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

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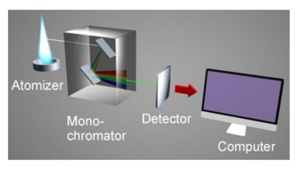
Introduction

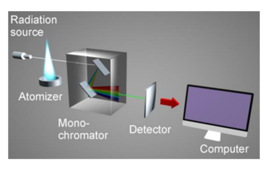
• Detection Technology of Atomic Processes

(i) Atomic Emission



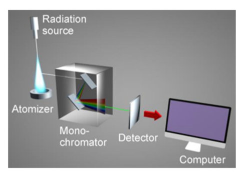
- After a short dwell time in a more energetic orbital, the electron return to its ground state. The energy difference released by this process is emitted all special directions in the form of electromagnetic radiation (or as a photon)

(ii) Atomic Absorption



- Absorption of photons (or electromagnetic radiations)

(iii) Atomic Fluorescence



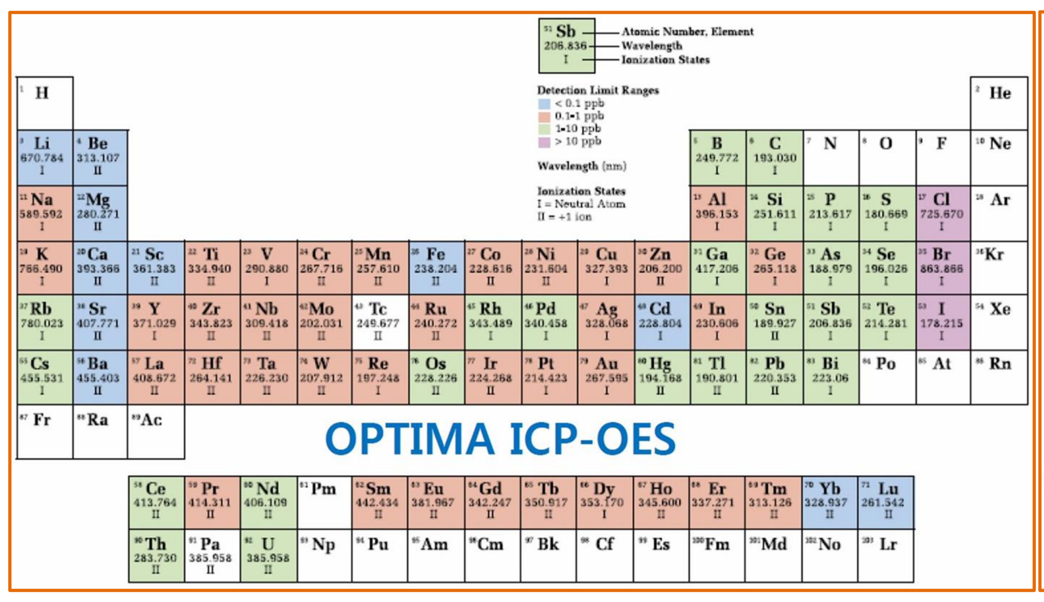
- When the amount of energy added by absorbing electromagnetic radiation is emitted in all special directions in the form of electromagnetic radiation

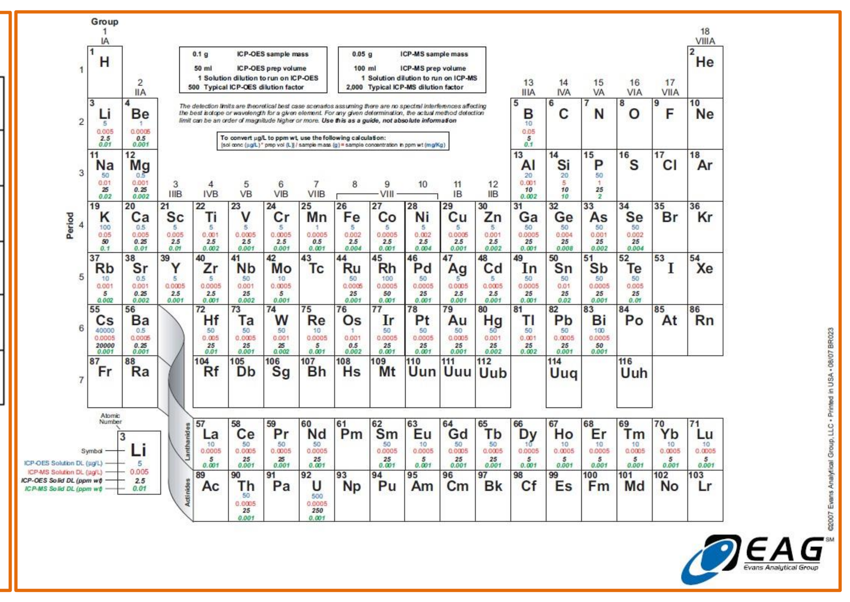
◆ 원자분광기(AS) 기술 특징

	AAS (원자흡수분광기)		MP-AES (마이크로웨이브 플라즈마-AES)	ICP-OES	ICP-MS	
	FAAS (불꽃AAS)	GFAAS (흑연불꽃AAS)			SQ (단일Quadrupole)	QQQ (Triple Quadrupole)
검출 한계	100's ppb	10's-100's ppt	ppb-10's ppb	100's ppt-ppb	<ppt	<ppt
측정 모드	순차 측정	순차 측정	순차 측정	동시 측정	순차 측정 (MS)	순차 측정 (까다로운 간섭 문제를 위한 MS/MS
최대 시료/일	100-200 (~6 원소)	100-200 (~2 원소)	100-200 (~10 원소)	2000-2500 (50+ 원소)	700-1000 (~50 원소)	500-750 (~50 원소)
유효 측정범위 (dynamic range)	3-4	2-3	4-5	7-8	10-11	9
작업자 기술 필요 수준	낮음	중간	낮음	중간	높음	가장 높음

- Note: ppm (parts-per-million, 10^{-6}), ppb (parts-per-billion, 10^{-9}), ppt (parts-per-trillion, 10^{-12}), ppq (parts-per-quadrillion, 10^{-15}) [g/L]

• Detection Limit Guidance





Instrumental Detection of ICP-OES Device

Key Technologies of ICP-OES

- Gas flow measurement & control
- Diffraction gratings
- Custom vacuum machining
- Integrated optical sub-assemblies
- Vibration isolation systems
- Optical components

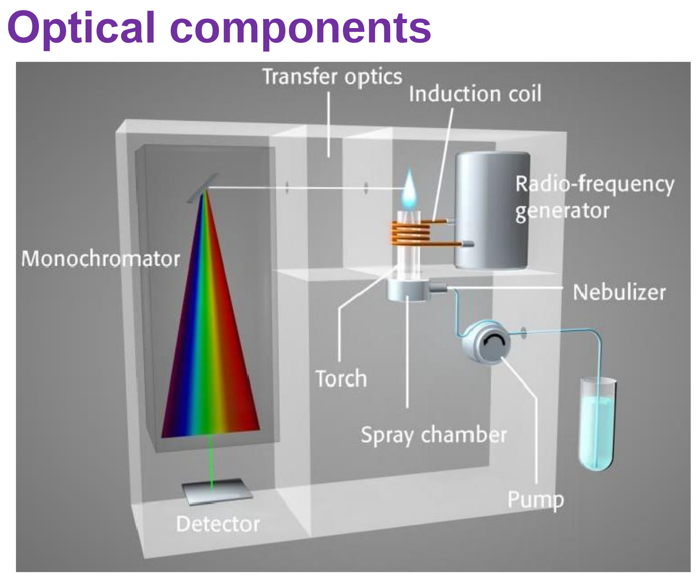


Fig. 1. Schematic structure of an ICP emission spectrometer

Characteristics of ICP (RFP) Torch

- RF Frequency : 27 ~ 56 MHz (by good energy transfer)
- RF Power : 0.7 ~ 1.5 kW
- Operating Gas (Plasma/Coolant Gas) : Ar (10~20 LPM)
- Plasma Temperature : 5,000 ~ 10,000 K
- Insulating Material : Quartz or Ceramic (for hydrofluoric acid solution)
- Injector Gas (Nebulizer Gas) : 0.5~2 LPM (as Aerosol, Fine mist of droplets)
- Auxiliary Gas : 0.5~2 LPM (if necessary)

Main Components of ICP-OES Device

○ ICP(RFP) Torch
- Energy needed to maintain the ICP plasma is provided by a RF generator

○ Spray Chamber
- Nebulizer turns the measuring solution into an aerosol, the larger droplets of which are subsequently removed inside the splay chamber

○ 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

○ 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 the radiation for each wavelength is registered by a detector

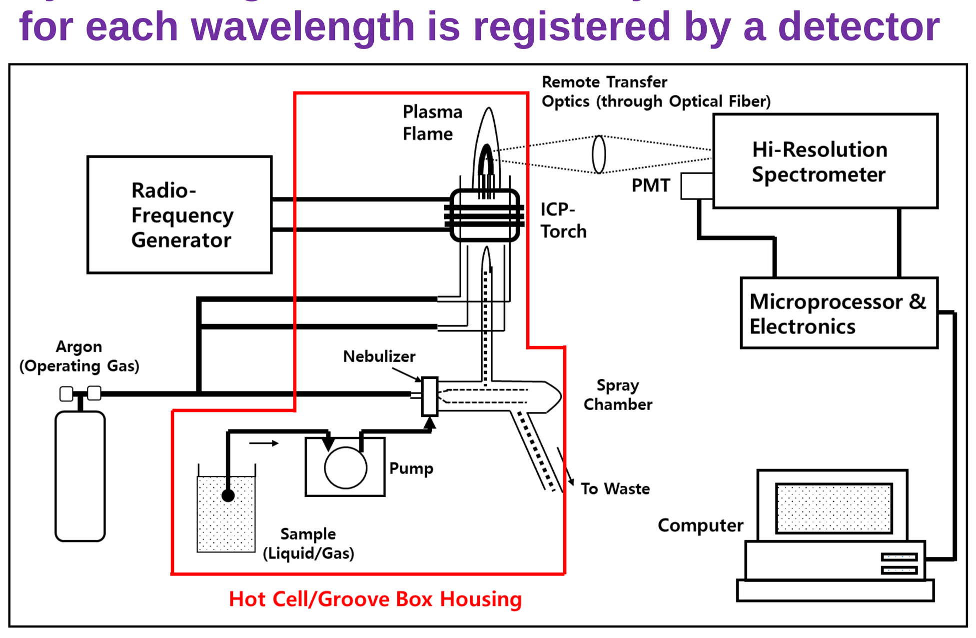


Fig. 2. Main components and typical layout of ICP-OES instrument

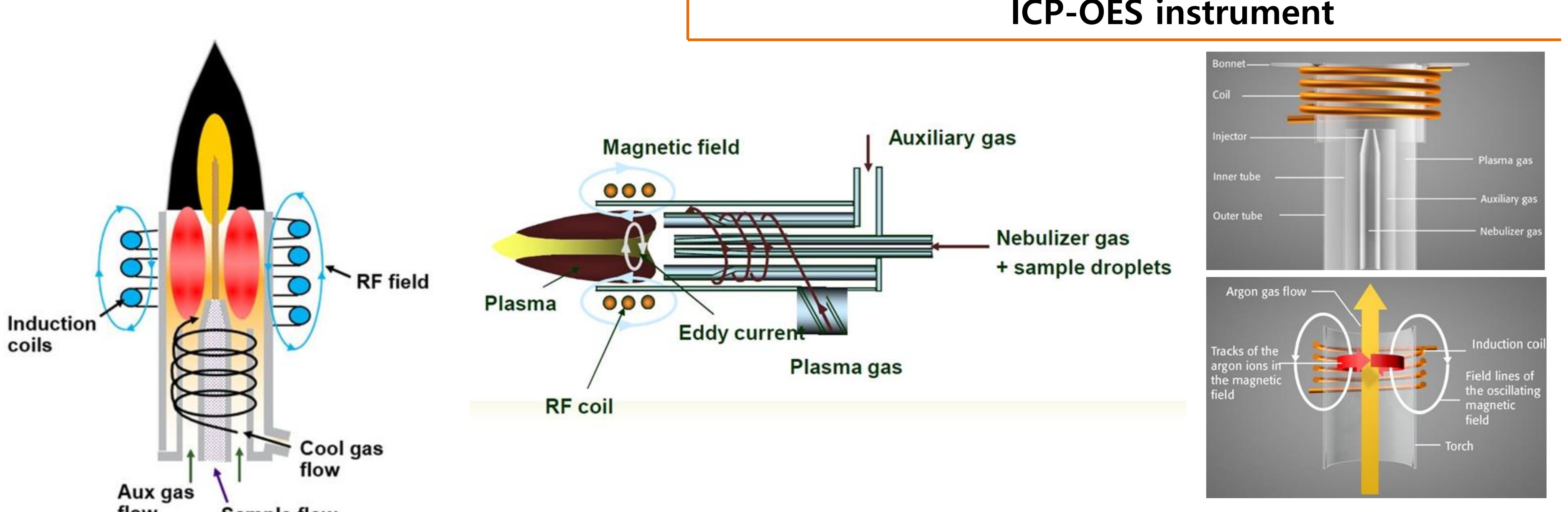


Fig. 3. Structure of ICP torch and schematics/functional principle of ICP

Nebulizer

- Convert a liquid into an aerosol, transported to the plasma
  - Separate between Pneumatic force and Ultrasonic mechanical force
- Popular types of ICP pneumatic nebulizer
  - 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)
- "Ultrasonic nebulization" means the liquid sample is pumped onto an oscillating piezoelectric crystal transducer, driven at 0.2~10 MHz
  - Used to break up liquid films into an aerosol
  - Efficiency of 10~20%, at least 10-fold greater than pneumatic nebulization

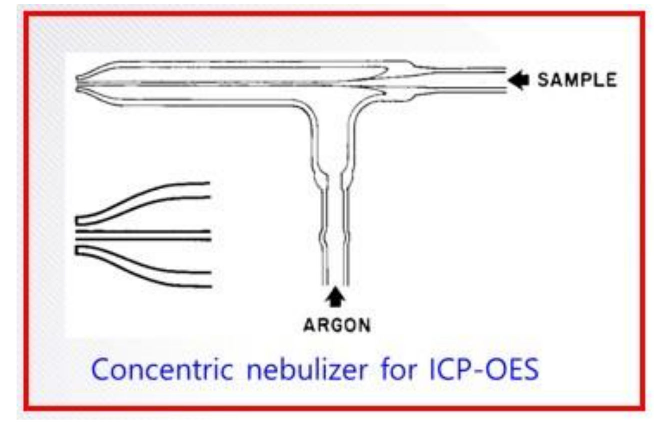


Fig. 4. The most common Nebulizer of ICP-OES

Spray Chamber

- Placed between the nebulizer and the torch
- To remove large droplets from the aerosol (a dimeter of 1~5 microns)
  - Plasma discharge is inefficient at dissociating large droplets (>10 micron~1x10-6 meter). The latter are eliminated by gravity and exit through a drain tube
- To smooth out pulses that occur during nebulization process, often due to pumping of the solution
- Efficiency of nebulizer/spray chamber system ~ 2%
  - Remainder of measuring solution(98%) is drained from the spray chamber, usually by pumping out the excess solution
- The greater the density of an aerosol, the lower of the intensity at the same analytic concentration
- The greater the viscosity of a solution, the lower of the intensity at the same analytic concentration

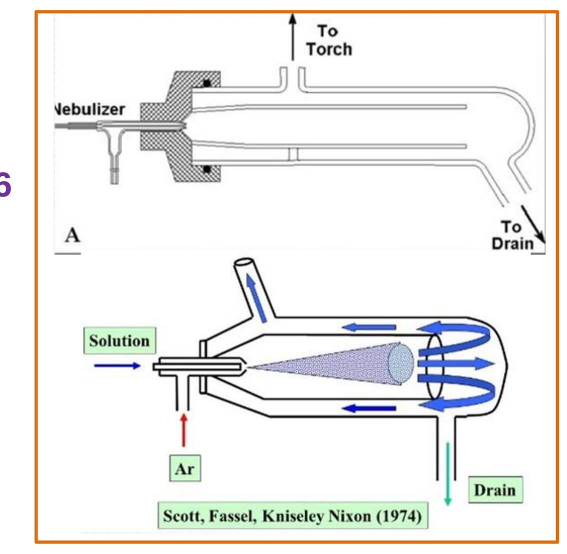
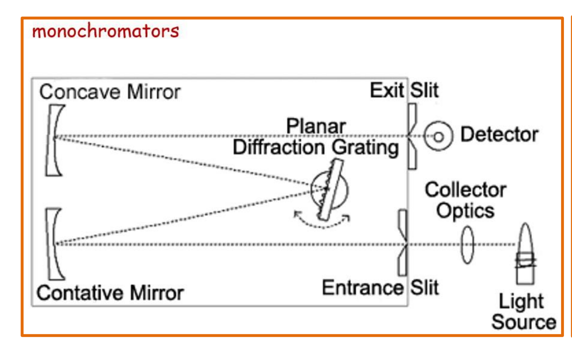
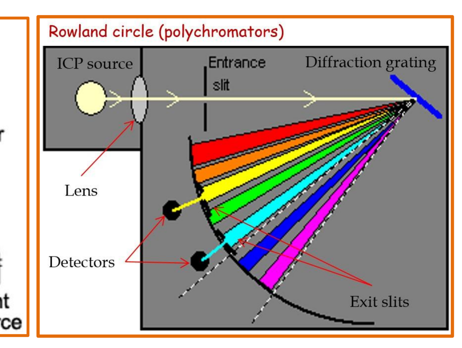


Fig. 5. Scott-double-pass Spray chamber

Transfer Optics

Available Devices
- Monochromators
  - Only isolate one line at any given instant
- Polychromators
  - Interrogate several different lines simultaneously
- Echelle spectrometer
  - Interrogate several different lines simultaneously





Instrumental Detection of LEP-OES Device

- Major isotopes of Cs in HALW (highly active liquid waste): ^{133}Cs, ^{134}Cs, ^{135}Cs, ^{137}Cs (long-life isotopes)
- ICP-OES(AES) cannot measure Cs at the sub-parts per million (ppm) level
  - Cs is ionized easily owing to its low ionization potential of 3.893 eV (Most Cs atoms are ionized at high electron temperatures (8,000~10,000 °K) of ICP
  - Energy provided by ICP is insufficient for exciting ionized Cs
  - Most sensitive emission line of neutral Cs (852.12 nm) is overlapped by emission line of Argon gas (852.14 nm)
  - Depletion of neutral Cs and overlapping of Argon emission are the reason of low sensitivity
- Typically detecting method of radio-Cs (^{134}Cs, ^{137}Cs)
  - Gamma spectrometer / ICP-MS
- LEP, as an attractive prospect for radiochemical analysis
  - Not require a plasma gas (ex. Ar), high-power source, and nebulizer
  - Discharge plasma generation between two liquid electrodes in a microchannel (or microchip), containing a sample solution
  - Confine a microchannel
  - Provide a more compact plasma source
  - Avoid spreading of the analyte (very important in radioactive element analysis)
  - Hourglass microchannels enhance the sensitivity of ICE-AES in detection of few elements
  - Mitigation of channel damage, caused by discharge plasma, by using an alternating current of a suitable frequency

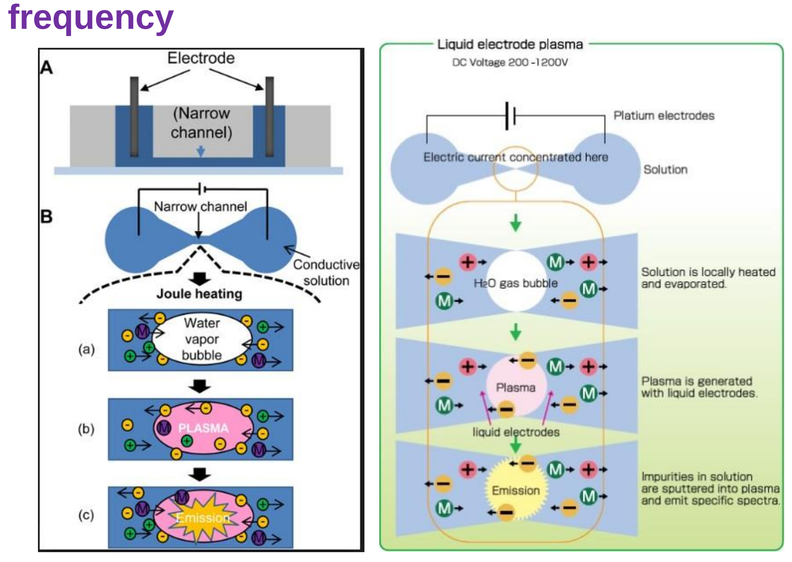


Fig. 6. Schematic principle of LEP-OES

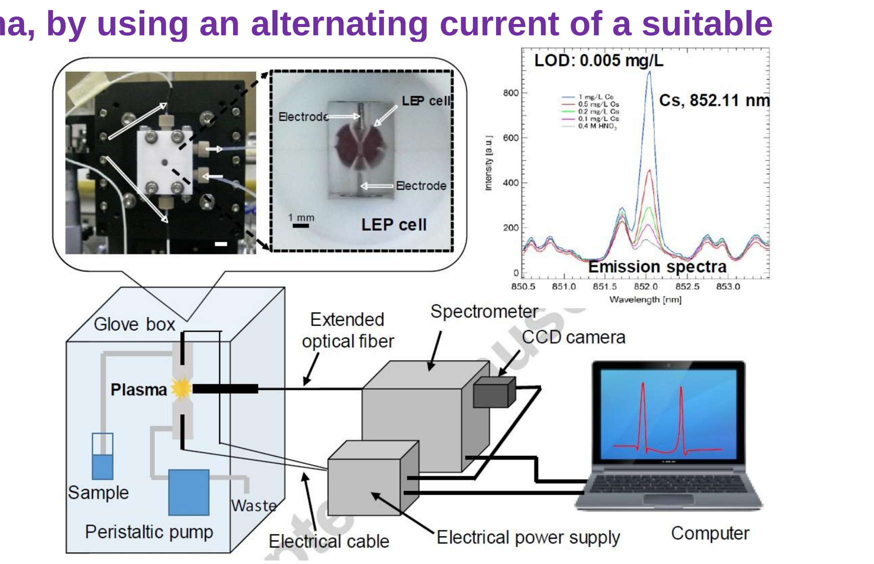


Fig. 7. Instrumentation of LEPLEP-OES for measurement of radioactive samples

Conclusions (& Basic Database)

◆ Database of Radioactive Nuclides from ICP-OES Experiments

Radioactive Nuclide	Sample Concentration [mg/L]	LOD/LOQ Level [μg/L, μg/Kg, ppb]	Detecting Wavelength [nm]	Year
$^{233-236}U/^{238}U$	~35	1~10	406.255/411.610/424.437	JAAS* 2011 26:293
^{237}Np	~1000	3~55	295~456	Microchemical J. 2014 117:225
$^{238-242}Pu$	~3.5	2~3	299~453	JAAS 2015 30:1655
$^{241-243}Am$	~1550	< 3	283~469	Microchemical J. 2013 110:425 JAAS 2014 29:817

*Journal of Analytical Atomic Spectrometry

◆ Database of Radioactive Nuclides from LEP-OES Experiment

Radioactive Nuclide	Sample Concentration [mg/L]	LOD/LOQ Level [μg/L, μg/Kg, ppb]	Detecting Wavelength [nm]	Year
Cs*	0.1~1.0	5~20	852.11	2018

*Talanta 2018 183:283

◆ 목표 분석(난분석) 핵종(사용현장 대응 이동형 장치 기반)
- 해체구조폐기물: ^{36}Cl, ^{41}Ca (^{55}Fe, $^{59/63}Ni$, ^{90}Sr)
- 콘크리트폐기물: ^{36}Cl, ^{60}Co, $^{152/154}Eu$
- 토양(해양)폐기물: ^{3}H, ^{60}Co, ^{90}Sr, ^{137}Cs

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