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Direct Analysis of Aerosol Particles by Atomic Emission and Mass Spectrometry

Hiroshi Kawaguchi, Tsutomu Nomizu, Tomokazu Tanaka and Satoshi Kaneco

Department of Materials Science and Engineering, Nagoya University, Nagoya 464-01, Japan

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Abstract : A method for the direct determination of elemental content in each of aerosol particles by inductively coupled plasma atomic emission (ICP-AES) or mass spectrometry (ICP-MS) is described. This method is based upon the introduction of diluted aerosols into an ICP and the measurement of either the flash emission intensities of an atomic spectral line or ion intensities. A pulse-height analyzer is used for the measurement of the distribution of the elemental content. In order to calibrate the measuring system, monodisperse aerosols are used. The potentials of the method are shown by demonstrating the copper emission signals from the aerosols generated at a small electric switch, a study of the relation between the decreasing rate of particle number density and particle size, and measurements of calcium contents in the individual biological cells.

Keywords : Inductively coupled plasma, Atomic emission spectrometry, Mass spectrometry, Aerosol particles, Monodisperse aerosol.

1. Introduction

Chemical composition and size distribution of aerosol particles are measured frequently in the study of environmental science and in the development of air pollution control technologies. Usually, particulate matter in air is collected on a membrane or glass fiber filter, and the collected materials are analyzed by various methods such as atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) after chemical decomposition. In these methods, however, lengthy sampling and dissolution time is required, and therefore, real time analysis of aerosols is impossible.

In the present paper, we will describe a direct method for the determination of elemental content in individual particles by introducing the aerosols into the ICP. In ICP-AES, the light flash from each particle is observed

by a monochromator and a pulse signal for the atomic emission is generated at the detector. The emission signal from each particle is proportional to the elemental content in the particle. Similarly, in ICP-MS, a group of ion signals from each of particle is observed as a single pulse by processing the ion signals with a preamplifier having a relatively large time constant. In these methods, sample aerosols are sufficiently diluted by carrier gas so that completely resolved flash signals of emission or ions from individual particles are measured. The detection limits obtained were 0.01 pg for calcium in ICP-AES and 0.003 pg for zinc in ICP-MS.

We first proposed this method in 1986 [1], and applied to the measurement of the relationship between the decreasing rate of the particle number density and the particle size [2]. The system is modified by incorporating a laser-scattering counter for the simultaneous measurement of the elemental content and size of particles [3]. The ICP-AES method was applied to the determination of calcium in individual biological cells [4]. Improvement of the sensitivity for the determination of elements in particles was proposed in 1993 [5] by using ICP-MS, and further optimization of the operating conditions was recently reported [6]. This paper will review these works carried out in our laboratory and discuss existing problems and potentials.

2. Experimental

Instruments in ICP-AES

A block diagram of the instruments we first employed for ICP-AES is shown in *Fig. 1* [1]. The ICP system is conventional one except for the signal processor. The plasma was projected by a quartz lens with unit magnification onto the entrance slit of a 0.5-m grating monochromator. Alternatively, a 1-m holographic grating monochromator (Seiko, SPS-1100H) was used for the biological cell analysis [4]. Signals from the photomultiplier were amplified by a preamplifier and a logarithmic amplifier. The signals were fed to a 1-kHz low-pass filter to reduce the shot noise and then to a pulse height analyzer which was constructed with an 8-bit A/D converter and a personal computer (Fujitsu, FM-8). The pulse height analysis and real time display on a cathode ray tube were executed by a program written in machine language. Air samples are introduced into the plasma at a rate of about 50 ml/min by the suction pressure of a nebulizer for liquid samples.

In order to calibrate the signals, monodisperse aerosols were used which were generated by a laboratory made aerosol generator of the vibrating orifice type. A 28.2 kHz ultrasonic horn was employed for the vibration of a 18-μm orifice in a stainless steel plate from which

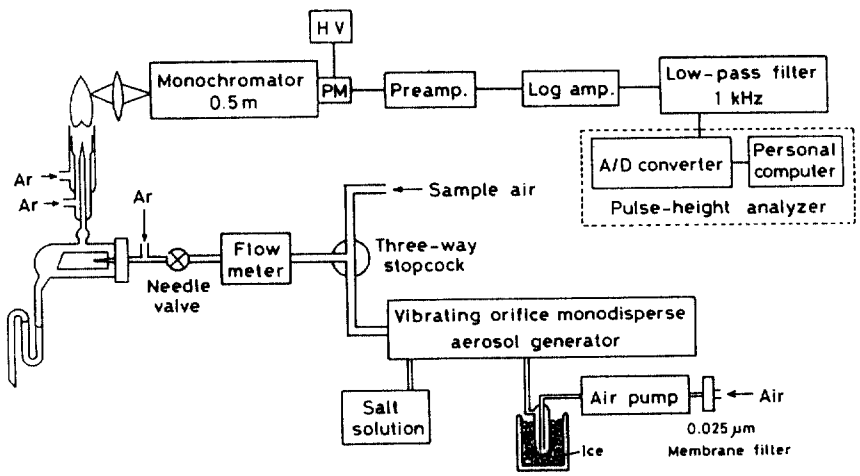

Fig. 1 A block diagram of the instruments.

a liquid jet of a salt solution is ejected. For example, when a solution of 10 μg/ml Na is fed at 48 μl/min, uniform liquid droplets with a diameter of 37.8 μm are generated and resulted monodisperse sodium chloride particles after drying the droplets have a diameter of 0.9 μm. A commercial monodisperse aerosol generator (TSI Inc. Model 3450, USA) was also used in the later experiments [2–5].

Although the flash emission from each of the aerosol particles is correlated to the elemental content, it cannot be converted to the elemental concentration unless the particle sizes are provided. A laser light-scattering counter was constructed and incorporated in the aerosol transport tube to the ICP [3]. A cross sectional view of the laser light-scattering cell is shown in *Fig. 2*. A semiconductor laser (Toshiba TOLD 9200, 670 nm, 2.7 mW) was used as light source and a photomultiplier (Hamamatsu Photonics, R1546) was used as detector. Scattered light at forward 60° was observed. Standard polystyrene latex beads aerosol (Japan Synthetic Rubber Inc., STADEX-SC series) was also used for the calibration of the scattering light intensities.

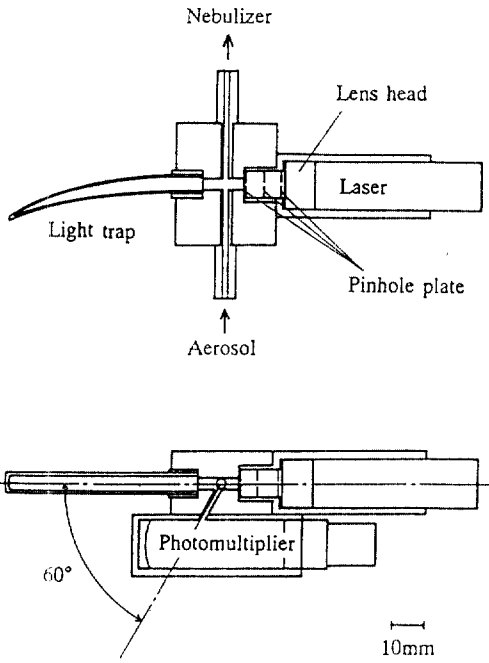

Fig. 2 Cross-sectional view of the light scattering cell.

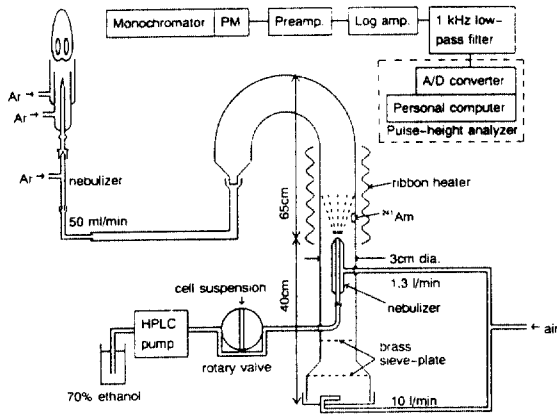

Fig. 3 Sample introduction system for biological cells.

For the analysis of biological cells, the sample introduction system as shown in *Fig. 3*[4] was employed. A 1-ml cell suspension in 70 % ethanol was injected into a 70 % ethanol stream through a rotary valve. The stream was fed to a concentric pneumatic nebulizer placed in the middle of a drying chamber at a flow rate of 0.2 ml/min by a HPLC pump. Moisture removed air was used to spray the cell suspension with the nebulizer and to dry the droplets at flow rates of 1.3 and 10 l/min, respectively. The outer wall of the drying chamber (Pyrex glass, 3 cm i.d.) was heated with a ribbon heater at ca. 70 °C. As shown in the figure, two brass sieve plates (3 mm bores) were incorporated into the chamber in order to minimize the turbulence of the air flow. To reduce the deposition of electrically charged cells on the wall of the chamber and feed tubes, the charge of the cells was neutralized by the irradiation of α-ray emission from 3.7 X 10^6 Bq (100 μCi) of ^{241}Am, which was attached to the inner wall of the chamber.

Instruments in ICP-MS

A commercial ICP mass spectrometer (Seiko Instr. Inc., SPQ 6500) was used [5, 6] except for the data processor. Signals from the electron multiplier was fed to a laboratory-made preamplifier having a relatively long time constant (0.33 ms) to obtain analog signals. The output signal was further smoothed by a dc

amplifier with a 1-kHz band-pass filter. The resulting peak profile of the single pulse had a 1-ms FWHM similarly in ICP-AES. The signal was then fed to the logarithmic amplifier and processed by the same system described in *Fig. 1*.

3. Results and Discussion

3.1 *Calibration by Monodisperse Aerosols*

The emission signal of the Ca II 393.36 nm line from the ICP is shown in *Fig. 4* [1] when a monodisperse aerosol of calcium is introduced. Emission pulses with almost uniform pulse height and about 1-ms pulse width are observed except a few strong pulses which may be due to the emission of two particles simultaneously introduced into the plasma. These uniform pulse height signals give sharp pulse-height spectrum as shown in *Fig. 5* [4]. These spectra were obtained by monodisperse calcium acetate aerosols containing 0.36, 0.11 and 0.036 pg of calcium. The channel number of the pulse height analyzer is proportional to the logarithmic conversion of the emission intensity since a logarithmic amplifier is used before the signals are measured by the pulse height analyzer.

The channel number of each peak in *Fig. 5* can be correlated to the calcium content in each of monodisperse aerosol particles as shown in *Fig. 6* [4]. The logarithms of Ca content are plotted linearly against

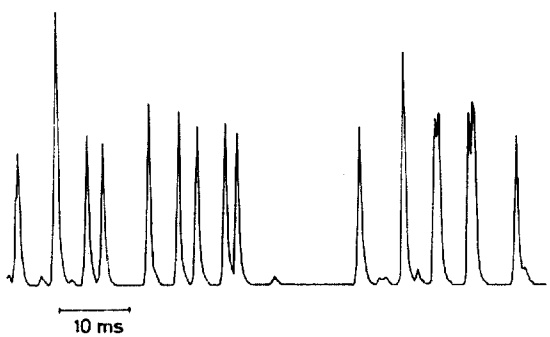

Fig. 4 Emission pulses from monodisperse aerosol of Ca particles.

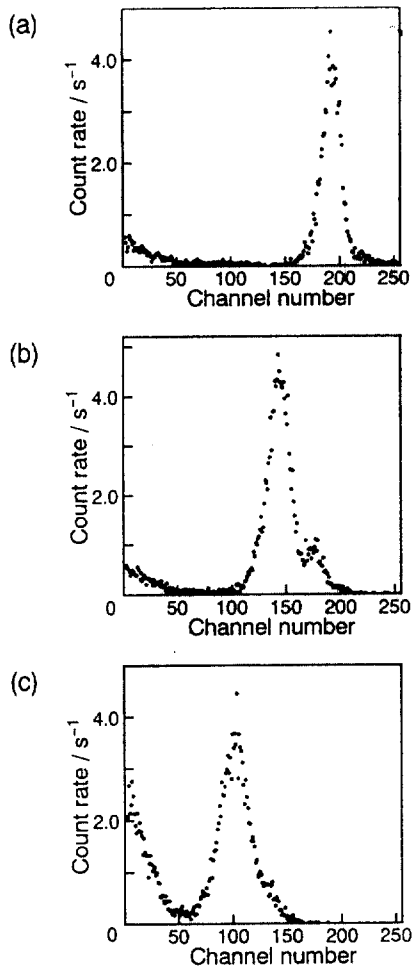

Fig. 5 Pulse height spectra for Ca emission from a) 0.36, b) 0.11 and c) 0.036 pg of Ca particles.

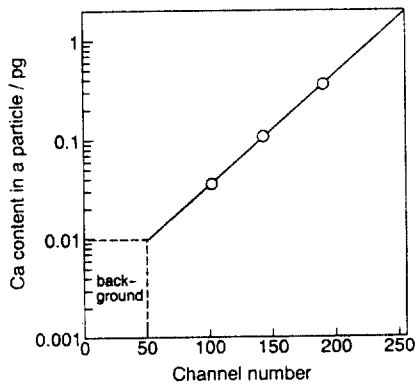

Fig. 6 Relation between Ca content and the channel number of pulse height analyzer.

the channel number. The relation can be used as a calibration curve for the determination of Ca content in each of aerosol particles. The signals below the channel 50 in *Fig. 6* can be regarded as the background signals derived form the continuum emission of the ICP. Therefore, the detection limit of Ca in this experiments is considered about 0.01 pg.

3.2 *Copper Aerosols Generated by a Switch*

When an electric switch turns off a lamp, a small arc is generated at the switch. Since the arc produces a copper aerosol, the present system was applied to measure the copper aerosols from the switch [1]. In *Fig. 7*, emission signals of the Cu I 324.75 nm line are shown when the copper aerosols were sampled three times and observed by an oscilloscope with bypassing of the logarithmic amplifier. A 200-W bulb was used as a load and the aerosol was sampled just above the switch. In the upper two examples in *Fig. 7*, the emission pulses are separated from each other but in the bottom example they are not resolved because too many copper particles were generated. The pulse height spectrum of these signals showed that the largest number of particles appeared at 0.7 μm in diameter.

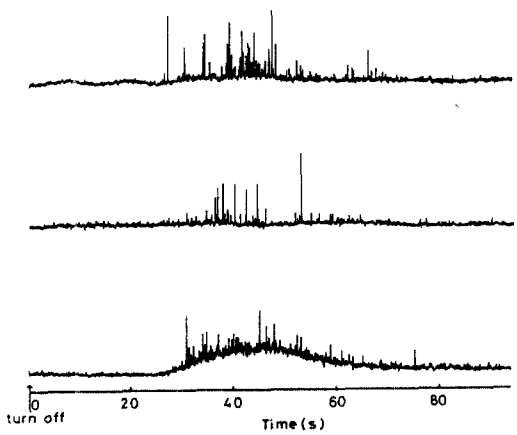

Fig. 7 Emission signals from Cu aerosols generated from an electric switch.

3.3 *Relation between the Decreasing Rate of Particle Number Density and Particle Size*

The present method was applied to the determination of the relation between the decreasing rate of particle number density and particle size for aerosols with known composition [2]. Particle number density of an aerosol decreases with time by either the gravitational precipitation or deposition at the wall of the vessel by the Brownian diffusion. Particle number densities, n, and size distribution of an aerosol filled in a cylindrical metal vessel were measured by periodically sampling the aerosol.

An example of the variation of the particle number density with time is shown in *Fig. 8* for a calcium carbonate aerosol filled in a stainless steel vessel (21 cm high, 21 cm i.d.). Samples obtained at different depth are plotted in a single line which shows the aerosol density in the vessel is homogeneous. Since the aerosol used in this experiment was a polydisperse aerosol prepared from a reagent grade powder, the variation of the aerosol densities were measured for different size fractions by dividing the channels of the pulse height analyzer into 7 groups. The resulted decreasing rates of $\log(n)$ with time are plotted against the particle diameter in *Fig. 9*. The diameter was calibrated by monodisperse aerosols described before.

The solid line in *Fig. 9* is derived from the theoretical

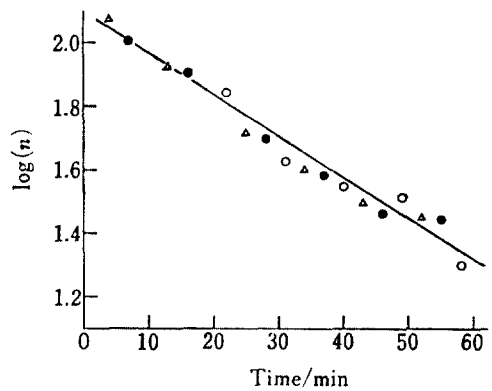

Fig. 8 Variation of logarithm of particle density as a function of time. Sampling depth 7.5, 10 and 15 cm.

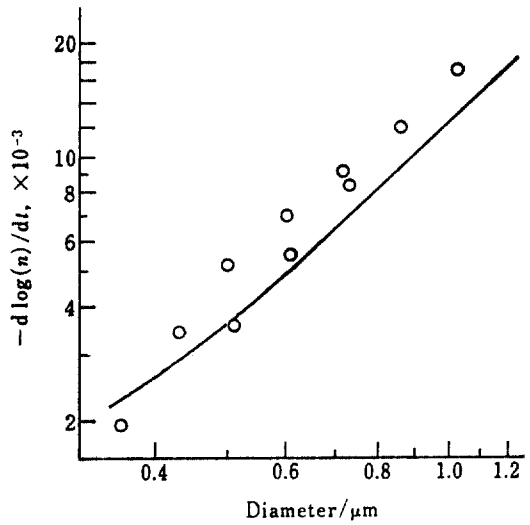

Fig. 9 Experimental and theoretical relations between $d\log(n)/dt$ and diameter for $CaCO_3$ particles.

calculation. The plots in the figure are reasonably agreed with the theoretical curve, which indicates the present method can be applied to the determination of particle size of aerosols without the compositional information.

3.4 *Simultaneous Measurement of Elemental Content and Size of Airborne Particles*

When a laser light-scattering counter as shown in *Fig. 2* is inserted into the transport tube of the aerosol to the ICP torch, scattering light pulses from the individual particles are observed [3]. From the intensity of the scattering light for each of the particles, its size can be calculated. The same pulse height analyzer was used alternatively both for the scattered-light pulses and emission pulses. If each of the atomic emission pulses can be correlated with the scattering-light pulse, elemental content and size of the particles are simultaneously measured.

The correlation of the emission pulse and the scattering pulse was carried out by measuring the time lag between these pulses. Since the particles are introduced into the scattering cell and then into the ICP through a thin tube, there was a relatively constant time

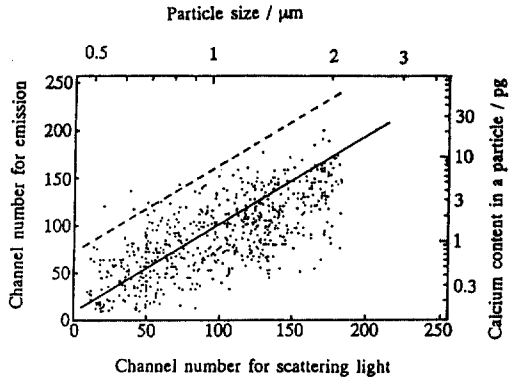

Fig. 10 Relation between pulse heights of scattered light and emission for polydisperse aerosol.

lag. By comparing the signals between the scattering and emission pulses using a monodisperse aerosol, the average time lag was calculated to be 134.4 ms with a standard deviation of 29.8 ms.

The search for an emission pulse corresponding to a scattered-light pulse was executed by a computer software and stored in the memories. An example of the correlation between these pulses is shown in *Fig. 10* for a polydisperse calcium acetate aerosol. The solid line in this figure is a calculated relation curve between the size and the calcium content for calcium acetate particles (Ca 22.7 wt%). Obviously, the plots are distributed along the solid line. The distribution, however, is rather broad, because the plots should be sharply aligned on the solid line for a polydisperse aerosol of a certain composition. The results shown in *Fig. 10* indicates the possibility of the simultaneous measurements of the elemental content and size of aerosol particles, although further improvements in the instruments are necessary.

3.5 *Determination of Calcium in Individual Biological Cells*

The ICP-AES system shown in *Fig. 1* was applied to the determination of the calcium content in individual biological cells [4]. Biological cell samples such as mouse fibroblast cells were suspended in 70% ethanol at a number density of 10^6-10^7 cells/ml. The solution was nebulized by a pneumatic nebulizer and the resulted

aerosol was dried with a large volume of clean air before the introduction into the ICP as shown in *Fig. 3*.

The calibration using monodisperse aerosols is based on the assumption that a pulse signal derived from a cell has almost the same pulse height as that from an aerosol particle containing the same amounts of calcium. From the pulse height spectra of cultured mouse fibroblast cells, the mean value of calcium content in individual cells was estimated to be 0.057 pg. Since the size of the cells ranged from 10 to 15 μm, the calcium concentration in the cell can be calculated to be in a range from 0.82 to 2.8 mM, assuming a spherical cell. The calculated value is close to the intracellular total calcium concentration, 1–2 mM, in a typical mammalian cell reported in the literature.

In *Table 1*, the mean values and the standard deviations of calcium content in individual cells are shown as well as the calculated intracellular calcium concentration for three cultured mammalian cell samples. All of the determined values are close to the literature values. Although calcium in individual cells can be determined by this method because it is one of the most sensitive elements in ICP–AES, application of the method to other elements was hampered by the insufficient sensitivity.

3.6 *Application to ICP–MS*

The ICP–AES is fairly sensitive for the measurement of main constituents in the aerosol particles, but it is not sufficient for the determination of minor elements in the particles. It was tried to apply the present principle to the ICP–MS [5]. Ion signals from the channel electron multiplier of a conventional ICP mass spectrometer were passed through a preamplifier with a relatively large time constant. The resulted pulse signals were corresponded to the elemental contents of the particles. Pulse-height spectra obtained with a monodisperse aerosols of zinc acetate are shown in *Fig. 11*. The spectra have a distribution with a relative standard deviation (RSD) of 27 % in the spectra (33 % RSD in size). Compared to the spectra shown in *Fig. 5* for ICP–AES, broadening of the distribution is apparent, although the sensitivity in ICP–MS is much higher than that in ICP–AES.

In order to improve the shape of the pulse height spectra, extensive optimization of the plasma operating

Table 1 Results of Ca determinations in cultured mammalian cells.

cell sample	diameter (μm)	measured content (pg/cell) mean value	std dev	calcd cellular concn[a] (mM)
mouse fibroblast cells	10–15	0.057	0.029	0.82–2.8
human pancreas cells	15–20	0.16	0.04	0.94–2.2
human endothelium cells	15–20	0.27	0.04	1.6–3.7

[a] Calculated from the cell diameter and the mean value of measured content for each cell sample by assuming a spherical cell.

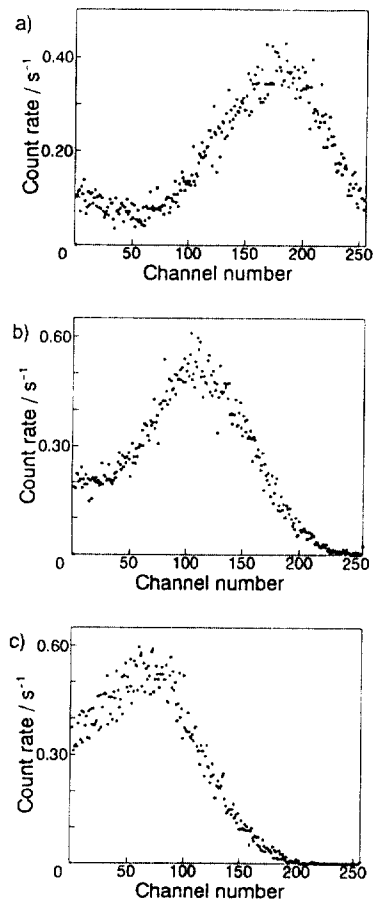

Fig. 11 Pulse-height spectra of $Zn(CH_3COO)_2$ particles in ICP–MS. a) 32, b) 12, c) 6.4 fg of Zn.

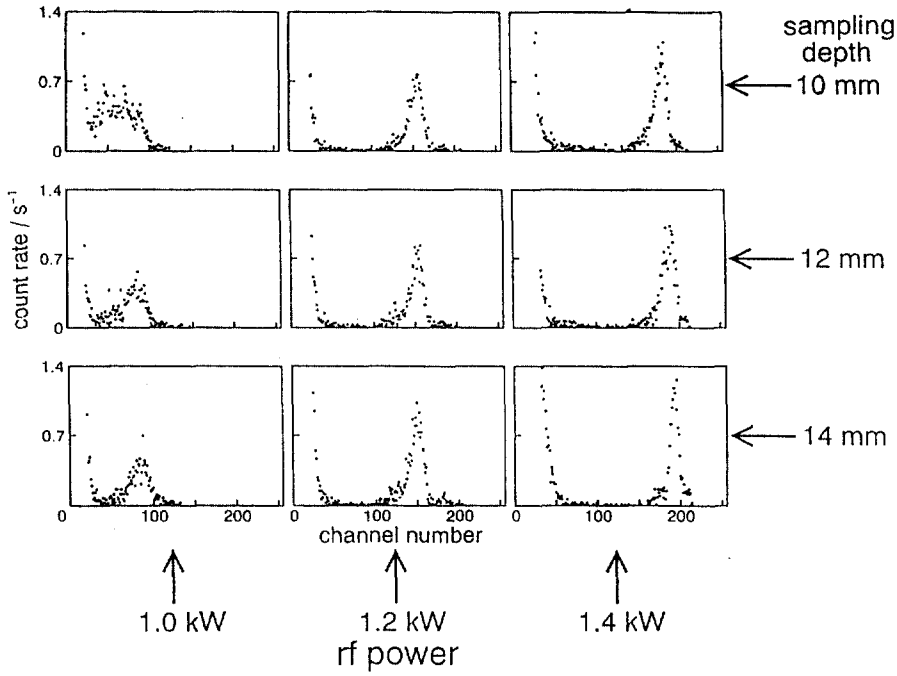

Fig. 12 Variation of pulse height spectrum for a monodisperse particle of 0.13 pg zinc as a function of rf power and sampling depth at a carrier gas flow rate of 0.8 l/min.

conditions were carried out [6]. The experiments with various combinations of rf power, sampling depth and carrier gas flow rate indicated that the critical optimization was necessary for the sharp pulse height spectra. Variation of pulse height spectrum as a function of rf power and sampling depth is shown in *Fig. 12* for a carrier gas flow rate of 0.8 l/min.

As the results, an rf power of 1.4 kW and sampling depth of 14 mm were selected as the optimum operating conditions under the gas flow rates of 16, 0.7 and 0.8 l/min for outer, intermediate and carrier gases, respectively. The signal distribution for a 30 fg zinc aerosol was 7.7 % RSD, which is even better than the typical RSD of 11 % in ICP-AES [3]. The detection limit of Zn by this method is estimated to be about 3 fg.

4. Conclusions

As a quite efficient atomization, excitation and ionization source, the ICP is excellent for the direct analysis of aerosol particles. By using extremely sensitive ICP-MS, the method will be further applied to various fields, especially to biological field.

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