Design and Performance of Glove-Box Adapted Inductively Coupled Plasma-Optical Emission Spectrometer for the Estimation of Elemental Composition of High Level Radioactive LiquidWaste at WIP Kalpakkam

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1. Introduction

Inductively Coupled Plasma–Optical Emission Spectrometer (ICPOES) is widely used for the qualitative and quantitative analysis for elemental composition of samples. ICPOES is based on the measurement of wavelengths and intensities of spectral lines emitted by secondary excitation. ICPOES is most preferred because of its high sensitivity, precision, and relative freedom from matrix effects. HighLevel Radioactive Liquid Waste (HLW) is immobilized in sodium borosilicate glass matrices by vitrification using a Joule Heated Ceramic Melter. Selection of composition of glass matrix is based on the elemental composition of HLW. The major elemental compositions of HLW depend on the burn-up of thenuclear fuel. It mainly contains fission products, activation products, minor actinides, corrosion products and added chemicals.

The concentration of rare earth elements, corrosion products, added chemicals, and platinum group metals are required to conform to stringent specification for safe disposal of Vitrified Waste Products (VWP) in Deep Geological Repository (DGR). For example, the amount of Na_2O has a significant role. It alters the glass structure by breaking Si-O bonds and provides non bridging oxygens, which alter the physical and chemical properties of glass [1]. Also, Rare Earth (RE) elements are abundant fission products in HLW, which may crystallize during melt cooling to form RE rich silicate phases such as apatite ($Ca_2RE_8(SiO_4)6O_2$) [2]. An increased elemental concentration HLW may alter the processing parameters (pouring temperature and viscosity) glass transition temperature (devitrification temperature) and strongly affect the chemical properties (leaching) of the vitrified product.

The commercially available ICP-OES cannot be readily employed for the analysis of HLW due to its high radioactivity content (~100 Ci/L). Hence, the commercial ICP-OES (Horiba JY-Ultima, Jobin Yvon, France) instrument was altered and installed in a suitably modified Glove Box (GB) for the analysis of radioactive liquids. The glove box satisfies the requirements of total containment of radioactive isotopes in solution as well as aerosol, easy operation during analysis, and helps to keep exposure to the operator within permissible limits. This abstract comprises the design of a suitable glove box to perform analysis of various streams of HLW and the JHCM feed by modified ICP-OES. Selection of elements, wavelength, method, calibration followed by its subsequent use for analysis have been discussed.

2. Glove Box Design and Modification of Instrumentation

A JY-Ultima ICP spectrometer was obtained from M/s Jobin Yvon, France, having a radial viewing configuration. The argon plasma source was powered with a solid-state 40.68MHz Radio frequency (RF) generator system that offers frequency stabilization, automatic initiation of the plasma, and reflected power regulation. The RF generator is isolated sufficiently to protect the plasma against RF leakage and electromagnetic interference. The coil has a self-enclosed water cooling system. The composite light emission from the plasma source is focused on the slit of the concave grating spectrometer with Czerny-Turner mounting, which disperses light into individual wavelengths. The spectrometer and plasma source are computer controlled, and the system can be programmed to monitor the individual analytical wavelengths sequentially.

The instrument was modified before its installation in the glove box to meet the specific requirements of analysis of HLW samples. The left side of the frame in which the torch compartment is located was separated. Only the detection system was retained inside the monochromator chassis and was thermo-regulated. A standard independent ICP torch cabinet was constructed including the ICP generator, match-box, Argon gas control, peristaltic pump, igniter and a torch. Tuning adjustment on the match-boxunit was positioned from the front side to the top and provided with extended cables. All electronic and optical components were placed outside the radioactive containment (GB) to prevent radiation-induced damage and also to facilitate easy maintenance. The entire assembly of the ICP torch, RF coil, nebulizer, spray chamber, peristaltic pump, and drainage system were placed inside the GB for the analysis of radioactive samples. To minimize acid attack during sample processing, a single module standard commercial glove box was connected with another specially designed stainless steel glove box. The specially designed GB incorporating these features is shown in Figure 1.All the modifications for the GB adaptation were achieved without any compromise on the analytical performance of the spectrometer which is one of the most important aspects during this work.

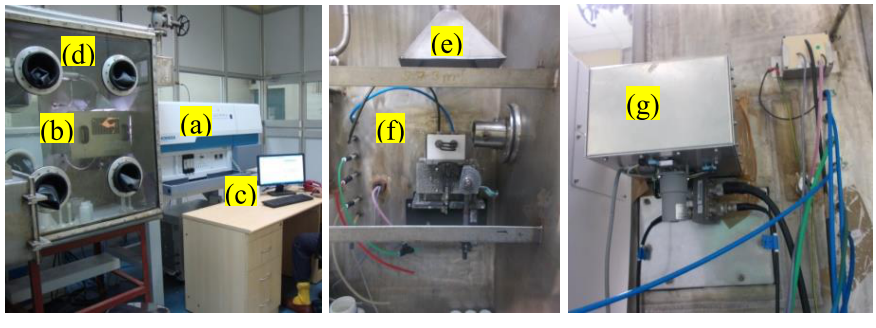

Figure 1. GB adopted ICP-OES (a) Spectrometer; (b) Torch cabinet; (c) monitoring system; (d) GB; (e) exhaust (-ve pressure max. 25mmWC) line; (f) RF coil; and (g) matching box

3. Calibration and Analysis of HLRW Streams

The measured acidity of diluted HLW, suitable for ICP-OES based on radiation dose, ranged between 0.1 and 0.3N. To minimize the effect of acid concentration on signal intensity of different elements, calibration standards, and samples were prepared in 0.2N HNO_3. For selected ionic lines for the elements of interest, the Background Equivalence Concentration (BEC), Limit of Detection (LOD) andRelative Standard Deviation (RSD) were calculated. The selected line and method was accurate and precise enough for the determination of elemental concentration in HLW as indicated by acceptable RSD values

(<1%). Moreover, the lines selected for analysis are mostly free from prominent interferences. For example, compared to other lines (385.958, 367.007, and 263.553 nm) of uranium (U II), the 409.014 is free of line interference (for ex. Ti, Fe, Ca, and Mg) and found to be accurate by using 40.68 MHz ICPAES (make: JY ULTIMA 2) [3]. The linear relationship was established for all elements with an acceptable coefficient of determination ($r^2 \geq 0.9999$) values in regression equations. Figure 2(a) shows an example of the relationship between concentration and the corresponding intensity values for uranium. Subsequently, the HLW elemental concentrations were estimated for various batches of the sample with suitable dilution. For the estimated concentrationfor the elements of interestareshown in Figure 2(b)-(d).

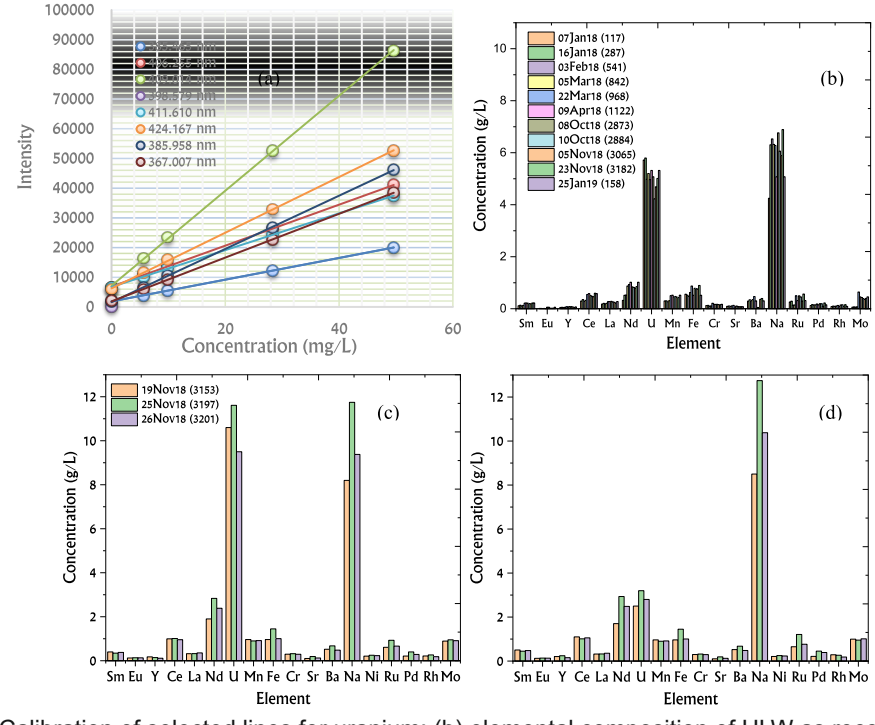

Figure 2. (a) Calibration of selected lines for uranium; (b) elemental composition of HLW as received at WIP-K, (c) elemental composition of HLW after evaporation; (d) elemental composition of HLW after uranium separation (JHCM feed)

4. Conclusion

The analysis of the HLW demonstrates the ability of the glove-box adapted ICP-OES unit. The installed excitation source inside the glove box offers an optimal configuration and capability for analysis of elements at trace levels (µg/mL).

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