# Measurement of Zeolite, Silicate, and Phosphate in Laundry Detergent Products by Inductively Coupled Plasma Atomic Emission Spectrometry

**Akihiko Kawauchi* and Masahiro Ishida**

Procter and Gamble Asia, Research and Development Department, Kobe Technical Center, Kobe, Japan

**ABSTRACT:** This paper reports the development of a method for simultaneously measuring zeolite, silicate, and phosphate in laundry detergent products by inductively coupled plasma atomic emission spectrometry. A sample is decomposed under alkaline oxidative conditions to decompose zeolite, silicate, phosphate, and organic substances. Then hydrochloric acid is added to the decomposed solution to dissolve aluminum hydroxide precipitate before analysis. This sample preparation procedure was investigated by using a total organic carbon analyzer and was confirmed to be applicable to simultaneous measurements of zeolite, silicate, and phosphate. Relative standard deviation for the analysis is less than 2.1%, recovery is more than 99.0%, and the calibration curve gives a correlation coefficient of $R = 1.000$. The detection limit of this method for aluminum and silicon is 0.1%, and for phosphorus, 0.2% by weight in the product. This method is applicable to various laundry detergent products that contain zeolite, silicate, or phosphate and is five times faster than the three wet chemical methods.

*JAOCS 73,* 131–135 (1996).

**KEY WORDS:** Aluminum, analysis, autoclave, inductively coupled plasma spectrometry, laundry detergent, phosphate, silicate, zeolite.

Before the modern synthetic detergent industry was developed, soap products were made with sodium salts of silicates and carbonates. These alkaline builders helped disperse the soap, enhanced their reaction with calcium and magnesium, and acted directly on fatty acid soils to increase their removal (1–4). These buffering builders are still important parts of modern detergent formulations.

Free calcium and magnesium hardness is present in surface water and is also found in home water supplies in varying amounts, depending on geographic area and type of water treatment used. The primary function of a detergent builder is to reduce the free calcium and magnesium ion concentrations in the washing solution. The successful development of synthetic detergents began with the invention of sodium tripolyphosphate as a builder for anionic surfactant systems. This phosphate species became a basic ingredient for essentially all heavy-duty laundry granule products throughout the world and was unequaled in its cleaning effectiveness, low cost, human safety, and good physical properties, until concerns about its contribution to the eutrophocation process were raised in heavily populated areas of developed countries.

The most commonly used nonphosphate builders are the sodium aluminum silicates, also known as zeolites (4). These materials are insoluble particles that can exchange sodium ions in their crystalline structure for calcium ions. Magnesium ions are not exchanged by zeolite, so other builders must also be used for the detergent for effective performance in most areas of the world.

The most widely used methods for zeolite, silicate, and phosphate quantitation are titration methodology for aluminum in zeolite, gravimetry for silicon in zeolite and silicate ,and colorimetry for phosphorus in tripolyphosphate (5). Zeolite is calculated based on the results for aluminum. The assumption of the conversion calculation made is that zeolite A ($Na_{12} Al_{12} Si_{12} O_{48} \cdot 27H_2O$) is used in detergent products (5). In fact, almost all detergent products with zeolite technology contain zeolite A because of its high calcium exchangeability and low price (6,7). If another type of zeolite is used in a detergent product, the conversion formula must be changed to reflect the difference in molecular formula. Silicate is calculated from the difference between total silicon and the silicon calculated to be contained in the zeolite based on the aluminum measurement. In previous methods used to quantify builders by inductively coupled plasma atomic emission spectrometry (ICP-AES), two different sample preparations were used for water-soluble (silicate and phosphate) and insoluble builders (zeolite) (8). Those solutions were then separately measured by ICP-AES.

The method described in this paper quantitates the three builders with one sample preparation. Surfactants are decomposed in the process of sample preparation, so no physical interference need be considered. The external standard method of quantitation can be applied to the analysis.

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*To whom correspondence should be addressed at Procter and Gamble Asia, Research and Development Department, Kobe Technical Center, 17, Koyocho, Naka 1-chome, Higashinada, Kobe 658, Japan.

## EXPERIMENTAL PROCEDURES

*Reagents and materials.* The following reagents were purchased from Wako Pure Chemical Co. (Osaka, Japan): aluminum, silicon, and phosphorus standard solutions (1,000 mg/L); potassium persulfate; sodium hydroxide; hydrochloric acid; sulfuric acid; dodecyl benzene sulfonic acid (sodium salt); zeolite (A-4) powder; sodium phosphate (anhydrous); sodium chloride; and sodium silicate. Sodium sulfate (anhydrous) and nitric acid were purchased from Kantoh Chemical Co. (Tokyo, Japan). Sodium carbonate and polyethylene glycol 2000 were purchased from Nacalai Tesque Co. (Kyoto, Japan). Deionized water was prepared with a Milli-Q SP reagent water system from Nippon Millipore Ltd. (Tokyo, Japan).

*Apparatus.* Aluminum, silicon, and phosphorus measurements were accomplished with an inductively coupled plasma atomic emission spectrometer (ICP-AES, model SPS-4000; Seiko Instruments, Tokyo, Japan) and a computer (PC-9801FA; NEC, Tokyo, Japan) for data collection. Sample decomposition was accomplished with an autoclave (Model SS-325; Tomy Seiko Co., Ltd., Tokyo, Japan) and a 100-mL teflon vessel (NR-216-05; Flonchemical Inc., Osaka, Japan). Total organic carbon (TOC) measurements were accomplished with a TOC analyzer (TOCA, model TOC-5000; Shimadzu Co., Kyoto, Japan). Analytical conditions of the ICP-AES were as follows: wavelengths used for measurements were Al (396.152 nm), Si (212.412 nm), and P (213.618 nm); measuring height was 10 mm; gas flows were carrier gas (1.0 L/min), plasma gas (16 L/min), and support gas (0.5 L/min); slit was 20 μm; integral time was 2 s × 3 times.

*Preparing standard solutions, blank solution, and decomposition reagent.* Standard solution A was prepared by mixing commercial traceable standard solutions (1,000 mg/L) of aluminum, silicon, and phosphorus and diluting them tenfold with 1:100 N hydrochloric acid. This solution contained 100.0 mg/L of Al, Si, and P.

Standard solution B was prepared by diluting standard solution A tenfold with 1:100 N hydrochloric acid. This solution contained 10.0 mg/L of Al, Si, and P.

Standard solution C was prepared by mixing 5 mL Al, 15 mL Si, and 8 mL P traceable standard solutions (1,000 mg/L) in a 100-mL volumetric flask, then made to volume with 1:100 N hydrochloric acid. This solution contained 50.0 mg/L Al, 150 mg/L Si, and 80.0 mg/L P.

A blank solution was prepared by mixing 30 g sodium dodecyl benzene sulfonate, 24 g sodium sulfate, 15 g sodium carbonate, and 1 g polyethylene glycol 2000. Three grams of this blank was weighed and transferred to a 1,000-mL volumetric flask with about 700 mL deionized water, then mixed well. The flask was then made to volume with deionized water and labeled as blank solution.

The decomposition reagent was prepared by dissolving 4.0 ± 0.1 g potassium persulfate and 5.0 ± 0.1 g sodium hydroxide in a 100-mL nalgene volumetric flask, then making it to volume with deionized water.

*Preparing test solutions for investigating residual TOC vs. initial organics concentration.* Twenty grams of a commercially available laundry detergent was weighed and transferred to a 1,000-mL volumetric flask with about 700 mL deionized water, then mixed well to dissolve. The flask was made to volume with deionized water and labeled as solution D.

Ten milliliters of solution D was pipetted into a 500-mL volumetric flask. The flask was then made to volume with deionized water and labeled as solution E.

Aliquots of solution D (2, 3.5, 5, 10, 25, and 50 mL) and of solution E (25 and 50 mL) were pipetted into eight teflon vessels. Ten milliliters of the decompositional reagent was added to each vessel and diluted to 60 mL with deionized water. Eight bottles were kept at 110°C for 1 h in an autoclave. After each vessel was cooled, 40 mL HCl solution (1:1) was added to it for TOC measurement.

*Preparing test solutions for investigating residual TOC vs. decompositional time.* Three grams of a commercially available laundry detergent was weighed and transferred to a 1,000-mL volumetric flask with about 700 mL deionized water, then mixed well. The flask was then made to volume with deionized water. Ten milliliters of this solution and 10 mL of decompositional reagent were pipetted into six teflon vessels. Forty milliliters of deionized water was added to each teflon vessel. Six bottles were sealed and separately kept at 110°C for 2, 5, 10, 30, 60, and 120 min in an autoclave. After each vessel was cooled, 40 mL HCl solution (1:1) was added for TOC measurement.

*Preparing test solutions for investigating residual TOC vs. chloride ion concentration.* Ten milliliters of blank solution and 10 mL of decompositional reagent were pipetted into six teflon vessels. Then, 10% sodium chloride solution was added to them as follows: 0.025, 0.050, 0.10, 0.20, 0.50, and 1.0 wt/vol% as chloride ion concentration; then the solutions were made to 100 mL. Each solution was diluted to 60 mL with deionized water. The teflon vessels were kept at 110°C for 1 h in an autoclave. After each vessel was cooled, 40 mL HCl solution (1:1) was added for TOC measurement.

*Preparing solutions for physical interferences investigation.* Ten milliliters of standard solution C was added to five 100-mL volumetric flasks. Hydrochloric acid and deionized water were put in the flasks as follows: 1, 2, 5, 10, and 17 wt/vol% as HCl concentration. In the same manner, standard solution C with sulfuric acid and with nitric acid solutions were prepared. A solution with no added acid was prepared by putting 10 mL standard solution C in a 100-mL volumetric flask, then making it to volume with deionized water. These 16 solutions were measured by ICP-AES for investigating physical interferences.

*Preparing test solutions for investigating zeolite decomposition.* One gram of zeolite was added to 9 g blank solution, then mixed well. Three grams of this mixture was weighed and transferred to a 1,000-mL volumetric flask, mixed to dissolve, and made to volume with deionized water. Ten milliliters of this solution, 10 mL decomposition reagent, and 40 mL deionized water were added into a teflon vessel. The vessel was kept at 110°C for 1 h in an autoclave. Then 40 mL HCl solution (1:1) was pipetted into the teflon vessel, and the solution was mixed for 20 min at room temperature. This solution was measured by ICP-AES for investigating zeolite decomposition.

*Preparing linearity-test solution.* Aliquots of standard solution A (6 and 18 mL) and of Standard solution B (1.0, 5.0, 10, and 30 mL) were pipetted into six 100-mL volumetric flasks. Ten milliliters of decomposition reagent and 40 mL HCl solution (1:1) were added into each volumetric flask and then made to volume with deionized water. These solutions contained 0.10, 0.50, 1.00, 3.00, 6.00, and 18.0 mg/L of Al, Si, and P.

*Preparing recovery-test solution.* Aliquots of standard solution A (6 and 18 mL) and of standard solution B (1.0, 5.0, 10, and 30 mL) were pipetted into six 100-mL teflon vessels. Ten milliliters of blank solution and 10 mL decomposition reagent were added into each teflon vessel and diluted to 60 mL with deionized water. The teflon vessels were kept at 110°C for 1 h in an autoclave, then cooled. Forty milliliters of HCl solution (1:1) were pipetted into each teflon vessel and mixed for 20 min at room temperature. The recovery test solutions were equivalent to 0.10, 0.50, 1.00, 3.00, 6.00, and 18.0 mg/L levels of Al, Si, and P.

*Sample preparation for commercial-product analysis.* Three grams of a commercial product sample were accurately weighed and transferred to a 100-mL volumetric flask, mixed to dissolve, and made to volume with deionized water. Ten milliliters of this solution, 10 mL decomposition reagent, and 40 mL deionized water were added into a teflon vessel. The vessel was kept at 110°C for 1 h in an autoclave. Then 40 mL HCl solution (1:1) was pipetted into the teflon vessel, and the solution was mixed for 20 min at room temperature. This solution was measured by ICP-AES.

## RESULTS AND DISCUSSION

*Investigating organic substances decomposition.* Surfactants change viscosity, surface tension of a solution, and also the particle size of any aerosol generated from a solution. This results in an intensity difference between the sample and a standard solution, unless the standard solution contains the exact amount of surfactants as the sample solution. It is not feasible to add the same amount of surfactants to a standard solution because the formula of the product may not be accurately known.

Decomposition of organic substances, such as surfactants, under the sample preparation conditions described in this paper, was investigated. Figure 1 plots initial sample concentration vs. residual organics with a fixed decomposition time. Figure 2 plots decomposition time vs. residual organics, provided that initial organics concentration remains constant.

Commercially available detergents contain chloride as an impurity. It usually comes from the process water or inorganic raw materials. Its level varies with each product, with a maximum 1.0%. In general, chloride ion is oxidized by persulfate in acidic conditions (9). Organic substances should be decomposed under alkaline conditions when a sample contains halide. Figure 3 plots initial chloride ion concentration vs. residual organics, provided that initial organics concentration remains constant. It shows that the presence of chloride ion does not interfere with the oxidization of organics when sample preparation is carried out as described in this paper.

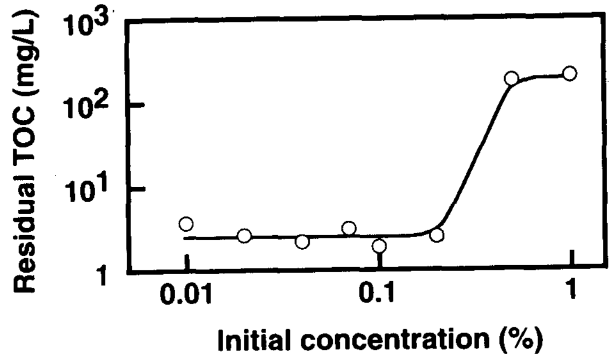

**FIG. 1.** Plot of initial sample concentration vs. residual organics; TOC, total organic carbon.

*Investigating physical interferences.* Solution viscosity, based on type and concentration of acid, affects particle size of the aerosol in an ICP nebulizer. This particle size is directly related to ICP signal intensity. This physical interference was investigated. Figures 4–6 plot ICP signal intensities vs. concentrations of hydrochloric, nitric, and sulfuric acids. These figures show that ICP signal intensities reached a plateau at 6% hydrochloric and nitric acids. Hydrochloric acid was used for this investigation.

*Investigating zeolite decomposition.* Decomposition of zeolite by the sample preparation procedure described in this paper was investigated. Zeolite was standardized by determining aluminum with the Japanese Industrial Standard (JIS) K-3362 method. Silicon in zeolite was calculated based on the zeolite A molecular formula ($Na_{12}\,Al_{12}\,Si_{12}\,O_{48}\cdot 27H_2O$). Table 1 shows the recovery of aluminum and silicon in zeolite. Percentage of recoveries of aluminum and silicon were more than 99% at any concentration. Both aluminum and silicon can be completely recovered with the sample preparation procedure described in this paper.

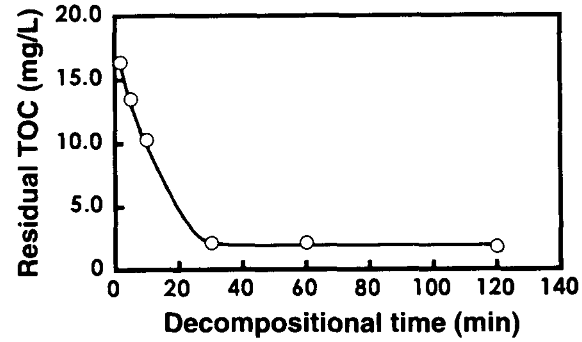

**FIG. 2.** Plot of decompositional time vs. residual organics. Abbreviation as in Figure 1.

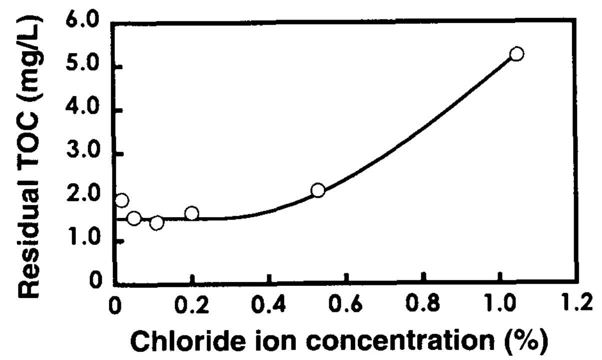

**FIG. 3.** Plot of chloride ion concentration vs. residual organics. Abbreviation as in Figure 1.

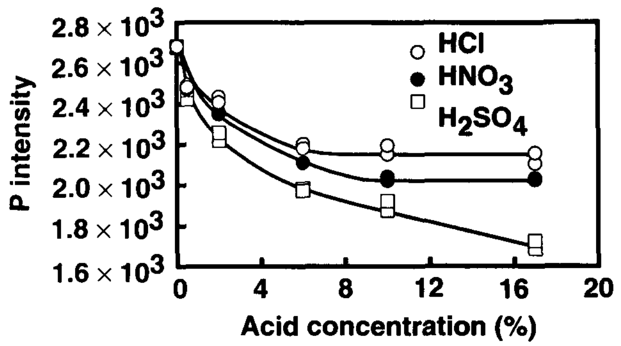

**FIG. 6.** Plot of acid concentration vs. inductively coupled plasma intensity of P.

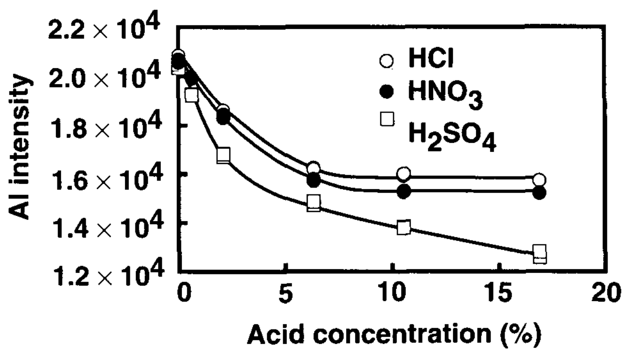

**FIG. 4.** Plot of acid concentration vs. inductively coupled plasma intensity of Al.

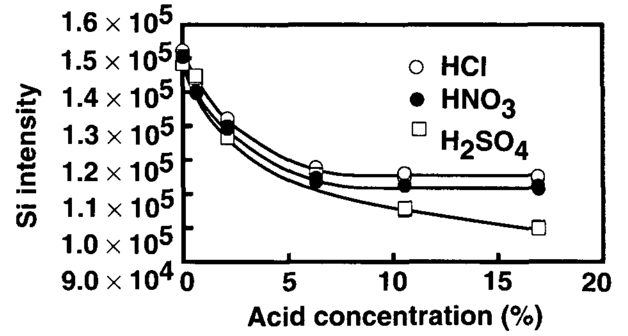

**FIG. 5.** Plot of acid concentration vs. inductively coupled plasma intensity of Si.

*Linearity and precision.* Calibration data obtained from the linearity test solution for aluminum, silicon, and phosphorus gave straight lines: aluminum, $Y = 5{,}100X + 14$ ($R = 1.000$); silicon, $Y = 7{,}500X + 1{,}300$ ($R = 1.000$); and phosphorus, $Y = 180X - 7.5$ ($R = 1.000$). Relative standard deviation of the measurements at each level is less than 3.0%. Based on the precision of those measurements, the limit of detections (LOD) were calculated as 0.1% for aluminum, 0.1% for silicon, and 0.2% for phosphorus (w/w) in the product.

The LOD was calculated from the following equation, where $yi$ is the number obtained empirically and $\hat{yi}$ is the number derived from the following calibration equation (10):

$$\mathrm{LOD} = 3 \times \left( \frac{\sum (yi - \hat{yi})^2}{n-2} \right)^{1/2} \qquad [1]$$

*Accuracy (investigating recovery and interferences).* Recovery data obtained from recovery test solutions for the three elements gave straight lines: aluminum, $Y = 5{,}100X - 160$ ($R = 1.000$); silicon, $Y = 7{,}500X + 950$ ($R = 1.000$); and phosphorus $Y = 180X - 11$ ($R=1.000$). As described in the Experimental Procedures section, a blank solution of known composition was used for this test to investigate the possibility of chemical and ionizational interferences between the three elements and the matrix. The recovery lines show that there are negligible interferences between the elements and the matrix, and an external standard quantitation method is applicable to this measurement.

**TABLE 1**

**% Recovery, Calculated by Dividing % Zeolite Determined by ICP Method with % Zeolite Determined by JIS K3362, Then Multiplying by 100**[a]

| Zeolite lot | % Zeolite determined by JIS K3362 | % Zeolite calculated with Al value determined by ICP method | % Recovery | % Zeolite calculated with Si value determined by ICP method | % Recovery |
|---|---|---|---|---|---|
| 1 | 99.2 | 98.6 | 99.4 | 99.8 | 100.6 |
| 2 | 98.9 | 98.5 | 99.6 | 99.5 | 100.6 |
| 3 | 99.2 | 98.3 | 99.1 | 98.8 | 100.6 |
| 4 | 98.7 | 98.4 | 99.7 | 98.4 | 99.7 |
| Average of % recovery | | | 99.5 | | 100.4 |

[a] ICP, inductively coupled plasma; JIS K3362, Japanese Industrial Standard (Ref. 5).

**TABLE 2**
**Six Commercially Available Products, Analyzed by Wet Chemical Methods[a] and the Method Described in This Paper**

| Sample | Method used | Zeolite (%) | Total silicate (%) | Phosphate (%) |
|---|---|---|---|---|
| A | Wet chemical method | 20.0 | 12.3 | |
| | ICP method | 20.5 | 11.9 | |
| B | Wet chemical method | 9.2 | 11.3 | |
| | ICP method | 8.9 | 11.3 | |
| C | Wet chemical method | 4.5 | 6.5 | 21.1 |
| | ICP method | 4.2 | 6.3 | 20.8 |
| D | Wet chemical method | 33.7 | | 3.5 |
| | ICP method | 33.3 | | 3.6 |
| E | Wet chemical method | | 14.1 | 6.9 |
| | ICP method | | 14.4 | 7.2 |
| F | Wet chemical method | | | 21.9 |
| | ICP method | | | 21.7 |

[a] Wet chemical methods used: titration methodology for zeolite (JIS K3362 5.15), gravimetry for silicate (JIS K3362 5.11), colorimetry for phosphate (JIS K3362 5.10); Methods as in Reference 5.

*Commercial product analysis.* Six commercial products were analyzed by three wet chemical methods and by the method described in this paper. The results are shown in Table 2. Results obtained from the method in this paper are in good agreement with those from the wet chemical methods. Total required time for the ICP-AES method of the six products was 5 h, including sample preparation, instrumental measurement, and preparation of the calibration curve. This was five times faster than the time required to prepare and measure the same samples by the three wet chemical methods.

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[Received March 21, 1995; accepted November 6, 1995]