Forensic Discrimination of Concrete Pieces by Elemental Analysis of Acid-soluble Component with Inductively Coupled Plasma–Mass Spectrometry

Masaaki Kasamatsu, Takao Igawa, Shinichi Suzuki, and Yasuhiro Suzuki

National Research Institute of Police Science, 6-3-1 Kashiwanoha, Kashiwa, Chiba 277-0882, Japan

Since fragments of concrete can be evidence of crime, a determination of whether or not they come from the same origin is required. The authors focused on nitric acid-soluble components in the fragments of concrete. As a result of qualitative analysis with ICP-MS, it was confirmed that elements such as Cu, Zn, Rh, Sr, Zr, Ba, La, Ce, Nd, and Pb were contained in the fragments. After the nitric acid-soluble components in the fragments of concrete were separated by dissolving them in nitric acid, the concentrations of these elements in the dissolved solution were quantitatively determined by ICP-MS. The concentration ratios of nine elements compared to La were used as indicators. By comparing these indicators, it was possible to discriminate between the fragments of concrete.

Keywords: Concrete, elemental analysis, forensic discrimination, ICP-MS

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Eight kinds of concrete pieces were collected or purchased randomly from available commercial samples, as shown in Table 2. One dry mortar premixed with cement and aggregate was also purchased and used for this research.

**Sample preparation**
A small piece of concrete was chiseled from five different points. Samples collected from each site were individually decomposed. Approximately 100 mg of a concrete piece was placed in a plastic tube; 1 mL of pure water and 1 mL of concentrated nitric acid were sequentially added and left overnight for obtaining an acid soluble fraction. The insoluble aggregate was removed by filtration (qualitative filter paper, ADVANTEC, Tokyo, Japan), and the filtrate—that is, the nitric acid soluble component of the concrete—was separated. The resulting solution was made up to 50 mL, further diluted if necessary, and qualitative and quantitative analyses were performed by ICP-MS. The insoluble aggregate was approximately 60 to 70% by weight for each concrete piece.

**Results and Discussion**

**Effect of curing the cement**
Concrete is prepared by mixing aggregate, cement, and water. The object to be analyzed is the concrete after curing. Here, since the curing of cement is a chemical reaction, there is a possibility that differences may result in the elements detected due to the influence of curing. Therefore, in order to confirm this point, pretreatment and analysis by this method were carried out on the dry mortar sample before and after curing. The obtained spectra are shown in Fig. 1. It should be noted that there was little difference in the shape of the spectra obtained. The detected element was quantified and the profile normalized with La concentration, as shown in Fig. 2. Thus, curing cement does not affect the obtained results.

**Qualitative analysis by ICP-MS**
In a homogeneous sample such as glass or metal, it is possible to discriminate by sampling a part of the material and completely dissolving and examining the trace elements. However, in heterogeneous samples, such as in the case of
concrete, variation of elemental composition due to the difference of sampling point is too large to get a representative value for discrimination between samples. For this reason, the acid-soluble components in the concrete were selected for analysis. As cement is mixed and agitated with aggregate and water when preparing concrete, the fluid part that includes the cement can be considered close to homogenous in the sample batch. Therefore, it was presumed that discrimination among these samples could be performed by utilizing elemental information of only the cement part of the concrete.

The qualitative analysis of the cement acid-soluble fraction confirmed that the fraction contained Cu, Zn, Rb, Sr, Zr, Ba, La, Ce, Nd, and Pb. An example of the result of the qualitative analysis by ICP-MS is shown in Fig. 3. Many peaks were observed in each sample in addition to the strong peaks of Sr and Ba. The same kinds of elements were found among different samples in this experiment. Thus, elements that could be used as indicators were selected and quantified.

Evaluation and discrimination method

In order to calculate the quantitative value from the measured value of the solution, it was premised that the weight of the sample dissolved was known. In this case, part of the sample was dissolved, and, considering the influence of moisture contained in the sample and foaming during dissolution, it was impossible to calculate the weight of only the dissolved part of the sample. However, even if the dilution factor was unknown, the proportion of contained elements should be constant. We surmised that indices could be obtained by standardization with specific elements. La was selected as the normalizing element, which had a high signal intensity and a small deviation in the sample. The result of normalizing each element with La is shown in Fig. 4. Each sample is shown as the mean ± SD of the normalized values. In addition to the measurement error, the error ranges were affected by heterogeneity due to the difference in sampling position; therefore, a large deviation might be observed. However, differences were found in the normalized values between the samples, and discrimination was performed using this value as an indicator.

Discrimination between the samples was performed by the following procedure with reference to the previous studies.25–27 First, a range of the average value ± 2SD was calculated for each sample, and the ranges between two samples were compared. If they did not overlap, a sufficient difference existed, and so it was determined that it could be discriminated.

Fig. 3 Mass spectrum of sample No. 3 by ICP-MS.

Fig. 4 Analytical results for different concrete samples by ICP-MS. The error bar for each column corresponds to SD.
If the ranges overlapped, a sufficient difference was not recognized between the examined samples and it was determined that it was difficult to distinguish. Discrimination between the two samples of interest was carried out for all combinations. The results are shown in Fig. 5. The symbol “D” indicates a discriminable pair determined by the method described above, and the symbol “N” indicates a non-discriminable pair. For example, the range of the indicator of Cu for samples 1 and 2 did not overlap, so they could be distinguished. Also, as the range of Ba for sample 8 was very large, it could not be discriminated in any sample.

In the case of using a single indicator, there were many combinations that could not be distinguished, and the discrimination power between samples was insufficient. Through considering the discrimination between samples, the discrimination power could be improved by combining the nine indicators. If there was more than one indicator that did not overlap in the range of 2 SD, they were judged as discriminable. The results are shown in Fig. 6. Out of 28 combinations, 26 pairs (about 93%) could be discriminated. In this way, by combining indices, the discrimination power was significantly improved. There were two indistinguishable combinations, but these might have been made from the same lot of raw materials. It was difficult to find differences in these products purchased from the same store because many commercially available concrete blocks might be produced at the same time. In fact, when analyzing three concrete blocks obtained from the same shelf, the samples were not distinguishable from each other (data not shown). This result not only shows that this method could distinguish different samples, but also that the samples from the same origin could be “the same”.

### Conclusions

We focused on acid-soluble components that were part of concrete pieces and found that forensic discrimination could be performed by comparing their combination of characteristic ratios. In order to minimize the influence of the aggregate, we did not completely dissolve the sample and targeted only the acid-soluble component—cement. Since cement could be considered close to homogeneous when making concrete, focusing on this part was appropriate for forensic discrimination. Because this is a comparison of ratio combinations, it is an excellent method that can be easily pretreated without concern for the dilution ratio of the sample.
References