

## JSCE-G 574-2005

### Test method for chemical element distribution in concrete using EPMA (draft)

#### 1 Scope

This standard specifies the requirements for carrying out an area analysis to determine various chemical elements in concrete (including mortar, paste and concrete surface coating material) using an electron probe micro analyzer (EPMA) of wavelength-dispersive type.

#### 2 References

By being cited herein, the following standards constitute part of the definition of this standard. This standard is based on the latest versions of these cited documents.

JIS R 6001 Bonded abrasive grain sizes

JIS R 6111 Artificial abrasives

#### 3 Definitions

The following terminology is used in this standard:

a) An electron probe micro analyzer (EPMA) of wavelength-dispersive type is an instrument for the analysis of multiple elements on the surface of a solid based on the information about characteristic X-rays emitted by the solid when irradiated with an electron probe.<sup>(1)</sup>

**Note** <sup>(1)</sup>: Two methods are in use to identify characteristic X-rays corresponding to the elements under investigation and to measure the characteristic X-ray intensities: wavelength-dispersive spectroscopy (WDS) involving spectroscopic measurement of characteristic X-rays by diffraction using a dispersion element; and energy-dispersive spectroscopy (EDS) in which the energy of characteristic X-rays is measured as electrical signals using a solid-state detector. The major differences between WDS and EDS are energy resolution and peak-to-background (P/B) signal ratio in the detection of X-rays. WDS has better energy resolution and P/B ratio so it is more suitable for the measurement of minor elements in concrete, such as chloride ions and alkalis, than EDS. This standard prescribes an area analysis method using WDS.

b) The term electron probe refers collectively to a focused beam of electrons used as a probe<sup>(2)</sup> and generated by an electron-optical device in the EPMA.

**Note** <sup>(2)</sup>: A probe is generally a needle or a similar device used for exploration. In the field of EPMA, the term electron probe means a focused beam of electrons.

c) Probe diameter is the diameter of the electron probe at the surface of the sample.

d) Electron-optical device is the component of the EPMA that produces the electron probe.

**e)** Probe current (beam current) is a measure of the quantity of electrons incident on the sample, expressed in the unit of current. Probe current density is the probe current per unit surface area.

**f)** Characteristic X-rays are X-rays of a wavelength characteristic of a particular chemical element. An atom of any element consists of an atomic nucleus with electrons orbiting it. When a high-energy electron beam is incident on an atom, inner-orbital electrons are scattered and electrons in outer orbitals drop down to fill the energy gaps. The X-rays produced during this process have a wavelength characteristic of the atom and corresponding to the difference in energy between the inner and outer orbitals and are referred to as characteristic X-rays.

**g)** A dispersion element is a component used to separate X-rays with the characteristic wavelength and isolate only the wavelength corresponding to the element under investigation. When characteristic X-rays are incident on the dispersion element, strong reflection takes place at a certain irradiation angle and the element of interest can be identified.

**h)** Point analysis refers to qualitative or quantitative analysis at a particular analysis point.

**i)** An analysis point is a point at which analysis is carried out.

**j)** Area analysis refers to a method of obtaining two-dimensional information about the kind and concentration of constituent elements by dividing the analysis area into elements called pixels and combining the results of point analysis at each analysis point.

**k)** Analysis area refers to an area in which an analysis is carried out.

**l)** Qualitative analysis refers collectively to any method of identifying the kind of constituent element at the point of analysis. In EPMA, the X-ray wavelength distribution is obtained by continuously changing the angle of the dispersion element and the position of the X-ray detector. The kind of element is then determined by comparing the wavelength distribution against the wavelength of a known element.

**m)** Quantitative analysis refers collectively to any analysis that determines the concentration of a constituent element at the point of analysis.

**n)** Pixel refers collectively to an element of a certain area obtained by dividing up the analysis area.

**o)** The peak is the specific irradiation angle at which the characteristic X-rays of the element under investigation peak in intensity when X-rays are incident on the dispersion element. Peak position refers to the dispersion element position at which the peak is obtained, corresponding to (a) in Figure 1.

p) Background refers to a range of irradiation angles around the peak over which X-ray intensities are at a constant low level. Background position refers to dispersion element positions used to evaluate the background X-ray intensity, corresponding to (b) and (c) in Figure 1.

q) Unit measurement time refers to the time taken to measure the intensity of characteristic X-rays on each pixel making up the area covered by area analysis. It is usually given in units of seconds.

r) Vapor deposition and sputtering are methods of depositing a thin film of conductive material on the surface of a non-conductive sample to provide it with conductivity. The vapor deposition method entails forming a thin film by heating a conductive material under high vacuum until evaporation and depositing the resulting vapor on the surface of the sample. Sputtering is a method in which atoms are dispersed from the surface of a conductive material through ion bombardment in a gas under low pressure and then deposited on the sample.

s) Vapor deposition material is the conductive material used in vapor deposition.

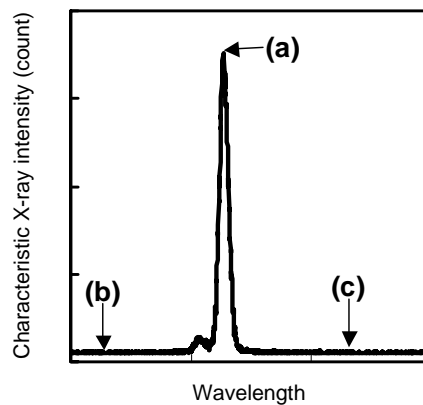


Figure 1 Peak (a) and background (b, c) of characteristic X-rays

#### 4 Principle

The area analysis of various elements in hardened concrete or mortar using EPMA involves the identification of the elements based on the characteristic wavelengths of X-rays emitted when a sample is irradiated with an electron beam. Information about element concentrations is obtained from characteristic X-ray intensities. When a solid sample is irradiated with an electron beam, each kind of atom present emits X-rays at its characteristic frequency. The elements present in the surface of the solid can be identified by analyzing the wavelengths of these characteristic X-rays. The intensity of each characteristic X-ray wavelength corresponds to the concentration of the constituent element at the point of irradiation. The concentrations of elements comprising the surface of the solid can therefore be determined by measuring characteristic X-ray intensities. Area analysis is carried out by sequentially irradiating the entire analysis area with an electron probe and measuring characteristic X-ray intensities. The results of this type of analysis are affected greatly by the method used to prepare samples and the analysis conditions.

## 5 Measuring equipment

The following equipment should be used to make measurements according to this standard.

### 5.1 EPMA

The EPMA consists of a wavelength-dispersive spectrometer, an electron-optical device, a sample chamber, a data processor and a vacuum pump as shown in Figure 2. The specifications of each item of equipment are described below.<sup>(3)</sup>

**Note** <sup>(3)</sup>: The EPMA should if possible be installed in an environment that undergoes minimal temperature variations, such as within  $\pm 2^\circ\text{C}$ .

#### a) Electron-optical device

The electron-optical device consists of an electron generator, an electron accelerator, a focusing lens to focus the electrons into the electron probe configuration, an objective lens, an aperture, an probe current meter and other components.<sup>(4)</sup>

**Note** <sup>(4)</sup>: Generally speaking, the electron beam accelerating voltage and probe current are in the range 5-25 kV and 1 nA-1  $\mu\text{A}$ , respectively. The electron-optical device must include a facility for measuring these values. Further, the device must allow for control of the electron probe diameter in the 1  $\mu\text{m}$  to 100  $\mu\text{m}$  range.

#### b) Sample chamber

The sample chamber must be large enough to allow analysis of the sample (that is, it must be twice as large as the sample) and include a mechanism for moving the sample.<sup>(5)</sup> The stage that supports the sample must have a clamping mechanism and at least three axes of movement in directions X, Y and Z.

**Note** <sup>(5)</sup>: The accuracy of stage position must correspond to the magnification factor: for instance, positional accuracy of the stage should be 1  $\mu\text{m}$  in a case where the stage moves over a measuring range of several centimeters.

#### c) Wavelength dispersive spectrometer

The wavelength dispersive spectrometer consists of a dispersion element and an X-ray detector to allow for analysis of the wavelengths and intensities of characteristic X-rays from the constituent elements.

#### d) Data processor

The data processor must save data output by the X-ray detector in digital form and provide functions for area and point analysis.

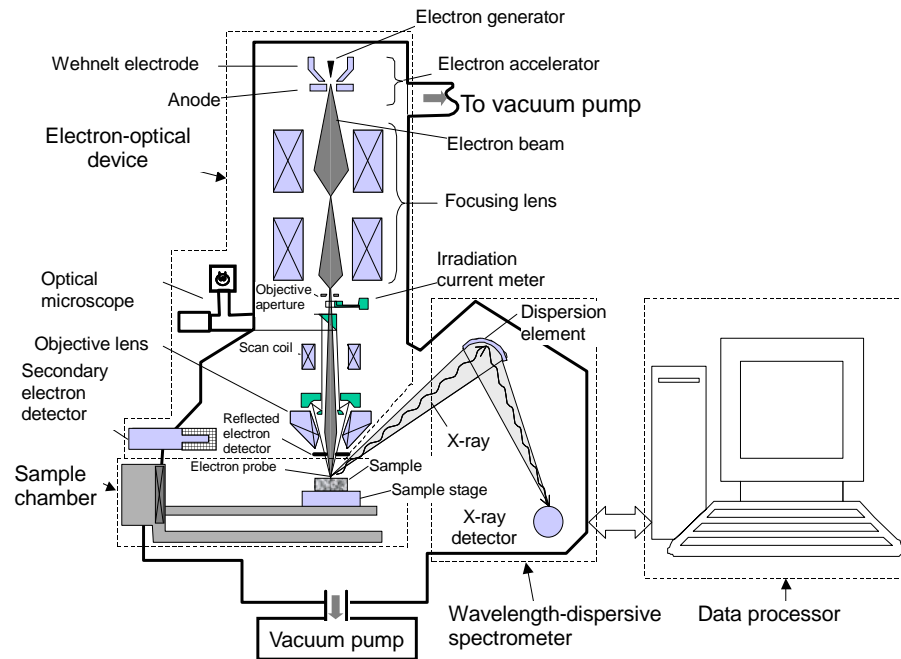


Figure 2 Configuration of EPMA

e) Vacuum pump

The vacuum pump must be capable of maintaining an appropriate vacuum in the EPMA chamber.<sup>(6)</sup>

**Note (6):** The EPMA chamber must be maintained under a vacuum at  $10^{-3}$ - $10^{-4}$  Pa.

## 5.2 Equipment for preparing samples for analysis

The equipment used to prepare samples for analysis should be as described below.

a) The concrete cutter must be capable of cutting a smooth-surfaced sample from a concrete specimen for analysis.<sup>(7)</sup>

**Note (7):** A dry or wet cutter is used according to the type of sample. A dry cutter is preferred because the movement of soluble elements is fully controlled during cutting. However, since the surface of the sample is ground in the next process, a wet cutter may be used except when the sample is porous. In this case, it is necessary to verify in advance that the elements to be measured are not affected by the cutting operation. If an oil cutter is used, it is necessary to pay attention to the cleaning and removal of oil from the sample.

b) The ultrasonic bath must be of suitable size for washing the entire sample.

c) The grinding machine must have sufficient capacity to grind the entire surface of the sample smooth.

d) The vacuum dryer should dry the sample under reduced pressure at normal temperature.<sup>(8)</sup>

**Note** <sup>(8)</sup>: The preferred pressure for vacuum drying is about  $10^{-3}$  Pa.

e) The vapor deposition or sputtering apparatus must be capable of depositing a suitable conductive material on the sample.

### 5.3 Reagents and abrasives

The reagents and abrasives used to prepare samples for analysis should be as described below.

a) Abrasives should have a suitable grain size and should finish the sample surfaces evenly.<sup>(9)</sup>

**Note** <sup>(9)</sup>: SiC powders (#240, #400, #800, #1500 and #3000), aluminum powders (#4000 and #10000) and diamond pastes (#4000 and #10000) may be used as abrasives.

b) Suitable organic solvents should be used in cleaning and grinding the sample.<sup>(10)</sup>

**Note** <sup>(10)</sup>: Kerosene and 2-propanol (isopropyl alcohol) are suitable for grinding and cleaning, respectively. Commercially available grinding solvents may also be used. Acetone and ethanol are not necessarily suitable because they dissolve alkalis.

## 6 Preparation of a sample for analysis

The standard procedure for preparing a sample for analysis is as follows.

a) Cut a sample<sup>(11)</sup> containing the analysis surface from the concrete specimen using a concrete cutter.<sup>(12)</sup> The size of the sample should be determined from the maximum aggregate size, the size of the EPMA sample chamber and the likely distribution range of elements to be measured.

**Note** <sup>(11)</sup>: Considering the ease of handling, samples should generally be 4 to 10 cm in width and 4 to 10 cm in length. Considering the drying time, possible drying deformation and ease of handling, samples should preferably be 1 to 2 cm in thickness. The analysis face and the opposite face must be as parallel as possible. The analysis face and the four adjoining sides must be cut as perpendicularly as possible to one another.

**Note** <sup>(12)</sup>: If a sample is easily misshapen or where the area to be analyzed is near the boundary between materials of different hardness, such as at the boundary between aggregate and cement paste, it is recommended that the sample be impregnated with resin. Before impregnating a cut sample with resin, it must be dried.

b) Grind the analysis surface smooth using a grinding machine. Obtain a smooth surface by grinding with abrasives of increasing fineness.<sup>(13), (14)</sup> When switching the abrasive grain size, as well as after grinding is complete, remove all abrasive material from the analysis surface using an organic solvent in the ultrasonic bath.

**Note** <sup>(13)</sup>: The smoothness of the analysis surface is crucial in area analysis. Hard aggregate particles are easily given a mirror finish whereas cement paste is readily scraped off by buffing, and this can cause a difference in level between the aggregate and paste.

**Note** <sup>(14)</sup>: Table 1 lists approximate standard abrasive grain sizes for final finishing according to the probe diameter.

Table 1 Approximate standard grain sizes for final finishing

Probe diameter	Grain size of abrasives
50-100 $\mu\text{m}$	#1000
10-50 $\mu\text{m}$	#3000
Order of one micrometer	#10000

c) Dry the ground sample completely in a vacuum dryer.<sup>(15)</sup>

**Note** <sup>(15)</sup>: The drying time varies with sample size and other factors. The estimated drying time for a 5 cm x 5 cm x 1 cm sample, for example, is over 24 hours. If drying is insufficient, it is likely that the required vacuum for vapor deposition or sputtering will not be obtained or the EPMA sample chamber may become contaminated with water vapor and other gases from the sample.

d) Deposit an appropriate conductive material<sup>(16)</sup> uniformly on the surface of the sample using a vapor deposition apparatus or a similar device.<sup>(17)</sup> Measure the thickness of the **vapor-deposited** conductive material using an appropriate method.<sup>(18)</sup>

**Note** <sup>(16)</sup>: The preferred conductive material is carbon, since variations in its thickness have little effect on characteristic X-ray intensities. Other suitable conductive materials include gold.

**Note** <sup>(17)</sup>: To prevent uneven deposition of, for instance, carbon, it is recommended that the sample be 10 to 15 cm distant from the **vaporization** point and that the sample be rotated perpendicular to the vapor flow during deposition.

**Note** <sup>(18)</sup>: To measure and ensure the thickness of **vapor deposition**, an opal glass having a droplet of diffusion pump oil on it is useful if it is set in the vapor deposition apparatus along with the sample. The **vapor deposition** thickness is measured and adjusted by comparing the color difference on the surfaces of the glass with or without a droplet of diffusion oil and with a separately prepared color sample.

## 7 Analysis of elements using the EPMA

a) In consideration of the analytical objectives, decide on the elements to be measured and the analysis conditions (accelerating voltage<sup>(19)</sup>, probe diameter, probe current, characteristic X-ray wavelengths, and the type of dispersion element).<sup>(20), (21)</sup>

**Note** <sup>(19)</sup>: The preferred accelerating voltage in the case of concrete is 15 kV.

**Note** <sup>(20)</sup>: The following points need to be taken into account in deciding on the analysis conditions.

(i) Probe diameter: From a macroscopic perspective, concrete comprises aggregate and cement paste, while on a microscopic level it consists of various fine minerals. Accordingly, the analytical objectives and the area of analysis need to be taken into account in deciding on the probe diameter.

(ii) Probe current: The intensity of X-rays to be measured is proportional to the probe current, so it is advantageous to increase the current in order to reduce measurement time and to measure trace elements. However, increasing the current excessively (to 1  $\mu$ A, for example) may result in damage to the sample or contamination of the sample chamber with emitted elements.

(iii) Kinds of elements to be measured: Samples containing such elements as Na, K, Cl and S (in the case of sulfates) are vulnerable to damage by electron probe irradiation, so characteristic X-ray intensities decrease after extended irradiation at high probe current densities. To measure these elements, it is necessary to choose a probe current density that is not too high and to increase the measurement time. Probe current density increases with a decrease in probe diameter at a constant probe current and with an increase in probe current at a constant probe diameter.

(iv) If characteristic X-ray intensities are too high, the emitted characteristic X-rays may be undercounted. Accordingly, it is necessary to adjust the analysis conditions so as to maintain characteristic X-ray intensities at an appropriate level. Alternatively, calibration calculations can be carried out to correct for the undercount.

**Note** <sup>(21)</sup>: Refer to Figure 3 for the procedure used to determine the conditions for area analysis.

**Remarks**: Table 2 lists standard measurement conditions for area and point analysis using EPMA.



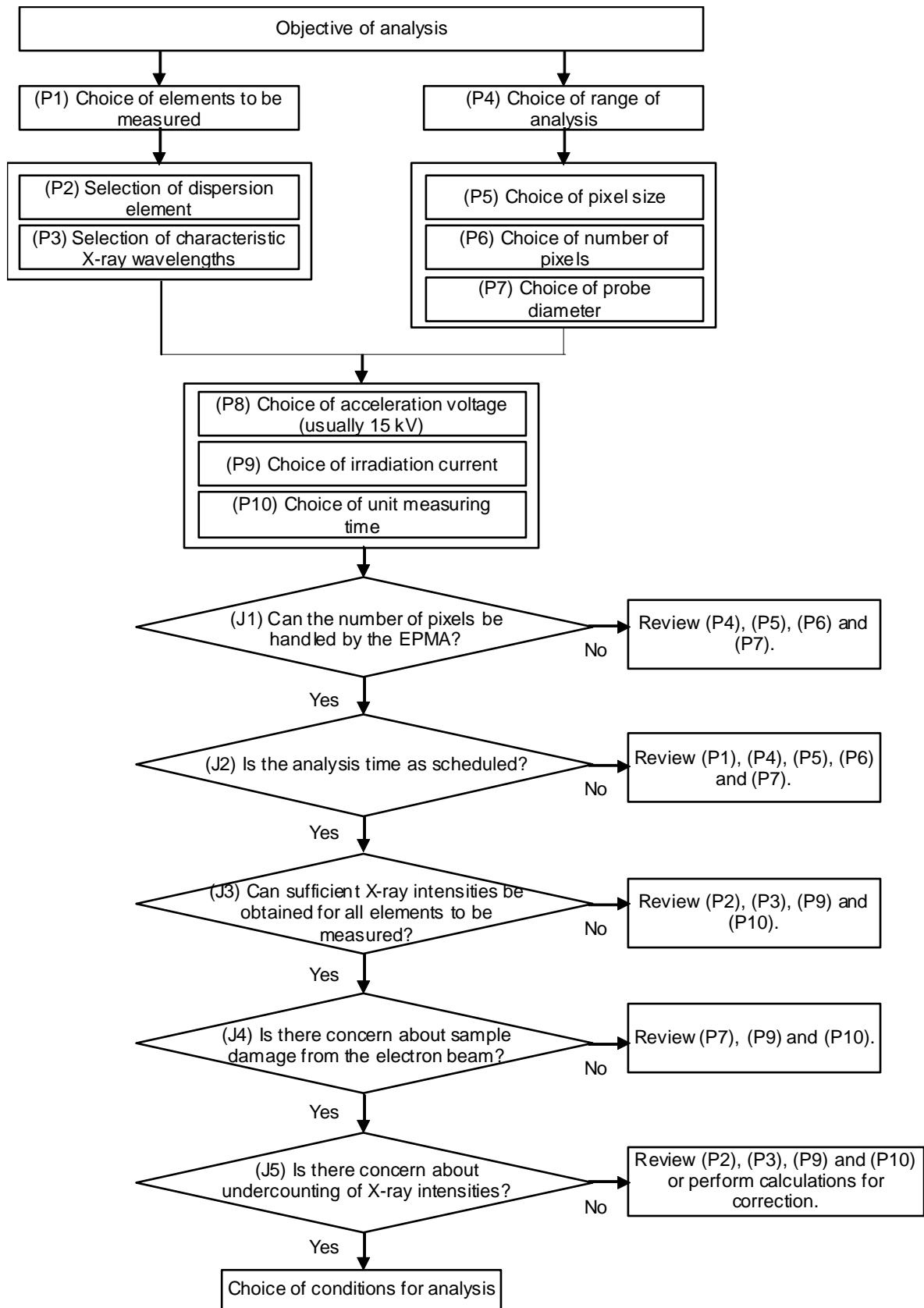


Figure 3 Flow diagram for determining area analysis conditions

Table 2 Standard measurement conditions for area and point analysis using EPMA

	Area analysis: Small area (cement paste and aggregate)	Area analysis: Large area (concrete and mortar sections)	Point analysis
Measuring range	0.4 x 0.4 to 4 x 4 mm	4 x 4 to 80 x 80 mm	ø0.1-10 µm
Pixel size	0.1-10 µm	10-100 µm	-
Accelerating voltage	15 kVA		15 kVA
Probe current	10-50 nA	50-300 nA	5-50 nA
Probe diameter	0.1-10 µm	10-100 µm	0.1-10 µm
Unit measuring time	30-50 ms		10-20 s
Movement of analysis point	Movement of sample stage		Fixed
Number of pixels (analysis points)	200 x 200 to 800 x 800		-

**b)** Before taking measurements, ensure that the probe current is stable.<sup>(22)</sup>

**Note** <sup>(22)</sup>: Because probe current is related proportionally to X-ray intensity, it is important to check that the current is stable. The probe current may vary if the vacuum changes during analysis. Accordingly, measurements should not be initiated until the current has stabilized. It is desirable to continue measuring the current even after the analysis is complete to make sure that it remains stable.

**c)** Secure the sample in a horizontal position on the sample holder<sup>(23)</sup> and adjust the holder until the electron probe is perpendicular to the analysis surface of the sample. Establish electric conductivity between the sample and the sample holder.<sup>(24)</sup>

**Note** <sup>(23)</sup>: Make sure the sample is firmly secured because the sample and holder unit move repeatedly in the EPMA sample chamber.

**Note** <sup>(24)</sup>: It is recommended that conductive paste or tape be used to establish electric conductivity between the sample and the sample holder.

**d)** After fitting the sample into the sample chamber, decide on the measurement range and confirm the coordinates of the sample.

**e)** Adjust the height of the sample using an optical microscope.

f) Carry out the point or area analysis according to the procedures below.

1) For point analysis, after confirming the characteristic X-ray wavelength of each element to be measured, first identify the peak and background positions. Once these are established, measure the X-ray intensities at the peak and background positions.

2) For area analysis, as with point analysis, first identify the peak and background positions for each characteristic wavelength. Then measure the X-ray intensities for each wavelength (element) at the peak and background positions to collect two-dimensional information on the plane to be measured.<sup>(25)</sup>

**Note** <sup>(25)</sup>: X-ray intensity is measured in the background position when it is necessary for quantitative analysis.

g) If quantitative analysis is required, carry out the analysis using one of the following three methods.<sup>(26)</sup>

1) Ratio method

A method of calculating the concentrations of elements in a sample based on measured characteristic X-ray intensities from a standard sample containing known concentrations of elements. This method is based on the assumption that the concentrations of elements in the analysis sample are proportional to the measured characteristic X-ray intensities obtained from the sample.

2) Linear calibration method

A method of calculating the concentrations of elements by preparing in advance several samples of similar chemical composition to the analysis sample but differing only in the concentrations of the elements to be measured. A calibration line is prepared based on the analysis results.

3) Theoretical correction method

A method of converting the measured characteristic X-ray intensities into the concentrations of elements in the sample using theoretical correction calculations based on the measured characteristic X-ray intensities obtained from a standard sample and the concentrations of elements in the standard sample.

**Note** <sup>(26)</sup>: Method 1) is a quick and simple quantitative analysis method applicable to various types of samples. A relative comparison can be made using a standard sample but absolute values are not necessarily guaranteed. Method 2) gives the most accurate values, but a sample with known concentration needs to be prepared. Method 3) is useful for the quantitative analysis of various samples from specific standard samples. As regards the accuracy of quantitative results, there is a long track record of quantitative analysis of minerals that do not contain voids or water. For minerals containing voids, such as cement hydrates, the accuracy of absolute values cannot be theoretically guaranteed, although it is possible to make relative evaluations.

h) Take measurements using standard samples when carrying out quantitative analysis by the ratio method or the theoretical correction method.<sup>(27)</sup>

**Note** <sup>(27)</sup>: It is desirable to use common materials as standard samples because the choice of a standard sample has a great influence on the quantitative determination. Example **elements** and standard samples are listed in Table 3.

Table 3 Example chemical elements and standard samples

Compound containing element to be measured	Standard sample	Chemical formula	Content (mass %)
SiO <sub>2</sub>	Wollastonite (tabular spar)	CaSiO <sub>3</sub>	50.9
Al <sub>2</sub> O <sub>3</sub>	Adularia (K-Feldspar)	KAlSi <sub>3</sub> O <sub>8</sub>	20.4
Fe <sub>2</sub> O <sub>3</sub>	Hematite (red hematite)	Fe <sub>2</sub> O <sub>3</sub>	99.9
CaO	Wollastonite (tabular spar)	CaSiO <sub>3</sub>	48.0
MgO	Periclase	MgO	99.99
SO <sub>3</sub>	Anhydrite (anhydrous gypsum)	CaSO <sub>4</sub>	58.8
Na <sub>2</sub> O	Albite (sodium feldspar)	NaAlSi <sub>3</sub> O <sub>8</sub>	11.5
K <sub>2</sub> O	Adularia (K-Feldspar)	KAlSi <sub>3</sub> O <sub>8</sub>	14.5
Cl	Halite (rock salt)	NaCl	60.7
TiO <sub>2</sub>	Rutile	TiO <sub>2</sub>	99.99
P <sub>2</sub> O <sub>5</sub>	Potassium titanium oxide phosphate	KTiOPO <sub>4</sub>	35.9
MnO	Manganosite	MnO	99.9
C	Calcite	CaCO <sub>3</sub>	12.0

1) Use the same probe diameter and probe current in measuring the standard sample as used with the analysis sample.<sup>(28)</sup>

**Note** <sup>(28)</sup>: The standard sample must be larger in size than the probe diameter and the surface to be measured must be even. Attention needs to be paid to the possibility of damage to the standard sample resulting from a high current density. Anhydrite (anhydrous gypsum) in particular is easily damaged. After a long period of irradiation or after irradiation at a high current density, Na and K exhibit a drop in X-ray intensity. Ideally, the area being measured should be changed every time a measurement is made. Great care needs to be taken in cases where the probe diameter is very small. If there is a great variation in element concentration between the standard sample and the analysis sample, the probe current may change.

2) For the measurement of the standard sample, first identify the peak and background positions for the elements to be measured and then measure characteristic X-ray intensities at the peak and background positions.<sup>(29)</sup>

**Note** <sup>(29)</sup>: To verify that measurement results do not vary widely, carry out measurements using the standard sample several times. The actual number of repeat measurements cannot be given definitively because it depends on the stability of the EPMA.

## **8 Data processing**

### **a) Point analysis**

Convert characteristic X-ray intensities into concentrations.<sup>(30)</sup>

### **b) Area analysis**

Convert characteristic X-ray intensities into concentrations with respect to each element to be measured by an appropriate method and express the concentrations in the form of a concentration distribution over the measured surface using a color scale.<sup>(30), (31)</sup>

**Note** <sup>(30)</sup>: Commercially available EPMA systems are outfitted as standard with data processing functions. The unit of concentration should be mass percentage or atomic percentage as appropriate in accordance with the analytical objectives.

**Note** <sup>(31)</sup>: To convert characteristic X-ray intensities into concentrations, the ratio method or linear calibration method is usually used. Refer to the appendixes for details. For the theoretical correction method, the software that comes standard with commercially available EPMA systems may be used.

## **9 Report**

### **9.1 Compulsory reporting**

The report must give the following information:

- a)** Name of the sample analyzed
- b)** Dimensions of the sample
- c)** Cutting method (wet, dry or other)
- d)** Grinding method (abrasive, solvent or other)
- e)** Type of **vapor-deposited** material
- f)** Image data and measurement conditions (name of analyzer, accelerating voltage, probe current, probe diameter, pixel size, unit measurement time, number of pixels and measurement range)
- g)** Data processing conditions (standard samples and method of quantitative determination)
- h)** Measurement results
- i)** Analysis data

### **9.2 As-needed reporting**

The report should give the following information where relevant:

- a)** Mix proportion of concrete specimen and surface coating material
- b)** Backscattered electron image of the analyzed sample
- c)** Photograph showing overall view of the concrete specimen before cutting out the sample for analysis
- d)** Conditions and results of data processing, if performed in accordance with **Appendix 3**

## Appendix 1: Method of converting area analysis data for elements into concentrations (Ratio method)

### 1 Scope

This appendix specifies the requirements for converting characteristic X-ray intensities obtained according to JSCE-G574-2005 "Area analysis method for chemical element distribution in concrete using EPMA" into mass percentages using the ratio method.

### 2 Standard samples

Standard samples corresponding to the elements to be measured as given in Table 3.

### 3 Required data

Characteristic X-ray intensities for each pixel and background X-ray intensities <sup>(1), (2)</sup> for each element in the analysis sample, as obtained in area analysis of the analysis sample, as well as mass percentages, characteristic X-ray intensities in the peak position and background X-ray intensities<sup>(1)</sup> of the elements in the standard sample.

**Note (1):** For background X-ray intensities, it is desirable to measure background intensity on both sides of the peak position and average the two measurements.

**Note (2):** For background X-ray intensities of elements in the analysis sample, measurements may be made at representative positions on the sample to reduce analysis time although intensities should ideally be measured in each pixel.

### 4 Conversion by the ratio method

**4.1** Determine first the relationship between characteristic X-ray intensity and mass percentage as shown in Figure 1 from the mass percentages, peak characteristic X-ray intensities and background X-ray intensities for each element in the standard sample. Then determine proportionality constant A as used in Equation (1).

$$I = A * C + B \tag{1}$$

where:

I = characteristic X-ray intensity of the element in the analysis sample (count/(ms•□A))<sup>(3)</sup>

C = mass percentage of element in the analysis sample (mass %)

A = characteristic X-ray intensity for the element in the peak position in the standard sample <sup>(3)</sup> minus the background X-ray intensity for the element in the standard sample <sup>(3)</sup> divided by the mass percentage of the element in the standard sample (count/(ms•mass %•□A))

B = background X-ray intensity of the element in the analysis sample (count/(ms•□A))<sup>(3)</sup>

**Note** <sup>(3)</sup>: A value normalized by measuring time (ms) and probe current (□A) is used as the unit of X-ray intensity.

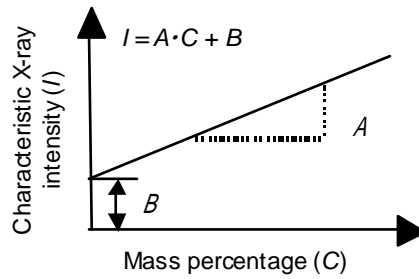


Figure 1 Relationship between characteristic X-ray intensity and mass percentage

**4.2** Use Equation (2) to convert characteristic X-ray intensities for the element in the analysis sample into mass percentages by the ratio method.

$$C = (I - B)/A \quad (2)$$

**4.3** Convert characteristic X-ray intensities in each pixel as obtained in the area analysis of the sample into mass percentages using Equation (2).<sup>(4)</sup>

**Note** <sup>(4)</sup>: Using the ratio method, relative concentrations of elements can be compared but absolute values cannot be guaranteed. However, the results of test measurements on an ordinary cement sample mixed with chloride ions indicate that the mass percentage determined by the ratio method agrees well with that determined by chemical analysis (Figure 2). That is, the mass percentage as determined by the method given here in Appendix 1 has a certain level of accuracy as an absolute value.

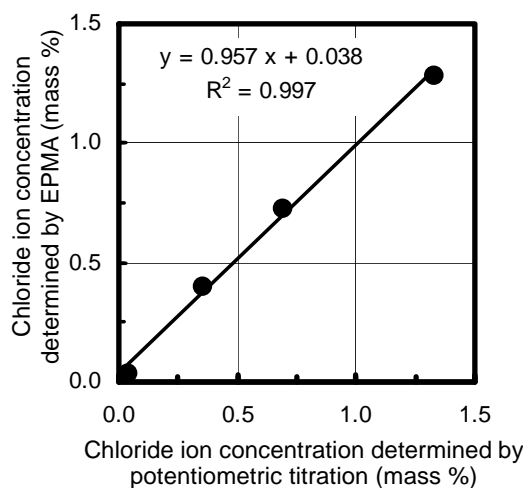


Figure 2 Comparison of mass percentage of chloride ions in ordinary cement paste determined by the ratio method with that by chemical analysis



## **Appendix 2 Method of converting area analysis data for elements into concentrations (Linear calibration method)**

### **1 Scope**

This appendix specifies the requirements for converting characteristic X-ray intensities obtained according to JSCE-G574-2005 "Area analysis method for chemical element distribution in concrete using EPMA" into mass percentages by the linear calibration method.<sup>(1)</sup>

**Note** <sup>(1)</sup>: The linear calibration method is used where mass percentages of the element are low, at several percent or less, or for trace elements. This method is effective for such elements in cement paste as Cl, S, Na and K.

### **2 Sample used for preparing calibration line**

**2.1** The sample used to prepare the calibration line (the standard calibration line sample) must be hardened cement paste containing the element to be measured. The mix proportion, type of powder (such as cement) and water-to-cement ratio of the standard calibration line sample must be equivalent to those of the analysis sample.<sup>(2), (3)</sup>

**Note** <sup>(2)</sup>: The preferred sample size is about 10 mm or greater in diameter. The standard calibration line sample must be prepared in the same manner as the sample for analysis.

**Note** <sup>(3)</sup>: If the mix proportion and the kind of cement in the analysis sample are unknown, ordinary Portland cement or other cement paste must be used in the standard calibration line sample. In this case, an error may be introduced. Accordingly, it is necessary to report on the standard calibration line sample used in Section 9.1 Compulsory reporting g).

**2.2** At least four standard calibration line samples with different concentrations of the element to be measured must be prepared, using concentrations in a range close to the concentration in the analysis sample.<sup>(4)</sup> Two sets of the standard calibration line samples must be prepared with each concentration, for chemical analysis and EPMA analysis.

**Note** <sup>(4)</sup>: It is desirable that the calibration line is prepared from data for the element in the same concentration range as in the analysis sample.

### **3 Required data**

Characteristic X-ray intensity in each pixel obtained from area analysis of the analysis sample and the calibration line obtained from the separately prepared standard calibration line samples.

### **4 Preparation of calibration line and conversion method**

Prepare the calibration line using the same EPMA equipment used to measure the analysis sample.

**4.1** Measure the mass percentages of the element in one set of the standard calibration line samples by chemical analysis.

**4.2** Carry out area analysis of each standard calibration line sample with the same EPMA equipment used to measure the analysis sample. Ensure the same measurement conditions are used in accordance with the methods specified in this standard.

**4.3** Average the characteristic X-ray intensities for all pixels obtained in the area analysis of each standard calibration line sample with a different concentration of the element. Plot the relationship between averaged characteristic X-ray intensity and mass percentage measured by chemical means in Section 4.1 for the standard calibration line samples, as shown in Figure 1. Derive a regression formula by linear regression and use the formula as the calibration line.

**4.4** Convert the characteristic X-ray intensity for each pixel obtained from area analysis of the analysis sample into mass percentages using the calibration line obtained in Section 4.3.

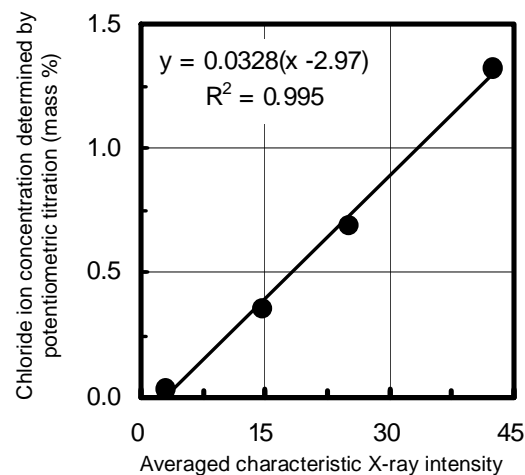


Figure 1 Example calibration line obtained by the use of a cement paste.

(The regression constant varies with measurement conditions.)

## **Appendix 3 Method of preparing concentration distribution of element in concrete using EPMA**

### **1 Scope**

This appendix specifies the requirements for preparing the concentration distribution of a specific element from the results of area analysis obtained according to JSCE-G574-2005 Appendix 1 or 2 and converting it into mass percentages of the element in the analysis sample.

### **2 Required data**

Results of area analysis obtained in Appendix 1 or 2 and converted into mass percentages.

### **3 Method**

Determine the orientation of the required concentration distribution in the area of analysis and average the concentration in each pixel in the direction perpendicular to the concentration distribution.<sup>(1), (2)</sup>

**Note (1):** An example is shown in Figure 1. To prepare a concentration distribution in the X direction, average measurements in the Y direction in Figure 1(a). It is desirable to average as large a number of pixels as possible.

**Note (2):** The data interval (positional resolution) in the direction of the required concentration distribution (the X direction in Figure 1(a)) may be changed as needed. As an example, Figure 1(b) shows a concentration distribution in the X direction obtained by averaging measurements in the Y direction based on the results of area analysis with a pixel size of 0.1 mm. Figure 1(c) shows the results of averaging data at five points in the X direction with a data interval of 0.5 mm. Smooth concentration distribution curves can be obtained by these methods.

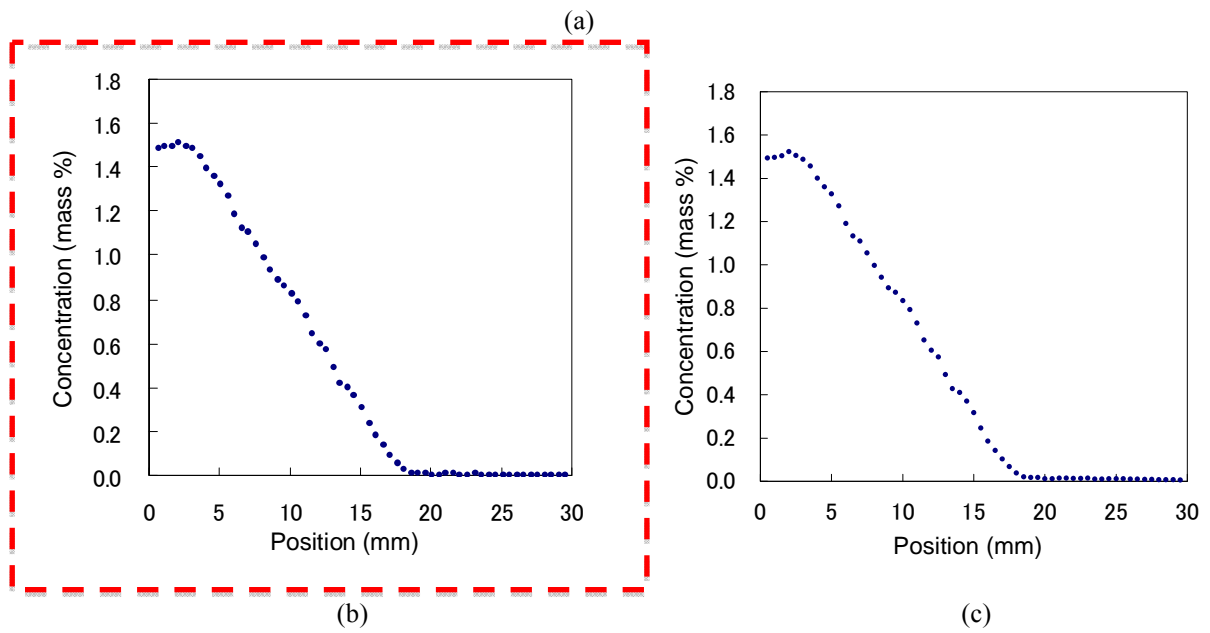
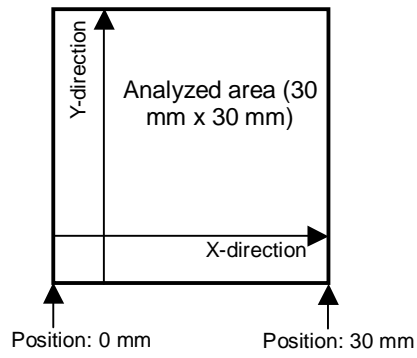


Figure 3-1 Example of concentration distribution preparation (a) Directions of analysis,  
 (b) Concentration distribution in the X direction (positional resolution: 0.1 mm),  
 (c) Concentration distribution in the X direction (positional resolution: 0.5 mm)