estimated mass fractions of all the components becomes 1. In addition, according to the above assumption, in a standard sample theoretical intensity calculation step **S2**C and an unknown sample theoretical intensity calculation step **S7**C, a theoretical intensity formula simply represented by the following formula (1) is used.

$$I_i^T = K_i W_i / \Sigma \mu_j W_j \tag{1}$$

[0005] In the formula (1), I_i^T is a theoretical intensity of fluorescent X-rays of a measurement component i, K_i is a constant of the fluorescent X-rays of the measurement component i, W_i is a mass fraction of the measurement component i, j is a total absorption coefficient of a component j (including the measurement component i) in the sample, and W_j is a mass fraction of the component j in the sample. On the assumption that a sum ΣW_j of mass fractions of all components is not 1 in the formula (1), if normalization is performed by dividing each of a numerator and a denominator of a right-hand side by ΣW_j so that the sum of the mass fractions of all the components becomes 1, the theoretical intensity I_i^T is represent as follows.

$$I_i^T = K_i W_i^N / \Sigma \mu_j W_j^N \tag{2}$$

[0006] In formula (2), each superscript N indicates that the corresponding value has been normalized. $W_i^N = W_i / \Sigma W_j$ represents a mass fraction of the measurement component i after normalization, and $W_i^N = W_j / W_j$ represents a mass fraction of the component j in the sample after normalization. A sum $\Sigma W_j^N = \Sigma(W_j / \Sigma W_j)$ of the mass fractions of all the components after normalization is 1. As is understood from comparison of the formula (1) with the formula (2), in the theoretical intensity formula used in the conventional FP method, the theoretical intensity I_i^T of the measurement component i does not depend on the absolute mass fraction W_j of each of the components j in the sample but depends on a proportion (W_1:W_2:W_3 . . .) of the mass fractions W_j among the components j in the sample. Therefore, if the proportion is the same, the same theoretical intensity I_i^T is calculated for the measurement component i regardless of whether or not the sum ΣW_j of the mass fractions of all the components is 1.

[0007] For example, in a sample composed of two components of Fe and Ni, when the mass fractions of Fe and Ni are 0.54 and 0.36, respectively, and the sum of the mass fractions is 0.9, the theoretical intensity of each of Fe and Ni becomes the same as in the case where the mass fractions of Fe and Ni are 0.6 and 0.4, respectively, and the sum of the mass fractions of all the components is 1 (each mass fraction is normalized in this case), because 0.54:0.36=0.6:0.4.

[0008] Meanwhile, a calibration curve method has been known as a method in contrast with the FP method. In a semi-fundamental parameter (SFP) method for the calibration curve method, a calibration curve is corrected by using matrix correction factors, relating to absorption of X-rays, obtained through theoretical intensity calculation (refer to Non-Patent Document 2). In a correction formula used in the SFP method, one component is used as a base component (so-called balance), and a mass fraction of the base component is set to a value obtained by subtracting, from 1, a sum of mass fractions of components other than the base component, thereby normalizing the mass fraction of each component so that the sum of the mass fractions of all the components becomes 1.

RELATED DOCUMENT

Non-Patent Document

[0009] [Non-Patent Document 1] J. W. Criss, L. S. Birks, "Calculation Methods for Fluorescent X-Ray Spectrometry", Analytical Chemistry, 1968, Vol. 40, p. 1080-1086

[0010] [Non-Patent Document 2] W. K. Jongh, "X-Ray Fluorescence Analysis Applying Theoretical Matrix Corrections. Stainless Steel", X-ray spectrometry, 1973, Vol. 2, p. 151-158

SUMMARY OF THE INVENTION

[0011] In a standard sample, the sum of the mass fractions of known components is often not 1. In the SFP method, when a calibration curve is made by using a standard sample in which the sum of the mass fractions of known components is 0.98 and an unknown sample having the same composition is analyzed, an adequate analysis result indicating that the sum of the mass fractions of all the components is substantially 0.98 is obtained. However, in the FP method, when a sensitivity constant is obtained by using a standard sample in which the sum of the mass fractions of known components is 0.98 and an unknown sample having the same composition is analyzed, an inadequate analysis result indicating that the sum of the mass fractions of all the components is substantially 1 is obtained because of the aforementioned reason regarding the theoretical intensity formula, which may result in a significant analysis error. Therefore, in the FP method, in order to realize accurate analysis, only a standard sample in which the sum of the mass fractions of known components is 1 or extremely close to 1 can be used.

[0012] The present invention has been made in view of the above conventional problems, and an object of thereof is to provide an X-ray fluorescence analysis method, an X-ray fluorescence analysis program, and an X-ray fluorescence spectrometer according to the FP method, which enable accurate analysis even when a standard sample in which the sum of the mass fractions of known components is not 1.

[0013] In order to attain the aforementioned object, an X-ray fluorescence analysis method according to a first aspect of the present invention includes: a standard sample measurement step of irradiating a standard sample, which contains elements or compounds as components and whose composition is known, with primary X-rays, and measuring an intensity of fluorescent X-rays generated from the component in the standard sample; a standard sample theoretical intensity calculation step of calculating a theoretical intensity of the fluorescent X-rays generated from the component in the standard sample, based on a mass fraction of the component in the standard sample, by using a predefined theoretical intensity formula; and a sensitivity constant calculation step of calculating a sensitivity constant, based on the intensity measured in the standard sample measurement step and the theoretical intensity calculated in the standard sample theoretical intensity calculation step.

[0014] Then, the X-ray fluorescence analysis method according to the first aspect includes: an unknown sample measurement step of irradiating an unknown sample, which contains elements or compounds as components and whose composition is unknown, with the primary X-rays, and measuring an intensity of fluorescent X-rays generated from the component in the unknown sample; a conversion step of converting the intensity measured in the unknown sample measurement step into a theoretical intensity scale by using the sensitivity constant, to obtain a converted measured intensity; and an initial value assumption step of assuming an initial value of an estimated mass fraction for the component in the unknown sample.

[0015] Further, the X-ray fluorescence analysis method according to the first aspect includes: an unknown sample theoretical intensity calculation step of calculating a theoretical intensity of the fluorescent X-rays generated from the component in the unknown sample, based on a latest estimated mass fraction, by using the predefined theoretical intensity formula; an update step of updating the estimated mass fraction, based on the theoretical intensity calculated in the unknown sample theoretical intensity calculation step and on the converted measured intensity obtained in the conversion step; a convergence determination step of performing convergence determination, based on the estimated mass fractions before and after update in the update step and on a predetermined convergence condition; and a result output step of outputting a latest estimated mass fraction as a mass fraction, to be obtained, of the component in the unknown sample. When a result of determination in the convergence determination step is "not converged", the convergence determination step is followed by the unknown sample theoretical intensity calculation step, whereas, when the result of determination in the convergence determination step is "converged", the convergence determination step is followed by the result output step.

[0016] Further more, in the X-ray fluorescence analysis method according to the first aspect, in the predefined theoretical intensity formula used in the standard sample theoretical intensity calculation step and the unknown sample theoretical intensity calculation step, the mass fraction of each component is normalized, only in an absorption term relating to absorption of X-rays, so that a sum of the mass fractions of all the components becomes 1.

[0017] The X-ray fluorescence analysis method according to the first aspect uses, in the FP method, the theoretical intensity formula in which, only in the absorption term relating to absorption of X-rays, the mass fraction of each component is normalized so that the sum of the mass fractions of all the components becomes 1. Therefore, the theoretical intensity of the measurement component depends on the absolute mass fraction of each of the components in the sample. Thus, even when a standard sample in which the sum of the mass fractions of known components is not 1 is used, accurate analysis can be performed.

[0018] In the X-ray fluorescence analysis method according to the first aspect, in the predefined theoretical intensity formula used in the standard sample theoretical intensity calculation step and the unknown sample theoretical intensity calculation step, the mass fraction of each component is normalized, only in the absorption term relating to absorption of X-rays, preferably by dividing the mass fraction of the component by the sum of the mass fractions of all the components. In this case, the mass fraction of each component in the absorption term can be easily normalized so that the sum of the mass fractions of all the components becomes 1.

[0019] In the X-ray fluorescence analysis method according to the first aspect, in the predefined theoretical intensity formula used in the standard sample theoretical intensity calculation step and the unknown sample theoretical intensity calculation step, the mass fraction of each component may be normalized, only in the absorption term relating to absorption of X-rays, by setting a mass fraction of a base component specified for each component to a value obtained by subtracting, from 1, a sum of mass fractions of components other than the base component.

[0020] A second aspect of the present invention is an X-ray fluorescence analysis program for causing an X-ray fluorescence spectrometer to execute the X-ray fluorescence analysis method according to the first aspect. A third aspect of the present invention is an X-ray fluorescence spectrometer provided with the X-ray fluorescence analysis program

according to the second aspect. Also in the X-ray fluorescence analysis program according to the second aspect and the X-ray fluorescence spectrometer according to the third aspect, the same operation and effect as those of the X-ray fluorescence analysis method according to the first aspect can be obtained.

[0021] Any combination of at least two constructions, disclosed in the appended claims and/or the specification and/or the accompanying drawings should be construed as included within the scope of the present invention. In particular, any combination of two or more of the appended claims should be equally construed as included within the scope of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] In any event, the present invention will become more clearly understood from the following description of preferred embodiments thereof, when taken in conjunction with the accompanying drawings. However, the embodiments and the drawings are given only for the purpose of illustration and explanation, and are not to be taken as limiting the scope of the present invention in any way whatsoever, which scope is to be determined by the appended claims. In the accompanying drawings, like reference numerals are used to denote like parts throughout the several views, and:

[0023] FIG. **1** is a flowchart showing an X-ray fluorescence analysis method according to a first embodiment of the present invention;

[0024] FIG. **2** is a flowchart showing an X-ray fluorescence analysis method according to a second embodiment of the present invention;

[0025] FIG. **3** is a schematic diagram showing an X-ray fluorescence spectrometer used for the X-ray fluorescence analysis methods according to the first and second embodiments; and

[0026] FIG. **4** is a flowchart showing an X-ray fluorescence analysis method according to a conventional FP method.

DESCRIPTION OF EMBODIMENTS

[0027] Hereinafter, an X-ray fluorescence analysis method according to a first embodiment of the present invention will be described. First, an X-ray fluorescence spectrometer used for the X-ray fluorescence analysis method will be described. As shown in FIG. **3**, this spectrometer is a sequential X-ray fluorescence spectrometer that irradiates a sample **1**, **14** (including both an unknown sample **1** and a standard sample **14**) with primary X-rays **3**, and measures intensities of generated secondary X-rays **5**. The X-ray fluorescence spectrometer includes: a sample stage **2** on which the sample **1**, **14** is placed; an X-ray source **4** such as an X-ray tube which irradiates the sample **1**, **14** with the primary X-rays **3**; a spectroscopic device **6** which monochromates the secondary X-rays **5** such as fluorescent X-rays generated from the sample **1**, **14**; and a detector **8** on which secondary X-rays **7** monochromated by the spectroscopic device **6** are incident and which detects the intensity of the secondary X-rays **7**. An output from the detector **8** is input, through an amplifier, a pulse height analyzer, a counting unit, and the like (not shown), to a control unit **11** such as a computer which controls the entire spectrometer.

[0028] The spectrometer is a wavelength dispersive and sequential X-ray fluorescence spectrometer, and includes an interlocking unit **10**, i.e., a so-called goniometer, which interlocks the spectroscopic device **6** with the detector **8** so as to change the wavelength of the secondary X-rays **7** incident on the detector **8**. When the secondary X-rays **5** are incident on the spectroscopic device **6** at a certain incident angle θ, an extended line **9** of the secondary X-rays **5** and the secondary X-rays **7** monochromated (diffracted) by the spectroscopic device **6** form a spectroscopic angle **2θ** which is twice the incident angle θ. To cause the secondary X-rays **7**, which are monochromated while the spectroscopic angle **2θ** is changed, to be incident on the detector **8** while changing the wavelength of the secondary X-rays **7**, the interlocking unit **10** rotates the spectroscopic device **6** around an axis O which passes the center of the surface of the spectroscopic device **6** and is perpendicular to the drawing sheet, and rotates the detector **8** around the axis O and around a circle **12** by an angle of twice the rotation angle of the spectroscopic device **6**. The value of the spectroscopic angle **2θ** (angle **2θ**) is input from the interlocking unit **10** to the control unit **11**.

[0029] The spectrometer is provided with one or a plurality of standard samples **14** whose compositions are known and different from each other so as to correspond to an expected unknown sample **1** to be analyzed. These samples are placed on the sample stage **2** and subjected to quantitative analysis. The control unit **11** has an X-ray fluorescence analysis program **13**A or **13**B which allows the X-ray fluorescence spectrometer to execute the X-ray fluorescence analysis method of the first embodiment or the later-described second embodiment. The X-ray fluorescence analysis program and the X-ray fluorescence spectrometer are also embodiments of the present invention. In the present invention, the X-ray fluorescence spectrometer may be a wavelength dispersive and simultaneous multi-elements analysis type X-ray fluorescence spectrometer, or may be an energy dispersive X-ray fluorescence spectrometer.

[0030] The X-ray fluorescence analysis method according to the first embodiment, using the aforementioned X-ray fluorescence spectrometer, will be described with reference to FIG. **1** showing a flowchart of the X-ray fluorescence analysis program **13**A. First, in a standard sample measurement step S**1**, the standard sample **14**, which contains elements or compounds as components and whose composition is known, is irradiated with the primary X-rays **3**, and an intensity I_i^{MS} of fluorescent X-rays **5** generated from the component i in the standard sample **14** is measured.

[0031] Next, in a standard sample theoretical intensity calculation step S**2**A, based on a known mass fraction W_j (a numerical value obtained by dividing the content that is the percentage concentration by 100) of a component j in the standard sample **14**, a theoretical intensity I_i^{TS} of the fluorescent X-rays (measurement line) **5** generated from the component i in the standard sample **14** is calculated by using a predefined theoretical intensity formula. The theoretical intensity formula used here is simply represented as the following formula (3) or (4) in which, unlike the formulae (1) and (2) used for the conventional FP method, only in an absorption term relating to absorption of X-rays (a denominator of a right-hand side), the mass fraction W_j of each component j is divided by the sum ΣW_j of the mass fractions of all the components to obtain W_j^N, thereby normalizing the mass fraction W_j of each component j so that the sum

$W_j^N N = \Sigma(W_j/\Sigma W_j)$ of the mass fractions of all the components becomes 1. The theoretical intensity I_i^T calculated for the standard sample **14** by the formula (3) is the theoretical intensity I_i^{TS}.

$$I_i^T = K_i W_i / \Sigma \mu_j (W_j / \Sigma W_j) \quad (3)$$

$$I_i^T = K_i W_i / \Sigma \mu_j W_j^N \quad (4)$$

[0032] In the formula (3), the denominator of the right-hand side is divided by the sum ΣW_j of the mass fractions of all the components. Since this is equal to multiplying the numerator of the right-hand side by the sum ΣW_j of the mass fractions of all the components, the formulae (3) and (4) are equivalent to the following formula (5).

$$I_i^T = (K_i W_i / \Sigma \mu_j W_j) \Sigma W_j \quad (5)$$

[0033] The theoretical intensity I_i^T according to the formula (5) is equivalent to one obtained by multiplying the theoretical intensity I_i^T according to the formula (1) used for the conventional FP method, by the sum ΣW_j of the mass fractions of all the components. In the present invention, as the predefined theoretical intensity formula, the formula (5) may be used instead of the formula (3).

[0034] Next, in a sensitivity constant calculation step S**3**, based on the intensity I_i^{MS} measured in the standard sample measurement step S**1** and the theoretical intensity I_i^{TS} calculated in the standard sample theoretical intensity calculation step S**2**A, a sensitivity constant A_i is calculated by the following formula (6). Alternatively, the sensitivity constant may be obtained through a least square method by using a plurality of standard samples, and selecting a linear expression or a quadratic expression instead of the formula (6).

$$A_i = I_i^{TS} / I_i^{MS} \quad (6)$$

[0035] Next, in an unknown sample measurement step S**4**, the unknown sample **1**, which contains elements or compounds as components and whose composition is unknown, is irradiated with the primary X-rays **3**, and an intensity I_i^M of fluorescent X-rays **5** generated from the component i in the unknown sample **1** is measured.

[0036] Next, in a conversion step S**5**, the intensity I_i^M measured in the unknown sample measurement step S**4** is converted to a theoretical intensity scale by using the sensitivity constant A_i calculated in the sensitivity constant calculation step S**3**, according to the following formula (7), thereby obtaining a converted measured intensity I_i^{MT}.

$$I_i^{MT} = A_i \times I_i^M \quad (7)$$

[0037] Next, in an initial value assumption step S**6**, an initial value $W_i(1)^N$ of an estimated mass fraction for the component i in the unknown sample **1** is assumed according to the following formulae (8) and (9), where I_i^P is a theoretical intensity of a pure substance of the component i.

$$W_i(0) = I_i^{MT} / I_i^P \quad (8)$$

$$W_i(1)^N = W_i(0) / \Sigma W_j(0) \quad (9)$$

[0038] Specifically, in the formula (8), the ratio of the converted measured intensity I_i^{MT} to the theoretical intensity I_i^P of the pure substance of the component i is regarded as a previous initial value $W_i(0)$. In the formula (9), the previous initial value $W_i(0)$ is divided by the sum $\Sigma W_j(0)$ of previous initial values of all the components, thereby normalizing the previous initial value $W_i(0)$ so that the sum $\Sigma W_j(1)^N = \Sigma(W_i(0)/\Sigma W_j(0))$ of the previous initial values of all the components becomes 1, and the normalized previous initial value $W_i(1)^N$ is assumed as the initial value $W_i(1)^N$ of the estimated mass fraction. In the estimated mass fraction $W_i(n)$, the numerical value n in round brackets is the number of iterations of estimation calculation with the initial value $W_i(1)^N$ being the first time.

[0039] Next, in an unknown sample theoretical intensity calculation step S**7**A in the iterative calculation, a theoretical intensity $I_i^T(n)$ of the fluorescent X-rays **5** generated from the component i in the unknown sample **1** is calculated based on a latest estimated mass fraction $W_i(n)$, according to the predefined theoretical intensity formula (3). That is, the theoretical intensity I_i^T calculated for the latest estimated mass fraction $W_i(n)$ through the formula (3) is the n-th theoretical intensity $I_i^T(n)$. Regarding the mass fraction W_i of the measurement component i for which a theoretical intensity I_i^T is to be calculated, normalization thereof is not performed during the iterative calculation but is performed, according to the formula (9), in the initial value assumption step S**6** immediately before entering the iterative calculation. Therefore, the latest estimated mass fraction $W_i(n)$ is normalized only in the first initial value $W_i(1)^N$.

[0040] Next, in an update step S**8**, the estimated mass fraction is updated from $W_i(n)$ to $W_i(n+1)$ according to the following formula (10), based on the theoretical intensity $I_i^T(n)$ calculated in the unknown sample theoretical intensity calculation step S**7**A and on the converted measured intensity I_i^{MT} obtained in the conversion step S**5**.

$$W_i(n+1) = W_i(n) \times I_i^{MT} / I_i^T(n) \quad (10)$$

[0041] Next, in a convergence determination step S**9**, convergence determination is performed according to the following formula (11), based on the estimated mass fractions $W_i(n)$ and $W_i(n+1)$ before and after update in the update step S**8** and on a predetermined convergence condition.

$$|W_i(n+1)/W_i(n) - 1.0| < \alpha \quad (11)$$

[0042] For example, if the formula (11) is not satisfied when $\alpha = 0.001$, the result of the determination is regarded as "not converged", and the procedure is returned to the unknown sample theoretical intensity calculation step S**7**A. Then, the steps from the unknown sample theoretical intensity calculation step S**7**A to the convergence determination step S**9** are repeated with $W_i(n+1)$ being the latest estimated mass fraction. On the other hand, when the formula (11) is satisfied, and then if the number of iterations of estimation calculation with the initial value $W_i(1)^N$ being the first time is three or more, that is, when $n+1 \geq 3$ ($n+1>3$ or $n+1=3$) is satisfied, it is determined that the result of the determination is "converged", and the procedure proceeds to a result output step S**10**.

[0043] In the result output step S**10**, the latest estimated mass fraction $W_i(n+1)$ is output as a mass fraction W_i, to be obtained, of the component i in the unknown sample **1**.

[0044] According to the X-ray fluorescence analysis method of the first embodiment and the conventional FP method, 11 elements in 5 standard samples **14** made of nickel alloy are analyzed. Table 1 shows: maximum and minimum contents of known chemical analysis values for each element; and accuracies for each element according to the respective methods. In Table 1, the "accuracy (before normalization)" of the conventional FP method is the accuracy obtained in the case where the latest estimated mass fraction $W_i(n+1)$, which is not yet normalized in the normalization step S**8**.**1**, is output in the result output step S**10**

of FIG. **4**. Meanwhile, in the conventional FP method, usually, the latest estimated mass fraction $W_i(n+1)^N$, which has been normalized in the normalization step S**8**.**1**, is output in the result output step S**10**, and the accuracy obtained in this case is the "accuracy (after normalization)".

TABLE

unit: mass %											
	Mn	Si	Cr	Ni	Co	Mo	W	Nb	Ti	Fe	Cu
Maximum content	1.28	0.94	21.62	72.6	20.8	4.5	2.4	4.98	3.09	27.4	0.077
Minimum content	0.23	0.083	17.4	20.26	0.06	0	0	0	0.001	1.4	0
Conventional FP method											
Accuracy (after normalization	0.007	0.021	0.239	0.768	0.115	0.042	0.003	0.026	0.036	0.149	0.007
Accuracy (before normalization)	0.036	0.064	0.218	0.392	0.151	0.092	0.024	0.072	0.085	0.173	0.038
FP method according to first embodiment											
Accuracy	0.002	0.020	0.070	0.16	0.031	0.010	0.000	0.001	0.017	0.030	0.007

[0045] In the 5 standard samples **14**, the sum of the contents of the 11 elements based on chemical analysis values ranges from 98.55% to 99.39%, that is, the sum of the mass fractions of the known components is not 1. Then, in each method, a sensitivity constant is obtained by using the standard samples **14**. Next, quantitative analysis is performed using the standard samples **14** as unknown samples **1**, thereby obtaining the accuracies based on quantitative errors from the known chemical analysis values. Each accuracy is a square root of a numerical value obtained by dividing a square sum of the quantitative errors of the standard samples **14** by **5** that is the number of the samples. As is apparent from Table 1, according to the X-ray fluorescence analysis method of the first embodiment, when the standard sample **14** in which the sum of the mass fractions of known components is not 1, the accuracy is significantly improved as compared with the conventional FP method.

[0046] As described, according to the X-ray fluorescence analysis method of the first embodiment, in the FP method, the theoretical intensity formula (3) is used in which, only in the absorption term relating to absorption of X-rays, the mass fraction W_j of each component j is normalized so that the total of the mass fractions of all the components becomes 1. Therefore, the theoretical intensity I_i^T of the measurement component i depends on the absolute mass fraction W_j of each of the components j in the sample. Thus, even when the standard sample **14** in which the sum of the mass fractions of the known components is not 1 is used, it is possible to perform accurate analysis on the unknown sample **1**. In addition, the normalization in the absorption term can be easily performed by dividing the mass fraction W_j of each component j by the sum ΣW_j of the mass fractions of all the components.

[0047] As for the X-ray fluorescence analysis method of the first embodiment, various modifications as follows are conceivable, and the same operation and effect as those of the first embodiment can be obtained also in the modifications. First, according to modification **1**, a normalization step S**8**.**1** may be provided between the update step S**8** and the convergence determination step S**9**, as in the conventional FP method. In the normalization step S**8**.**1**, normalization is performed according to the following formula (12) such that the estimated mass fraction $W_i(n+1)$ of each component i, which has been updated in the update step S**8**, is divided by the sum $\Sigma W_j(n+1)$ of the estimated mass fractions of all the components to obtain $W_i(n+1)^N$, whereby the sum $\Sigma W_i(n+1)^N = \Sigma(W_i(n+1)/\Sigma W_j(n+1))$ of the estimated mass fractions of all the components becomes 1.

$$W_i(n+1)^N = W_i(n+1)/\Sigma W_j(n+1) \tag{12}$$

[0048] In the modification **1**, in the convergence determination step **S9**, convergence determination may be performed based on either the non-normalized estimated mass fractions $W_i(n)$ and $W_i(n+1)$ before and after update or the normalized estimated mass fractions $W_i(n)^N$ and $W_i(n+1)^N$ before and after update. Also in the result output step S**10**, as the mass fraction W_i, to be obtained, of the component i in the unknown sample **1**, either the latest non-normalized estimated mass fraction $W_i(n+1)$ or the latest normalized estimated mass fraction $W_i(n+1)^N$ may be output. However, in the case where the determination result in the convergence determination step **S9** is "not converged" and the procedure is returned to the unknown sample theoretical intensity calculation step S**7**A, the latest estimated mass fraction is the latest normalized estimated mass fraction $W_i(n+1)^N$.

[0049] Further, although departing from the present invention, in modification **2**, the theoretical intensity formula used in the unknown sample theoretical intensity calculation step S7A of modification **1** may be changed from the formula (3) to the formula (1) used in the conventional FP method.

[0050] Next, an X-ray fluorescence analysis method according to a second embodiment will be described with reference to FIG. **2** showing a flowchart of the X-ray fluorescence analysis program **13**B shown in FIG. **3**. The X-ray fluorescence analysis method of the second embodiment is identical to the X-ray fluorescence analysis method of the first embodiment except that a predefined theoretical intensity formula used in a standard sample theoretical intensity calculation step S2B and an unknown sample theoretical intensity calculation step S7B is different from the predefined theoretical intensity formula (3) used in the standard sample theoretical intensity calculation step S**2**A and the unknown sample theoretical intensity calculation step S**7**A in the X-ray fluorescence analysis method of the first embodiment. Since the rest of the configuration of the second embodiment is the same as that of the first embodiment, only the theoretical intensity formula will be described.

[0051] The theoretical intensity formula is represented by the following formulae (13) and (14), in which, only in an absorption term relating to absorption of X-rays (a denominator of a right-hand side in formula (13)), a mass fraction W_{ib} of a base component ib specified for each component i is set to a value obtained by subtracting, from 1, a sum $\Sigma_{j\neq ib}W_j$ of mass fractions of components other than the base component ib, thereby normalizing the mass fraction W_j of each component j so that the sum ΣW_j of the mass fractions of all the components becomes 1.

$$I_i^T=K_iW_i/(\Sigma_{j\neq ib}\mu_jW_j+\mu_{ib}W_{ib}) \quad (13)$$

$$W_{ib}=1.0-\Sigma_{j\neq b}W_j \quad (14)$$

[0052] The X-ray fluorescence analysis method of the second embodiment is verified through simulations as follows. First, a standard sample **14** is assumed which is composed of two elements, Fe and Ni, and in which a mass fraction W_{Fe} of Fe is 0.50, a mass fraction W_{Ni} of Ni is 0.49, and the sum of the mass fractions of all the components is not 1 but 0.99. Fluorescent X-rays to be measured are Fe—Kα line and Ni—Kα line. A measurement intensity I_{Fe}^{MS} of Fe—Kα line is 200.0, and a measurement intensity I_{Ni}^{MS} of Ni—Kα line is 100.0. As for Fe, Ni is specified as a base component. As for Ni, Fe is specified as a base component.

[0053] According to the above setting, a theoretical intensity I_{Fe}^{TS}=2753.6 of Fe—Kα line and a theoretical intensity I_{Ni}^{TS}=1278.1 of Ni—Kα line are calculated in the standard sample theoretical intensity calculation step S**2**B, and a sensitivity constant A_{Fe}=13.768 of Fe—Kα line and a sensitivity constant A_{Ni}=12.781 of Ni—Kα line are calculated in the sensitivity constant calculation step S**3**.

[0054] Next, the standard sample **14** assumed as described above is used as an unknown sample **1**, and the measurement intensities I_{Fe}^{M} and I_{Ni}^{M} of Fe—Kα line and Ni—Kα line are similarly set to 200.0 and 100.0, respectively. Converted measurement intensities I_{Fe}^{MT} and I_{Ni}^{MT} obtained in the conversion step S**5** are equal to the theoretical intensities I_{Fe}^{TS} and I_{Ni}^{TS} calculated for the standard sample **14**, respectively, that is, the converted measured intensity I_{Fe}^{MT} of Fe—Kα line is 2753.6, and the converted measured intensity I_{Ni}^{MT} of Ni—Kα line is 1278.1. In the initial value assumption step S**6**, first, theoretical intensities I_{Fe}^{P} and I_{Ni}^{P} of pure substances of Fe and Ni are calculated to be 4615.2 and 5343.5, respectively, and initial values $W_{Fe}(1)^N$=0.7138 and $W_{Ni}(1)^N$=0.2862 of estimated mass fractions are obtained through formulae (8) and (9).

[0055] Table 2 shows the theoretical intensity $I_i^T(n)$ obtained in the unknown sample theoretical intensity calculation step S7B and the estimated mass fraction $W_i(n+1)$ after update in the update step S**8**, up to n=10, during the subsequent iterative calculation. In Table 2, a superscript B indicates that the corresponding value is not normalized.

TABLE 2

		Fe mass fraction	Fe theoretical intensity	Ni mass fraction	Ni theoretical intensity
Measured intensity (theoretical intensity scale)	I_i^{TM}		(2753.6)		(1278.1)
Pure substance theoretical intensity	I_i^P		4615.2		5343.5
Initial mass fraction (normalized)	$W_i^B(1)$	0.7138		0.2862	
Theoretical intensity	$I_i^T(1)$		3569.1		626.8
Estimated mass fraction	$W_i^B(2)$	0.5507		0.5835	
Theoretical intensity	$I_i^T(2)$		2953.5		1670.4
Estimated mass fraction	$W_i^B(3)$	0.5135		0.4464	
Theoretical intensity	$I_i^T(3)$		2807.3		1118.5
Estimated mass fraction	$W_i^B(4)$	0.5037		0.5101	
Theoretical intensity	$I_i^T(4)$		2768.3		1356.4
Estimated mass fraction	$W_i^B(5)$	0.5010		0.4807	
Theoretical intensity	$I_i^T(5)$		2757.7		1242.8
Estimated mass fraction	$W_i^B(6)$	0.5003		0.4943	
Theoretical intensity	$I_i^T(6)$		2754.7		1294.6
Estimated mass fraction	$W_i^B(7)$	0.5001		0.4880	
Theoretical intensity	$I_i^T(7)$		2754.0		1270.4
Estimated mass fraction	$W_i^B(8)$	0.5000		0.4909	
Theoretical intensity	$I_i^T(8)$		2753.7		1281.7
Estimated mass fraction	$W_i^B(9)$	0.5000		0.4896	
Theoretical intensity	$I_i^T(9)$		2753.7		1276.4
Estimated mass fraction	$W_i^B(10)$	0.5000		0.4902	
Theoretical intensity	$I_i^T(10)$		2753.6		1278.8
Estimated mass fraction	$W_i^B(11)$	0.5000		0.4899	

[0056] As is apparent from Table 2, according to the X-ray fluorescence analysis method of the second embodiment, even when the standard sample **14** in which the sum of the mass fractions of known components is not 1 is used, the estimated mass fraction is appropriately converged to a true value.

[0057] Also in the X-ray fluorescence analysis method of the second embodiment, in the FP method, the theoretical intensity formulae (13) and (14) are used in which, only in the absorption term relating to absorption of X-rays, the mass fraction W_j of each component j is normalized so that the total of the mass fractions of all the components becomes 1. Therefore, the theoretical intensity I_i^T of the measurement component i depends on the absolute mass fraction W_j of each of the components j in the sample. Thus, even when the standard sample **14** in which the sum of the mass fractions of known components is not 1 is used, accurate analysis of the unknown sample **1** can be performed.

[0058] In the X-ray fluorescence analysis method of the first embodiment, the simple formula (3) or (5) in which primary X-rays have a single wavelength, and which does

not include the intensity of fluorescent X-rays due to secondary excitation, is used. However, the X-ray fluorescence analysis method of the first embodiment may use the following formulae (5-1), (5-2), (5-3), (5-4) and (5-5), or the following formulae (5-6), (2-2), (2-3) and (2-4) so as to include wave range integration of primary X-rays and the intensity of fluorescent X-rays due to secondary excitation.

$$R_{ip} = W_i \int_{\lambda_{min}}^{\lambda_e^i} \frac{I_0(\lambda)\tau_{ip}(\lambda)}{m'(\lambda)+m'(\lambda_{ip})}\left[1+\frac{1}{2}\sum_{jq} W'_j F(jq,\lambda) \left\{\frac{\log\left(1+\frac{m'(ip)}{\mu'(jq)}\right)}{m'(ip)}+\frac{\log\left(1+\frac{m'(\lambda)}{\mu'(iq)}\right)}{m'(\lambda)}\right\}\right]d\lambda \quad (5\text{-}1)$$

where the X-ray intensity is R_{ip}, and in the formula (1), corresponds to the X-ray intensity obtained when the mass fraction of the i element is 1.0, that is, $R_{ip}=I_i/K_i$ is satisfied.

[0059] However, each symbol with an apostrophe is represented by the mass fraction normalized by the sum of the mass fractions of all the components, as described below.

$$m'(\lambda)=\Sigma_k(\lambda)W'_k/\sin\phi \quad (5\text{-}2)$$

$$m'(ip)=\Sigma_k\mu_k(ip)W'_k/\sin\psi \quad (5\text{-}3)$$

$$\mu'(jq)=\Sigma_k\mu_k(jq)W'_k \quad (5\text{-}4)$$

$$W'_k=W_k/\Sigma_l W'_l \quad (5\text{-}5)$$

[0060] The above formulae are rewritten as follows.

$$R_{ip} = W_i \int_{\lambda_{min}}^{\lambda_e^i} \frac{I_0(\lambda)\tau_{ip}(\lambda)}{m(\lambda)+m(\lambda_{ip})}\left[1+\frac{1}{2}\sum_{jq} W_j F(jq,\lambda)\left\{\frac{\log\left(1+\frac{m(ip)}{\mu(jq)}\right)}{m(ip)}+\frac{\log\left(1+\frac{m(\lambda)}{\mu(iq)}\right)}{m(\lambda)}\right\}\right]d\lambda\sum W_k \quad (5\text{-}6)$$

[0061] However, the term relating to absorption of X-rays is calculated by the following formulae.

$$m(\lambda)=\Sigma_k\mu_k(\lambda)W_k/\sin\phi \quad (2\text{-}2)$$

$$m(ip)=\Sigma_k\mu_k(ip)W_k/\sin\psi \quad (2\text{-}3)$$

$$\mu(jq)=\Sigma_k\mu_k(jq)W_k \quad (2\text{-}4)$$

[0062] In formula (5-1), the theoretical intensity of the fluorescent X-rays due to secondary excitation is included in the theoretical intensity of the fluorescent X-rays to be calculated. When, only in the absorption term relating to absorption of X-rays, the mass fraction of each component is normalized so that the sum of the mass fractions of all the components becomes 1, not only the absorption term relating to absorption of fluorescent X-rays due to secondary excitation (the term in curly brackets in formula (5-1), for example) but also the term relating to the mass fraction of the secondary-excited component (W'_j in square brackets in formula (5-1), for example) is included in the object to be normalized.

[0063] Likewise, in the X-ray fluorescence analysis method of the second embodiment, the simple formula (13) or (14) in which primary X-rays have a single wavelength, and which does not include the intensity of the fluorescent X-rays due to secondary excitation, is used. However, the X-ray fluorescence analysis method of the second embodiment may use the following formulae (2-1), (14-1), (14-2) and (14-3) and the aforementioned formula (14) so as to include wave range integration of primary X-rays and the intensity of fluorescent X-rays due to secondary excitation.

$$R_{ip} = W_i \int_{\lambda_{min}}^{\lambda_e^i} \frac{I_0(\lambda)\tau_{ip}(\lambda)}{m(\lambda)+m(\lambda_{ip})}\left[1+\frac{1}{2}\sum_{jq} W_j F(jq,\lambda) \left\{\frac{\log\left(1+\frac{m'(ip)}{\mu'(jq)}\right)}{m'(ip)}+\frac{\log\left(1+\frac{m'(\lambda)}{\mu'(iq)}\right)}{m'(\lambda)}\right\}\right]d\lambda \quad (2\text{-}1)$$

$$m(\lambda)=\left(\sum_{k\neq ib}\mu_k(\lambda)W_k+\mu_{ib}(\lambda)W_{ib}\right)/\sin\phi \quad (14\text{-}1)$$

$$m(ip)=\left(\sum_{k\neq ib}\mu_k(ip)W_k+\mu_{ib}(ip)W_{ib}\right)/\sin\psi \quad (14\text{-}2)$$

$$\mu(jq)=\sum_{k\neq ib}\mu_k(jq)W_k+\mu_{ib}(jq)W_{ib} \quad (14\text{-}3)$$

[0064] In formula (2-1), "½" and the subsequent portion in square brackets correspond to the term relating to secondary excitation, W_j is the mass fraction of the component to be secondarily excited, and F(jq,λ) corresponds to the product of photoelectric absorption coefficient, transition probability, fluorescence yield, and jump ratio. The product of W_j and photoelectric absorption coefficient is the degree of photoelectric absorption of the primary X-rays into the secondary-excited component. Meanwhile, a portion in curly brackets corresponds to the term relating to absorption of fluorescent X-rays due to secondary excitation (Reference Document: Y. Kataoka, "STANDARDLESS X-RAY FLUORESCENCE SPECTROMETRY (Fundamental Parameter Method using Sensitivity Library)", THE RIGAKU JOURNAL, 1989, Vol. 6, No. 1, p. 33-39).

[0065] Although the present invention has been fully described in connection with the preferred embodiments thereof with reference to the accompanying drawings which are used only for the purpose of illustration, those skilled in the art will readily conceive numerous changes and modifications within the framework of obviousness upon the reading of the specification herein presented of the present invention. Accordingly, such changes and modifications are, unless they depart from the scope of the present invention as delivered from the claims annexed hereto, to be construed as included therein.

REFERENCE NUMERALS

[0066] **1** . . . unknown sample
[0067] **3** . . . primary X-rays
[0068] **5** . . . fluorescent X-rays
[0069] **13**A, **13**B . . . X-ray fluorescence analysis program
[0070] **14** . . . standard sample
[0071] **S1** . . . standard sample measurement step
[0072] **S2**A, **S2**B . . . standard sample theoretical intensity calculation step
[0073] **S3** . . . sensitivity constant calculation step
[0074] **S4** . . . unknown sample measurement step

[0075] S**5** . . . conversion step

[0076] S**6** . . . initial value assumption step

[0077] S7A, S7B . . . unknown sample theoretical intensity calculation step

[0078] S**8** . . . update step

[0079] S**9** . . . convergence determination step

[0080] S**10** . . . result output step

What is claimed is:

1. An X-ray fluorescence analysis method comprising:

a standard sample measurement step of irradiating a standard sample, which contains elements or compounds as components and whose composition is known, with primary X-rays, and measuring an intensity of fluorescent X-rays generated from the component in the standard sample;

a standard sample theoretical intensity calculation step of calculating a theoretical intensity of the fluorescent X-rays generated from the component in the standard sample, based on a mass fraction of the component in the standard sample, by using a predefined theoretical intensity formula;

a sensitivity constant calculation step of calculating a sensitivity constant, based on the intensity measured in the standard sample measurement step and the theoretical intensity calculated in the standard sample theoretical intensity calculation step;

an unknown sample measurement step of irradiating an unknown sample, which contains elements or compounds as components and whose composition is unknown, with the primary X-rays, and measuring an intensity of fluorescent X-rays generated from the component in the unknown sample;

a conversion step of converting the intensity measured in the unknown sample measurement step into a theoretical intensity scale by using the sensitivity constant, to obtain a converted measured intensity;

an initial value assumption step of assuming an initial value of an estimated mass fraction for the component in the unknown sample;

an unknown sample theoretical intensity calculation step of calculating a theoretical intensity of the fluorescent X-rays generated from the component in the unknown sample, based on a latest estimated mass fraction, by using the predefined theoretical intensity formula;

an update step of updating the estimated mass fraction, based on the theoretical intensity calculated in the unknown sample theoretical intensity calculation step and on the converted measured intensity obtained in the conversion step;

a convergence determination step of performing convergence determination, based on the estimated mass fractions before and after update in the update step and on a predetermined convergence condition; and

a result output step of outputting a latest estimated mass fraction as a mass fraction, to be obtained, of the component in the unknown sample, wherein

when a result of determination in the convergence determination step is “not converged”, the convergence determination step is followed by the unknown sample theoretical intensity calculation step, whereas, when the result of determination in the convergence determination step is “converged”, the convergence determination step is followed by the result output step, and

in the predefined theoretical intensity formula used in the standard sample theoretical intensity calculation step and the unknown sample theoretical intensity calculation step, the mass fraction of each component is normalized, only in an absorption term relating to absorption of X-rays, so that a sum of the mass fractions of all the components becomes 1.

2. The X-ray fluorescence analysis method as claimed in claim **1**, wherein

in the predefined theoretical intensity formula used in the standard sample theoretical intensity calculation step and the unknown sample theoretical intensity calculation step, the mass fraction of each component is normalized, only in the absorption term relating to absorption of X-rays, by dividing the mass fraction of the component by the sum of the mass fractions of all the components.

3. The X-ray fluorescence analysis method as claimed in claim **1**, wherein

in the predefined theoretical intensity formula used in the standard sample theoretical intensity calculation step and the unknown sample theoretical intensity calculation step, the mass fraction of each component is normalized, only in the absorption term relating to absorption of X-rays, by setting a mass fraction of a base component specified for each component to a value obtained by subtracting, from 1, a sum of mass fractions of components other than the base component.

4. An X-ray fluorescence analysis program to cause an X-ray fluorescence spectrometer to execute the X-ray fluorescence analysis method as claimed in claim **1**.

5. An X-ray fluorescence spectrometer provided with the X-ray fluorescence analysis program as claimed in claim **4**.

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