

Ultrasensitive Trace Determination of Pb by Two-Color Resonance Ionization Mass Spectrometry

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Received September 5, 1994

The resonance ionization mass spectrometry (RIMS) system with angular reflectron type time-of-flight mass spectrometer (AREF-TOFMS) has been developed and characterized. The system is applied for the ultratrace determination of Pb element. The 2-color 3-photon laser ionization scheme is adopted for the study and the mass resolution of the system is determined as $T/\Delta T=1680$. The calibration curve for Pb is obtained in the range of 100 ppb to 0.01 ppb by using standard solutions. The minimal amount of detection for the present RIMS system is determined as less than 100 femtograms (10^{-13} gram).

Introduction

The development of ultrasensitive detection method for atoms and molecules has been desired for a long time. Resonance Ionization Mass Spectrometry (RIMS) is recognized as one of the newest and the most sensitive technologies in the field of trace determination of elements in these years.¹⁻³ RIMS has been applied for many different types of samples such as heavy metal atoms, rare earth elements, etc. for more than a decade. In this study Pb is chosen as a sample for the test of detection limit of newly-built pulsed RIMS system. The Pb is one of the heavy metal elements which has notorious effects on human as well as environment. Analysis of Pb has been studied for the determination of Pb concentration in antarctic ice by Bolshov *et al.*⁴ They utilized the laser induced fluorescence technique and the detection limit is reported as ppt level. Although this fluorescence study showed a very good detection limit, no information on isotopes can be obtained. The detection of ²¹⁰Pb isotope by RIMS with continuous wave lasers have been studied by Burshaw *et al.*^{5,6} This study did not utilize a mass spectrometer, while it adopted a very narrow band cw lasers. In the present study, more convenient and less expensive pulsed laser systems with broad bandwidths and a time-of-flight mass spectrometer are adopted for the determination of isotopes of Pb.

The detection of Pb by RIMS has been tested for a while in this laboratory and a preliminary result has been already published.⁷ In the previous work, a linear TOF mass spectrometer and Nd:YAG laser pumped dye lasers have been used in the two step RIMS schemes. The detection limit obtained was 10 picograms. In the present study details of new RIMS setup which brings improvement of the detection limit and the characterization of the system are presented. In this system a newly developed resistive heating filament atomizer with a slide-in type mount is specially designed for the collimation of atomic beam. The mass resolution of the present RIMS system is found to be high enough to completely separate all Pb isotopes. In addition, data on nuclear hyperfine structure of ³P₁ state of Pb with narrow bandwidth pulsed dye laser has been utilized to improve the isotope selectivity. The minimal amount of Pb sample which

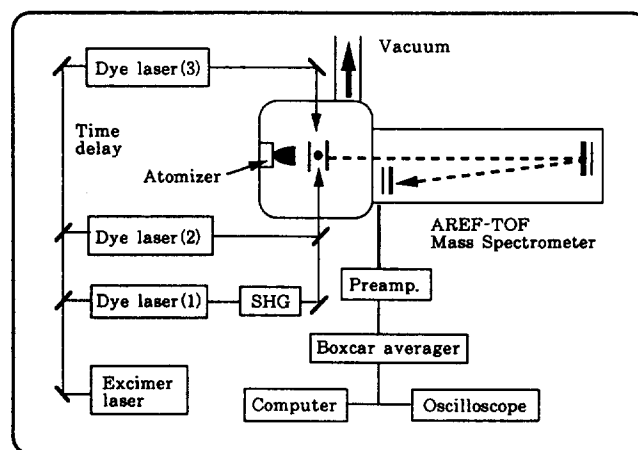


Figure 1. Schematic diagram of 2-color 3-photon RIMS setup.

can be detected in our RIMS system is determined as smaller than 100 femtograms. This detection limit is 100 times better than the previously reported result.⁷ This detection limit is obtained with the new atomizer, new AREF-TOF mass spectrometer, and better ionization efficiency.

Experiment

RIMS setup. The RIMS spectrometer, which is developed in our laboratory, is composed of several systems and the details are described as following. The overall schematic diagram of the experiment is shown in Figure 1.

(1) The laser system is a key part in RIMS and consists a pumping laser and two dye lasers (Lumonics HD-300 and HD-500). The pumping laser is a high power excimer laser (Lumonics 748, XeCl, 300 mJ/pulse, 1-200 Hz). One of the dye laser outputs is frequency-doubled by a second harmonic generator (Inrad model Autotracker II) which is equipped with KDP and BBO crystals to generate ultraviolet light. The laser system is operated at the repetition rate of 10-30 Hz. The bandwidth of the first dye laser (excitation) is measured as 1 GHz, while that of the second dye laser (excitation and ionization) is 3 GHz. These two dye lasers are arranged to spatially overlap in the ionization region and

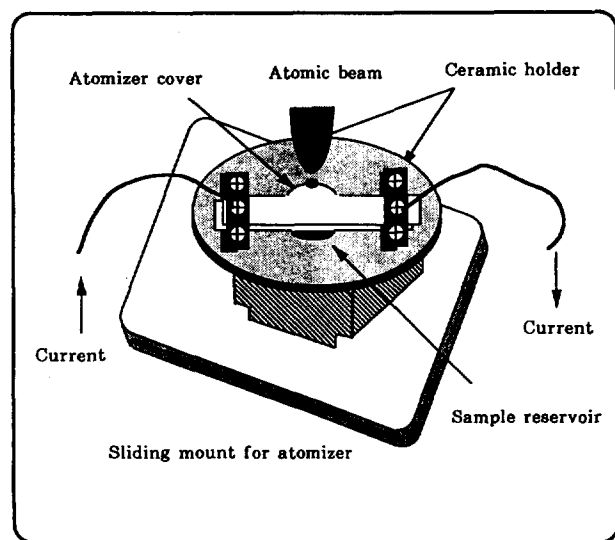


Figure 2. Schematic diagram of electrothermal heating type atomizer placed on top of sliding base. The maximum temperature obtainable is 1500 °C.

to maintain the time delay from 0 ns to 9 ns.

(2) The atomizer is made of various metal foils such as tungsten (W), molybdenum (Mo) and tantalum (Ta). Among these metals only tungsten filament is measured to contain no contamination of Pb. Atomizers made of Ta and Mo contain at least a few hundred picograms of Pb as an impurity. This atomizer is constructed with two plates, where one plate is used as the sample reservoir and the other is used for the cover of atomizer as well as the nozzle with a hole of 1 mm diameter. The heating of the atomizer is accomplished by an electrothermal heating method and can be heated up to 1500 °C. The metal filaments are located on the top of a specially designed slide-in type atomizer mount. The slide-in type mount makes the exchange of samples more convenient and fast. The schematic diagram of atomizer is depicted in Figure 2. Atomic beam is arranged to meet laser beams at the right angle. In this configuration atomic beam faces to the TOF mass spectrometer.

(3) The mass spectrometer used for the detection of isotopes is an angular reflectron type time-of-flight mass spectrometer (AREF-TOFMS). The schematic diagram of the mass spectrometer is shown in Figure 3. The flight distance for ions from an ionization region to the dual microchannel plate detector is 185 cm. The ions of target element are produced by multi-color multi-photon laser ionization. After the ions are produced, the repeller plate (A_1), which is loaded with 1000 V, and acceleration grid (A_2), which is loaded with 700 V, accelerate the ions toward ion reflector assembly. The Einzel lens, which focuses the ion beam to improve the mass resolution, and two deflection plates, which controls the ions in XY direction to be efficiently collected at the dual microchannel plate (MCP) detector are attached right after the acceleration plate.

After the ions pass through the deflection plates, they experience a field free region (160 cm). These ions are reflected by ion reflector assembly which has a retarding grid (700 V) and twenty plates with meshes and a reflectron grid (1200 V). After the ions are reflected, a 40 mm dual microchannel

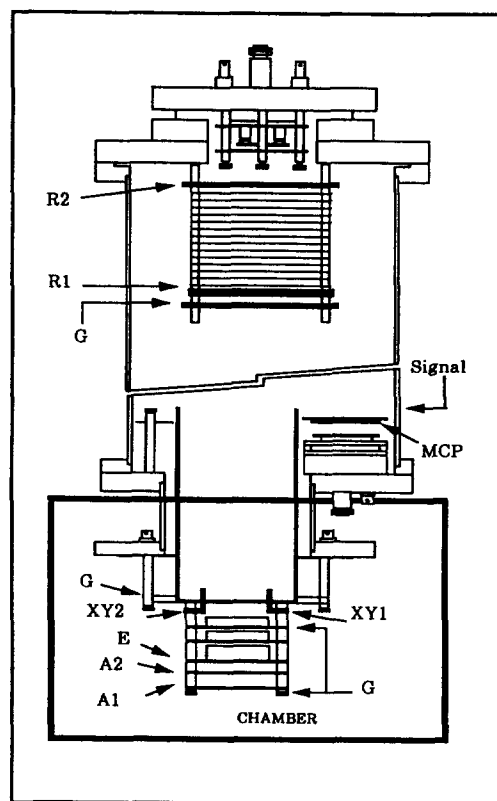


Figure 3. Schematic diagram of AREF-TOF mass spectrometer. A1: Repeller plate, A2: Acceleration grid, E: Einzel lens, G: Ground potential, XY1: Deflection plates, R1: Retarding grid, R2: Reflectron grid, MCP: Microchannel plate

plate is used to detect the ions. The chamber is kept under vacuum with a 10 inch turbopump (Alcatel TPU 5900, 880 L/s) and a mechanical backing pump (Alcatel 2033, 765 L/min) and the vacuum is measured as about 1.0×10^{-8} torr without vaporization of samples. During the experiment, however, the pressure is increased ten times (1.0×10^{-7} torr) due to the atomic beam. Under this vacuum condition no impurities other than Pb are detected.

(4) The detected ions are amplified by a fast preamplifier (Stanford Research System model SR240) and integrated by a boxcar integrator (Stanford Research System model SR 250). A digital oscilloscope (Hewlett Packard model 53505B, 400 Megasamples/sec) is used to detect ion signals. Ion signals are transferred through a GPIB board (CEC model) to a host computer. All these procedures are controlled by a IBM 466 DX2/D personal computer.

Experimental procedure. The present experiments are performed by two-color RIMS schemes. The $7s^2P_1$ state is chosen as the first excited state, which is located at 35287.2 cm^{-1} from the ground state level. This radiative transition has relatively high excitation cross section compared to other excited energy levels. The fluorescence lifetime of the state is reported as 5.8 ns.⁸ The samples of Pb are prepared from the 1000 ppm atomic absorption standard solution (Johnson Matthey) by stepwise dilutions. The concentration range of the samples used is between 0.01 ppb and 100 ppb. The sample amount used for the determination was 10 mL. The solvent of sample is evaporated with an IR lamp. After the

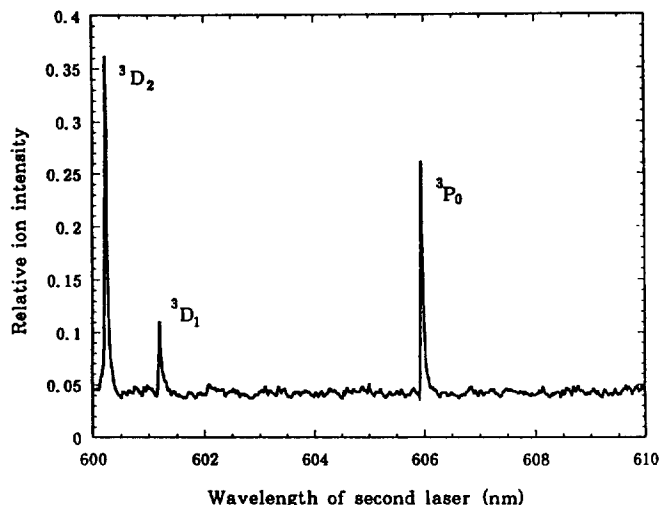


Figure 4. Ionization spectra of Pb between 600 nm and 610 nm. The transitions starts from 35287.2 cm^{-1} excited state for $m/z=208$ isotope

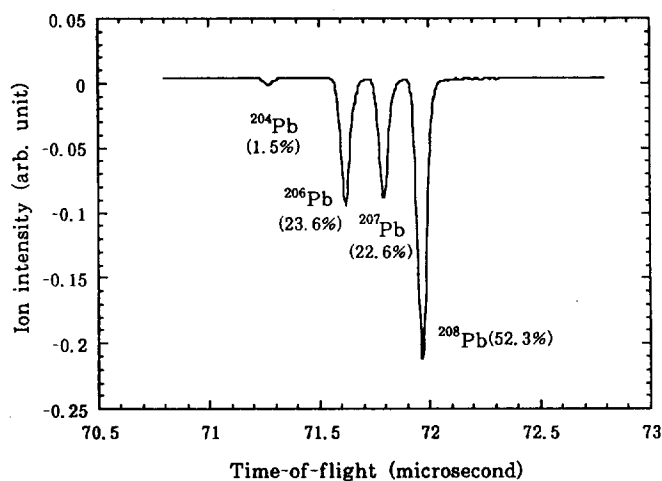


Figure 5. Mass spectrum of Pb isotopes. The numbers inside the parenthesis indicate measured relative intensities.

solvent is dried completely, the atomizer loaded with sample is introduced to the vacuum chamber. The analysis of one sample takes about ten minutes, while it takes approximately 20 minutes for chamber to be evacuated below 1×10^{-7} torr.

Results and Discussion

Search for the efficient excitation/ionization schemes. In the process of multi-color multiphoton RIMS it is important to identify and utilize second excited states to obtain the maximum ionization efficiency. In general if the overall ionization probability increases, detection sensitivity also increases. We have identified several higher excited states which can be excited from $7s^3P_1$ state. Five levels are observed in the wavelength range of Rhodamin 610 and Coumarin 500 dye. These are $8p^3P_0$, $8p^3D_1$, $8p^3D_2$, $9p^3P_1$ states and one unidentified state. Figure 4 shows part of these energy levels of highly excited states. Among these possible candidates for the second excited state, $8p^3D_2$ state, which

Table 1. Experimental Condition of Pb Determination

Experimental variables	Specifications
First laser wavelength	283.3 nm
Second laser wavelength	600.2 nm
Time delay between the two lasers	1 ns
Amount of sample	10 μL
Solvent evaporation	IR lamp
Laser power	Saturation energy
Temp. of atomizer	600-900 $^{\circ}\text{C}$
Rep. rate of laser	10 Hz
MCP detector voltage	-1950 V (-2200 V max)

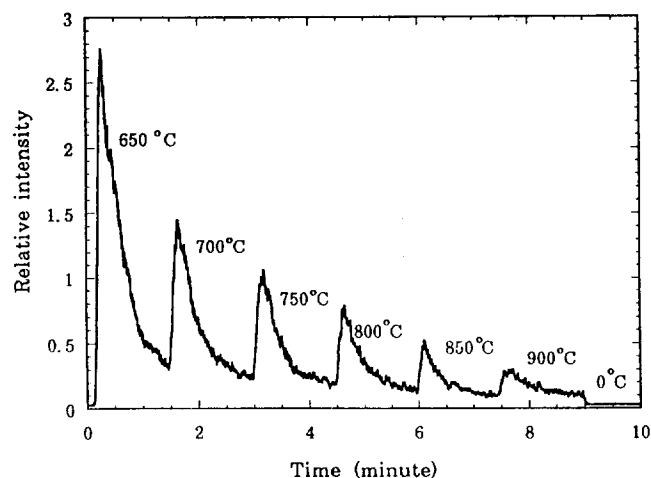


Figure 6. Analytical signals of 100 ppb Pb standard solution by using stepwise heating method. Duration of heating at one temperature is optimized with preliminary experiments.

is located at 51994 cm^{-1} , has the largest excitation cross section when the transition starts from $7s^3P_1$ state. Consequently, the determination of Pb is performed with 2-color 3-photon (283.3 nm+600.2 nm) resonance ionization scheme utilizing $8p^3D_2$ state.

Mass resolution of the RIMS system. A mass spectrum of Pb measured by two-color RIMS is shown in Figure 5. Pb has four stable isotopes ($m/z=204, 206, 207, 208$). The present result shows that ratio of each isotope is in good agreement with the natural abundances. In general one of the well recognized disadvantage of laser RIMS method in mass detection is the difficulty of obtaining accurate mass ratio due to the hyperfine structures of atoms. In the present case, however, very accurate isotope ratio for Pb isotopes is observed. This is because the transition to $7s^3P_1$ from the ground state is well saturated so that all the hyperfine levels are excited together by laser pulses. The FWHM of each isotope peak is measured as 40 ns, while the flight time is near 72 μs . Therefore mass resolution ($M/\Delta M$) of the system is calculated as 1680 from the $T/\Delta T$. This mass resolution is good enough to study isotope selective RIMS of any atomic species.

Determination of Pb. Determination of Pb has been tried with 2-color 3-photon RIMS. All the experimental con-

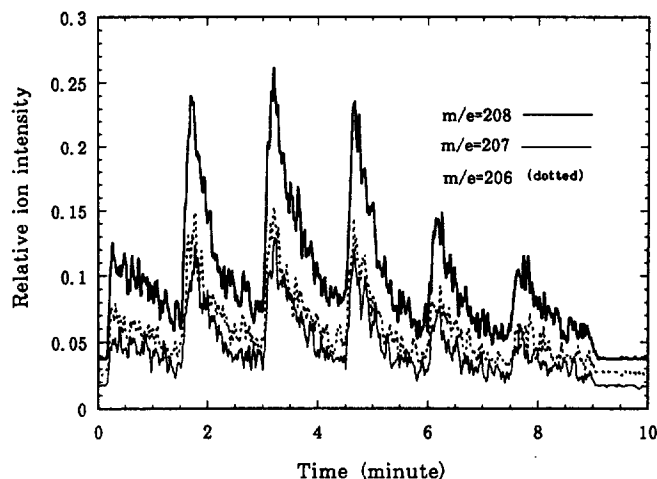


Figure 7. Analytical signals of 10 ppb Pb standard solution. Different background levels are arbitrarily set to plot ion signals of three isotopes in one figure.

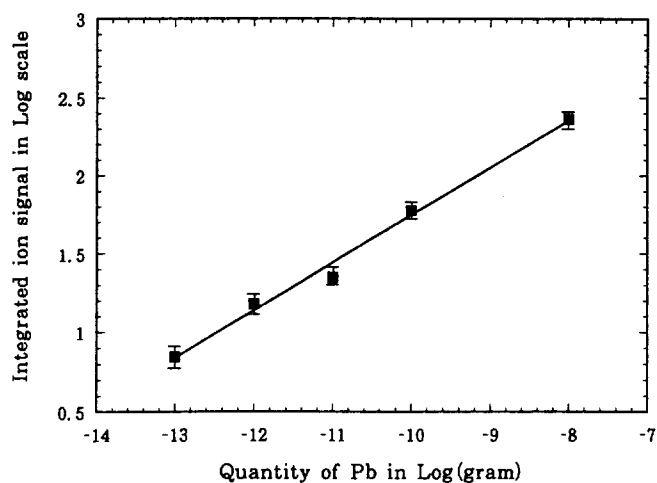


Figure 8. Calibration curve obtained from Pb standard solutions. The detected signal is sum of signals for three isotopes. The detection limit is measured as 0.01 ppb (100 femtograms). The correlation coefficient for linearity is calculated as 0.99153. The error bars indicate standard deviations for each data point.

dition is listed in Table 1. The samples used in the present experiment range from 100 ppb to 0.01 ppb. Figure 6 shows the analytical signal obtained by a stepwise heating method. The atomizer temperature is raised from 600 °C to 900 °C in seven steps. The stepwise heating method shows better detection sensitivity compared to the continuous heating at a specific temperature.⁷ This is because at low temperature the signal intensity level is similar to the noise level, while at high temperature sample is evaporated so fast that the detection sensitivity gets bad. Figure 7 is the analytical signal for 10 ppb sample. The three traces represent signal for each isotope. The analytical signal is big enough to determine 10 ppb sample. In this study 0.01 ppb sample is the lowest concentrated solution the present system can detect. In this analysis process it was necessary to check whether there is any Pb contamination in the atomizer. No Pb ion

signal is observed with empty atomizer only. Same procedures are taken for the pure water which is used as solvent for the preparation of standard solution. In this measurement, however, some contamination of Pb in water is detected. The ion signal from water is regarded as a background in this determination. The quality of water was the one of the main reason which prevent us from detecting less than 100 femtograms of Pb sample. One of the method to determine the background and noise levels is to check ion signals with the laser frequency tuned to the off-resonance line. We have checked the noise level by tuning the dye laser to the off-resonance line. No ion signal is detected. Therefore we conclude that no noise is present in this study, while background signals are present due to the impurities of solvent.

The calibration curve is obtained by integrating all ion signals for each isotope with subtracting background signals. In addition more than 20 measurements have been made for each sample and averaged. Figure 8 shows the calibration curve obtained in the present study with 2-color 3-photon resonance ionization. It shows good linearity within the measured concentration range. One data point, 1 ppb data, is out of linearity. This may be due to the experimental error such as normalization of laser power used for the study. This plot has been calculated by least square fit. The correlation coefficient of linearity is 0.9915 and the fitting standard error is 0.0623. The absolute minimum quantity of Pb the present system can detect is determined as less than 100 femtogram.

Conclusions

The trace determination of Pb has been demonstrated with RIMS system which is set up in this laboratory. The several excited states are identified and the $8p^3D_2$ is determined as the most appropriate second excited level for the resonance ionization. The ionization scheme adopted is 2-color 3-photon ionization through $7s^3P_1$ and $8p^3D_2$ excited states. The newly built RIMS system is capable of mass resolution as $T/\Delta T = 1680$ or better. The minimum quantity of Pb which can be detected with the present RIMS system is determined as less than 100 femtograms. For the improvement of the detection sensitivity of the system further studies on pulsed atomizers, autoionization states, collimation of atomic beam as well as utilization of high repetition rate laser should be investigated.

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Simultaneous Preconcentration and Determination of Trace Elements in Water Samples by Coprecipitation-Flotation with Lanthanum Hydroxide [La(OH)₃]

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Received October 10, 1994

The preconcentration and determination of trace Cd(II), Cu(II), Pb(II), Mn(II) and Zn(II) in water samples were studied by the precipitate flotation using La(OH)₃ as a coprecipitant. The analytes were quantitatively coprecipitated by adding 3.0 mL of 0.1 M La(III) solution in a 1,000 mL water sample and adjusting the pH to 9.5 with NaOH solution. After the addition of the 1:8 mixed surfactant solution of each 0.1% sodium oleate and sodium lauryl sulfate, the solution was stirred with a magnetic stirrer for 10 minutes. The precipitates were floated to the surface by bubbling with nitrogen gas and collected in a small sampling bottle. The precipitates were dissolved in nitric acid and then the solutions were diluted to 25.00 mL with a deionized water. The analytes were determined by flame atomic absorption spectrometry. This procedure was applied to the waste water analysis. This technique was simple, convenient and especially rapid for the analysis of a large volume of sample. And also, from the recoveries of better than 92% which were obtained from real samples, this method could be judged to be applicable to the preconcentration and quantitative determination of trace elements in water samples.

Introduction

Even though at trace levels, several heavy elements are fatally harmful to living things, but are sometimes necessary in their metabolism. And water is indispensable to keep the life of all the creatures. There are many kinds of elements in a water, especially natural water inflowed from various sources. And also the elements are absorbed into organisms together with water and cause various physiological phenomena.^{1,2} Therefore, the information about such elements in waters is very important.

The requirement for the accurate determination of trace heavy elements has been increasing in environmental pollution studies. For it, the preconcentration is needed from bulk water prior to their measurements by a proper method. The volatilization, solvent extraction, adsorption, ion-exchange, and coprecipitation are commonly applied as the preconcentration techniques for the atomic spectrometric determination of them in water samples.³⁻⁸ However, these methods need relatively long time and cumbersome operations for a large volume of sample by some techniques such as gentle heating, phase separation, filtration, elution and so forth.

In this work, a precipitate flotation technique was applied for the preconcentration of hydroxide-forming elements, in which the precipitates of hydrated metal oxide are floated with the aid of surfactant and small inert gas bubbles.⁹⁻¹³ This technique is rapid and convenient compared to other

concentration techniques and also the flotation of flocculent precipitates can be performed with an unskillful technique. Besides, it has another advantage to concentrate many elements, simultaneously.

Kim and Zeitlin¹⁰ had determined trace Cu(II) and Zn(II) in a sea water by the flotation of them coprecipitated with iron(III) hydroxide precipitates at pH 7.6 using dodecylamine as a surfactant. Mizuike and Hiraide¹¹ also used iron(III) hydroxide as a coprecipitant for the flotation of Sn(IV), Cu(II) and Zn(II) in an aqueous solution at pH 6-8 with paraffinic solution. On the other hand, hydrated zirconium oxide,¹² aluminum hydroxide and indium(III) hydroxide¹³ as a coprecipitant as well as sodium oleate and sodium lauryl sulfate as a surfactant were used for the determinative flotation of various elements. And Ti(OH)₄, Bi(OH)₃, Th(OH)₄, CdS, PbS and so on have also been used.¹⁴

In this study, trace amounts of Cd(II), Cu(II), Pb(II), Mn(II), and Zn(II) were simultaneously floated by the coprecipitation with lanthanum hydroxide and nitrogen gas bubbling. But lanthanum hydroxide has not been used as a gathering agent for the flotation of multi-elements up to present. Not only the lanthanum forms very desirable flocculent precipitates, but also it has good capability to reduce the chemical interferences in the flame atomic absorption spectrometry. The various experimental parameters such as coprecipitant, surfactant, solution pH and bubbling rate of nitrogen gas were investigated as well as the interferences of concomitant