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Technical Explanation

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Introducing the ZA4000 Series of Polarized Zeeman Atomic Absorption Spectrophotometers

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1. Introduction

Atomic absorption spectrophotometers, instruments that measure the concentrations of elements in liquids, are used in many fields, including those related to the environment and food production. Atomic absorption spectrophotometers typically atomize elements via one of two methods depending on the concentration to be measured: the *flame* method, in which elements are atomized by a chemical flame, or the graphite method, in which elements are atomized in an electric furnace. Atomic absorption spectrophotometers exploit the fact that atomized elements absorb light at specific characteristic wavelengths; to determine the concentration of a given element in an unknown sample, the sample's light absorption (or absorbance) is measured, and the absorbance values are converted to concentration values using calibration curves, rules relating absorbance to concentration that are prepared using standard solutions with known concentrations. If other substances are also present in the sample, they will absorb light at specific wavelengths that are known to produce errors in measured values; this is known as background. To mitigate the impact of the background, Hitachi's atomic absorption spectrophotometers—including instruments in the ZA4000 series—implement the method of polarized Zeeman correction using permanent magnets to obtain highly accurate measured values. The lineup of instruments in this series has also been augmented by the addition of the ZA4800, which offers rapid sequential flame capabilities to allow sequential measurements of multiple elements; this increases throughput compared to conventional flame methods, which measure only one element at a time. The full lineup of ZA4000 series instruments is shown in Figure 1.



Fig. 1 Full lineup of instruments in ZA4000 series.

2. Key Features of ZA4000 Series

2-1. Polarized Zeeman method for background correction

Atomic absorption spectrophotometers determine element concentrations from absorbance values, which quantify the extent to which light at specific wavelengths is absorbed by the element in question. In some cases the measurement sample may contain additional "impostor" substances that also absorb light at those wavelengths, possibly affecting experimental results. This is known to constitute one source of background errors; to correct these errors, the instrument is used to measure both the *apparent* absorption (absorption by the target element plus absorption by impostor substances) and the *background* absorption (absorption by impostor substances only) and the latter is subtracted from the former. Hitachi's atomic absorption spectrophotometers implement a polarized-Zeeman background-correction method that uses permanent magnets and is the legacy of a nearly 50-year history of painstaking development. This technique enables instruments to provide a stable baseline immediately upon turning on the hollow

cathode lamp that serves as the light source—and allows background correction for all elements. The principles of this correction technique are illustrated in Figure 2.

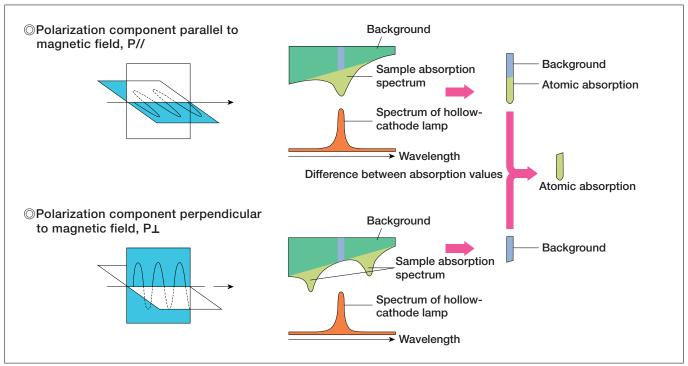


Fig. 2 Principles of polarized Zeeman background correction.

2-2. Dual-detector optical system for high sensitivity

Figure 3 shows the optical system of ZA4000 series instruments. The system includes two detectors to allow separate, independent measurements of apparent absorption and background absorption. This increases the flux of light that may be detected per unit time, yielding low-noise signals for high-sensitivity measurements.

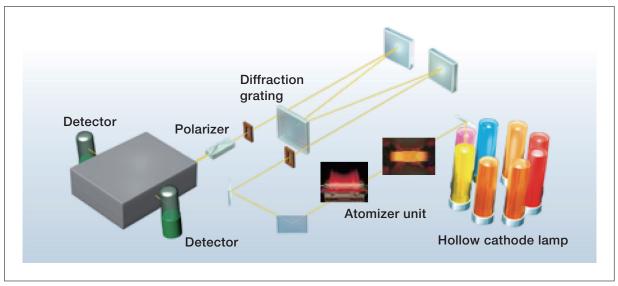


Fig. 3 Optical system of ZA4000 series instruments

3. Sequential Measurements of Multiple Elements via Flame Method

3-1. Introducing a new measurement technique: rapid sequential measurement

Atomic absorption spectrophotometers typically measure one element per sample. The ZA4000 series includes the newly-released ZA4800, which boasts the novel ability to make sequential measurements of multiple elements, via the flame method, for a single sample insertion. This technique is known as *rapid sequential measurement* (RS

measurement). In RS measurement, 4 hollow-cathode-lamp light sources may be active simultaneously, allowing sequential measurement of as many as 12 elements. Atomic absorption spectrophotometers use diffraction gratings to split the light absorbed by target elements, with light flux measured by detectors; in RS measurement, the diffraction grating is actuated at high speed using a newly-developed mechanism while the measurement is in progress. The wavelength of the light received by the detector is varied to perform sequential measurements of multiple elements. In conjunction with this, the hollow-cathode lamps are switched as appropriate for a given target element. For measurements of 5 or more elements, a compound lamp is used to emit light from multiple elements. As one example, Figure 4 compares the use of conventional flame measurement and RS measurement procedures for an experimental task requiring measurements of 6 elements for each of 20 samples. To complete this task via conventional flame measurements, we would fix a set of measurement conditions, measure the first element for each of the 20 samples, switch to the second element and measure the second element for each of the 20 samples, and similarly for all 6 elements. This requires a total of 120 separate sample insertions. In contrast, the RS measurement approach allows measurements for all 6 elements to be made sequentially, with measurement conditions configured separately for each measurement, with just a single sample insertion. Thus, the RS approach allows the full measurement to be completed with only 20 sample insertions. This not only reduces the workload for instrument operators, but also reduces the measurement time by approximately 30% depending on measurement conditions.

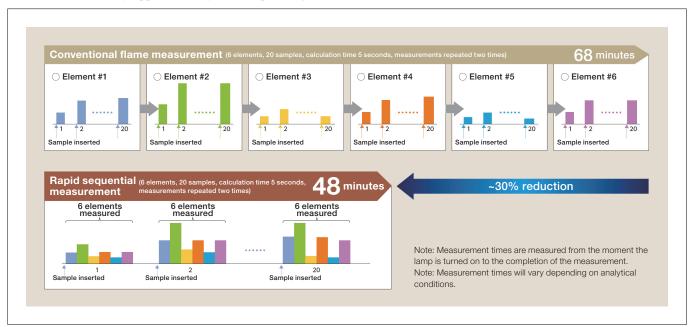
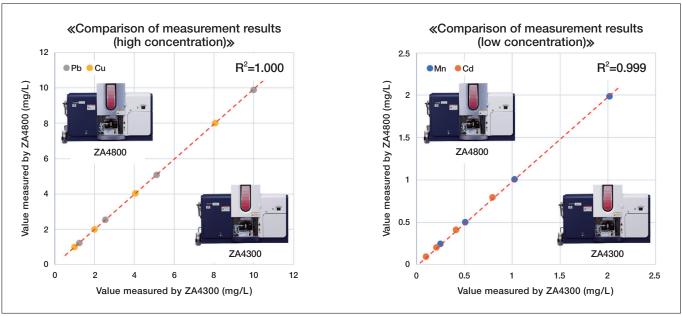


Fig. 4 Comparison of conventional flame measurement and rapid sequential measurement for experimental task involving 6 elements and 20 samples.

Rapid sequential measurement vs. conventional flame measurement: Comparison of measurement results

To confirm that RS measurements and conventional flame measurements yield identical results, we measure the same solution in two ways: via RS measurement using the ZA4800, and via conventional flame measurement using the ZA4300. Results of these measurements are compared in Figure 5. The left plot shows the results of Pb and Cu measurements for concentrations in the range 1–10 mg/L. The results produced by the two measurement procedures are in good agreement, with an excellent value of 1.000 for the coefficient of determination (R²). The right plot shows the results of Mn and Cd measurements for concentrations in the range 0.1-2 mg/L. For this lower-concentration measurement we again find good agreement between the results of the two measurement methods. This demonstrates that RS measurement is compatible with conventional flame measurement.



Comparison of measured data obtained via conventional flame measurement and via rapid sequential measurement.

Conclusions

In the nearly 70 years since the original proposal of atomic absorption spectroscopy by Walsh and Alkamade in 1955, atomic absorption spectrophotometers have progressed in many ways; one key milestone was Hitachi's release of the world's first polarized Zeeman atomic absorption spectrophotometer, the 170-70, in 1978. The historical evolution of Hitachi's atomic absorption spectrophotometers is depicted graphically in Figure 6. The ZA4000 series builds on the robust technological legacy made possible by this history—and advances its frontier by introducing the new technique of rapid sequential measurement. We are confident that atomic absorption spectrophotometers will remain widely-used tools with applications spanning a broad range of fields.

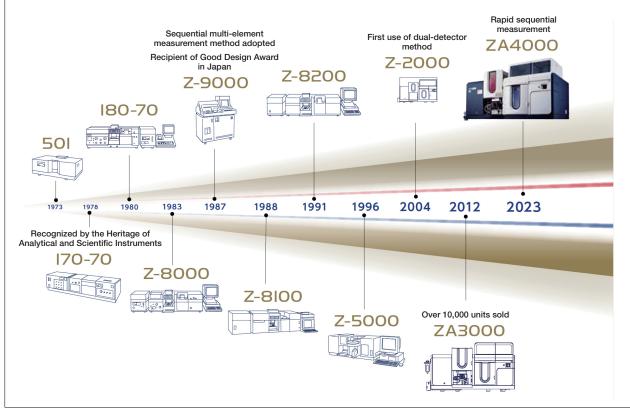


Fig. 6 Historical evolution of Hitachi's atomic absorption spectrophotometers.

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