

Introduction to Detection Technology of Radioactive Multi-Nuclides by using Portable ICP-OES and LEP-OES Instruments

Doo-Hee Chang*, Duck-Hee Kwon, Sun-Ho Kim

Nuclear Physics Application Research Division, Korea Atomic Energy Research Institute, Daejeon 34057, Korea

*Corresponding author: doochang@kaeri.re.kr

1. Introduction

There are three kinds of detection method under the atomic processes, such as the atomic emission, atomic absorption, and atomic fluorescence. For the atomic emission process, the electron return to its ground state after a short dwell time in a more energetic orbital. The energy difference released by this atomic emission is emitted all special directions in the form of electromagnetic radiation (or as a photon). There is an absorption process (or electromagnetic radiation) under the atomic absorption. Otherwise, when the amount of energy added by absorbing electromagnetic radiation is emitted in all special directions in the form of electromagnetic radiation under the atomic fluorescence process [1].

The atomic emission spectroscopy (AES or OES) uses quantitative measurement of the optical emission from excited atoms to determine analytic concentration [2]. Analyzed radioactive atoms in solution are aspirated into the excitation region where they are desolved, vaporized, and atomized by a flame, discharge, or plasma. These high-temperature atomization sources provide sufficient energy to promote the atoms into high energy levels. The atoms decay back to lower levels by emitting light. Since the transitions are between distinct atomic energy levels, the emission lines in the spectra are narrow. The spectra of multi-elemental samples can be very congested, and spectral separation of nearby atomic transitions requires a high-resolution spectrometer (HRS). Since all atoms in a sample are excited simultaneously, they can be detected simultaneously, and is the major advantage of AES compared to atomic-absorption (AA) spectroscopy.

The chemical analysis of highly active liquid waste (HALW) has been a major concern in the field of nuclear waste treatment. Major isotopes of Cs in HALW include ^{133}Cs , ^{134}Cs , ^{135}Cs , and ^{137}Cs because other short-life isotopes disappear during storage. The inductively coupled plasma-AES (ICP-AES) cannot measure Cs, in usual, at the sub-parts per million (ppm) level [3]. Cs is ionized easily owing to its low ionization potential of 3.893 eV. Consequently, most Cs atoms are ionized at high electron temperatures (8,000~10,000 K) of ICP. However, the energy provided by ICP is insufficient for exciting ionized Cs. Moreover, the most sensitive emission line of neutral Cs at 852.12 nm is overlapped by an emission line of Argon gas at 852.14 nm. The depletion of neutral Cs and the overlapping of argon emission are the main reason of low sensitivity.

To overcome the low sensitivity, the liquid electrode plasma (LEP) with a few unique features may be an attractive prospect for radiochemical analysis since these miniaturized plasma sources are expected to be alternatives for ICP to simplify the plasma generation process to ensure it does not require a plasma gas (ex., Ar) and a high power source [4].

2. Instrumental Apparatus of Portable ICP-OES

The key technologies of portable ICP-OES are as shown in Fig. 1: Gas flow measurement & control, diffraction gratings, custom vacuum machining, integrated optical subassemblies, vibration isolation systems, and optical components [1, 2].

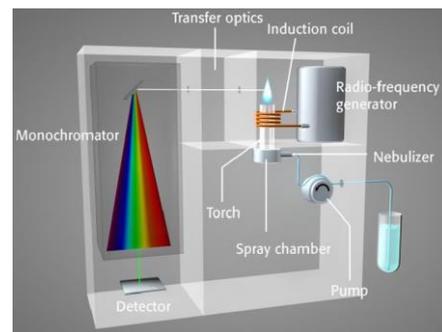


Fig. 1. Schematic structure of an ICP optical emission spectrometer (OES).

Main components of ICP-OES device are summarized as the following (see Fig. 2):

- (i) ICP (RFP: RF plasma) torch: Energy needed to maintain the ICP plasma is provided by a RF generator
- (ii) Nebulizer & Spray chamber: Nebulizer turns the measuring solution into an aerosol, the larger droplets of which are subsequently removed inside the spray chamber
- (iii) Injector: Inject the aerosol into the plasma, where the substance is dried extremely and quickly. The dried solid residue is melted and finally vaporized. The gas molecules are then atomized and the atoms ionized
- (iv) Transfer optics: Electromagnetic radiation which is emitted as a result of the simultaneously occurring excitation is directed to the dispersing (wavelength-resolving) optics. The optics separates the light by wavelength, and the intensity of radiation for each wavelength is registered by a detector

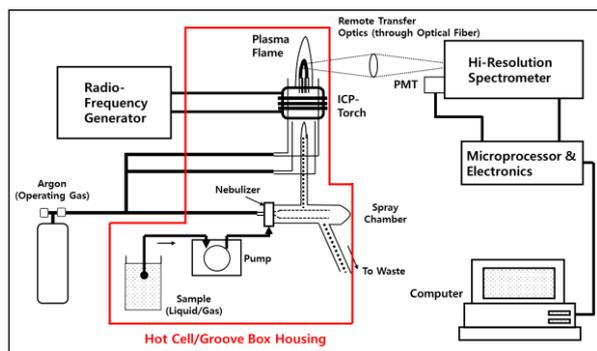


Fig. 2. Main components and typical layout of portable ICP-OES instrument.

2.1 ICP/RFP Torch

The characteristics of typical ICP(RFP) torch are summarized, as the following:

- (i) RF frequency: 27~56 MHz (by good energy transfer)
- (ii) RF power: 0.7~1.5 kW
- (iii) Operating gas (Plasma/Coolant gas): Ar (10~20 LPM)
- (iv) Plasma temperature: 5,000 ~ 10,000 K
- (v) Insulating material: Quartz or Ceramic (for hydrofluoric acid solution)
- (vi) Injector gas (Nebulizer gas): 0.5~2 LPM (as aerosol, fine mist of droplets)
- (vii) Auxiliary gas: 0.5~2 LPM (if necessary)

2.2 Nebulizer

The nebulizer converts a liquid into an aerosol, transported to the plasma, and separates between a pneumatic force and an ultrasonic mechanical force. The "Pneumatic" uses a gas as the driving force. The popular types of ICP pneumatic nebulizer are as the following: Concentric glass, Concentric PFA, Fixed cross-flow, Lichte (modified), Micro-concentric glass, Adjustable cross-flow, High-pressure fixed cross-flow (MAK), Babington V-groove (high solids), GMK Babington (high solids), Hildebrand dual grid (high solids), Ebdon slurry (high solids), Cone Spray (high solids). The "Ultrasonic nebulization" means the liquid sample is pumped onto an oscillating piezoelectric crystal transducer, driven at 0.2~10 MHz. The ultrasonic mechanical force is used to break up liquid films into an aerosol with the efficiency of 10~20% and at least 10-fold greater than pneumatic nebulization.

2.3 Spray Chamber

Once the sample aerosol is created by the nebulizer, it must be transported to the torch so it can be injected into the plasma. Because only very small droplets in the aerosol are suitable for injection into the plasma, a spray chamber is placed between the nebulizer and the torch. The primary function of the spray chamber is to remove large droplets from the aerosol. A secondary purpose of

the spray chamber is to smooth out pulses that occur during nebulization, often due to pumping of the solution.

In general, spray chambers for the ICP are designed to allow droplets with diameters of about 10 μ m or smaller to pass to the plasma. With typical nebulizers, this droplet range constitutes about 1~5% of the sample that is introduced to the nebulizer. The remaining 95~99% of the sample is drained into a waste container. The material from which a spray chamber is constructed can be an important characteristic of a spray chamber. Spray chambers made from corrosion-resistant materials allow the analyst to introduce samples containing hydrofluoric acid which could damage glass spray chambers.

2.4 Transfer Optics

The emission radiation from the region of the plasma known as the normal analytical zone (NAZ) is sampled for the spectrometric measurement. Until recently, the analytical zone was observed from the side of the plasma operating in a vertical orientation. This classical approach to ICP spectroscopy is referred to as a radial or side-on viewing of the plasma. In the early 1990's, a new "look" at the normal analytical zone of the ICP was commercialized. The plasma is rotated to a horizontal position and the zone is observed from the end of the plasma. This configuration has become known as an axial or end-on viewing of the ICP. Recently, instruments that combine both radial and axial viewing, called dual view, have been introduced.

No matter whether the ICP is a side-on or end-on viewing type configuration, the radiation is usually collected by a focusing optic such as a convex lens or a concave mirror. This optic then focuses the image of the plasma onto the entrance slit of the wavelength dispersing device or spectrometer. In some side-on configured instruments, the focusing optic is used in conjunction with mirrors that allow measurement of emission at different heights within the plasma. This viewing height adjustment makes the instrument more flexible, although it is not necessary for most analyses. For the end-on viewing ICPs, the ability to measure the emission at different heights is immaterial for most applications. However, the ability to adjust the mirror simplifies torch alignment.

3. Instrumental Apparatus of Portable ICP-OES

In the analysis of liquid samples, reliable methods such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS) are widely used. However, the need for a gas increases the analytical cost, and the complex instruments require frequent maintenance, which make these methods difficult to

apply in the field and in real-time analysis [5]. One method that overcomes these issues is the use of micro-plasma sources especially for liquid sample analysis.

The working principle of liquid electrode plasma atomic emission spectroscopy (LEP-AES) is as follows (as shown in Fig. 3). A liquid sample with

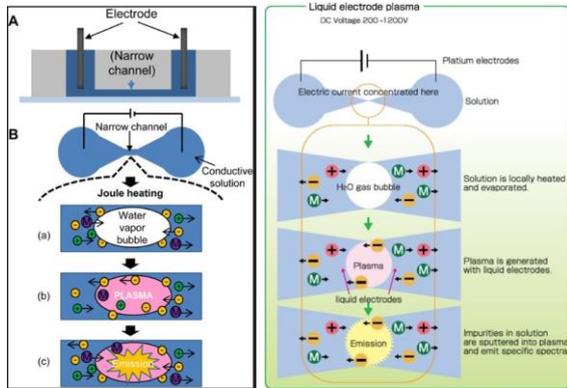


Fig. 3. The schematic principle of LEP-OES system.

electrolytes is filled inside a microchannel having a narrow center and then high-voltage DC/AC pulse powers are applied with electrodes on both sides of the microchannel. As a bubble generated by Joule heating at the narrow-center part expands, the bubble liquid interfaces work as liquid electrodes for discharge inside the bubble. Compared to conventional ICP-AES, LEP-AES uses very small plasma without gas, resulting in lower analytical cost, less maintenance, and smaller instrument size, which makes it easy to be applied in the field and in real-time analysis. In several research studies using the LEP-APS, microchannels made of polydimethylsiloxane, resin, and silica were used, and with salts or nitric acid as typical solutions, 0.2 to 2.5 kV was applied for the emission.

A rapid and simple analytical method using the LEP-OES for determination of Cs in highly radioactive liquid sample was already developed, as shown in Fig. 4 [3].

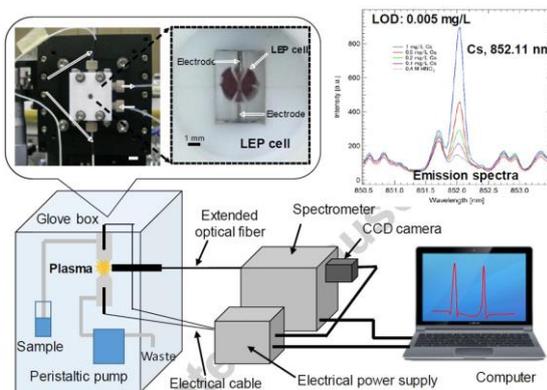


Fig. 4. Instrumental apparatus of LEP-OES: Hourglass LEP cell, setup of cell with holder, and arrangement of LEP-OES for measurement of radioactive sample.

The limit of detection (LOD) and limit of quantification (LOQ) are 0.005 mg/L and 0.02 mg/L, respectively. The measurement time is about three minutes. And, no sample treatment other than dilution is needed in the LEP-OES process.

4. Conclusions

The instrumental apparatus of ICP-OES and LEP-OES systems are reviewed for the element analysis of radioactive multi-nuclides with the portable & fast detection and sensitive analysis methods. The ICP-OES and LEP-OES methods are available and useful for the quantitative element analysis of radioactive nuclides.

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