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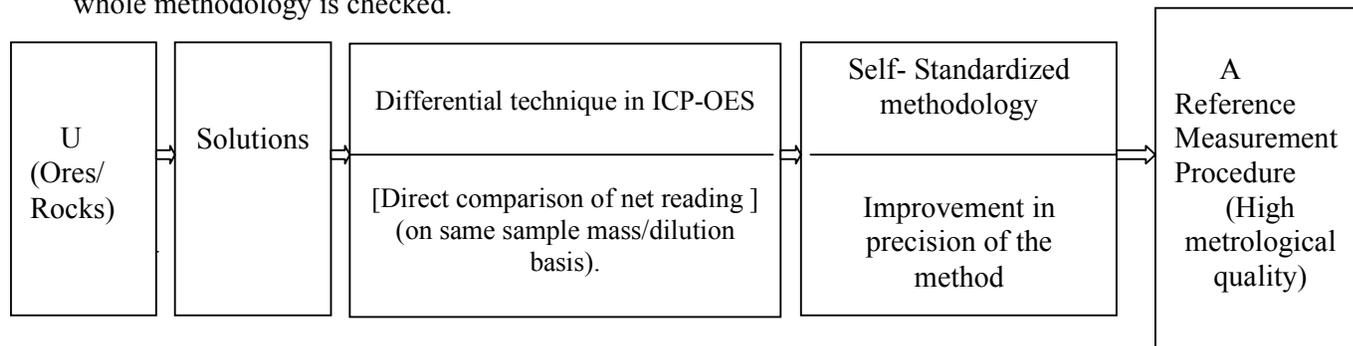
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Graphical abstract:

Application of a differential technique in ICP-OES measurement procedure for the determination of total uranium mass fraction is based on the comparison of the net intensity/indication of the reference solutions or certified reference materials with a sample of similar but unknown concentration on the same sample weight or dilution basis, wherein all samples are subjected to exactly the same procedures and measurement steps such that the whole methodology is checked.



Differential technique fulfills the essential requirements of both equipment and method calibration, and also guarantees the quality of an analytical result (accuracy, high precision, reliability, comparability and traceability).

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Application of a differential technique in inductively coupled plasma emission spectrometry:
Presentation of a relative reference measurement procedure for the determination of total mass
fraction of uranium in mineralised rocks and similar matrices

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Abstract A relative reference measurement procedure for the determination of total mass fraction of uranium in mineralized rocks, ores and similar matrices using application of a differential technique in inductively coupled plasma emission spectrometry at 409.014 nm wavelength is presented, based on the comparison of net reading or indication of reference ore solutions with a sample of similar but unknown mass fraction of uranium on the same sample weight or dilution basis. Under standard operating conditions of the instrument, ICP-OES measurements were performed at 409.014 nm wavelength after checking the instrument stability by C-Ar test, robustness of plasma and linearity response using aqueous standard U₃O₈ solutions. The estimated relative measurement uncertainty values obtained using the results of replicate analyses (“top-down” approach) in ICP-OES procedure for mass fraction of uranium in low grade uranium ore -IAEA samples, and CANMET-reference uranium ore, are, S1, 0.0015, S2, 0.002, S3, 0.002, S4, 0.0015, and BL-2a, 0.001, respectively. Both approaches show low measurement uncertainty in the determination of total mass fraction of uranium without any chemical separation or extraction steps using differential technique in ICP-OES measurement procedure and are comparable with differential technique in laser-induced fluorimetry (DT-LIF). Differential technique in spectrophotometry/laser fluorimetry/ICP-OES has inherent high metrological quality. Differential technique in ICP-OES measurement procedure will be useful for the analysis of uranium in ores, certification of reference materials, borehole core assay, and other diverse applications in nuclear fuel cycle.

Keywords: Differential technique; Inductively coupled plasma emission spectrometry; Reference measurement procedure; Measurement uncertainty; Mineralised rocks; Uranium.

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Introduction

Rapid and reliable determination of the uranium mass fraction in various naturally occurring diverse matrices has been the subject of studies[1] and is of great importance from an economic standpoint [2-7]. Reliable analytical results are often the basis for critical discussions in assessing nuclear operations, environmental pollution, minerals resource potential, production of high quality reference materials, and for worldwide inter-laboratory comparison (ILC)[8]. It has been now well recognized that the quality of measurement result is of highest importance and depends on the realization of the method (strict adherence to the number of steps) into practice [9].

The metrological concepts have been elaborated in the ‘International vocabulary of metrology-basic concepts and associated terms’ (VIM) JCGM200:2008 [10] and IUPAC technical report [11]. Meyer [12] reviewed various aspects of the estimation of the measurement uncertainty of all validated analytical test procedures as an added value.

Recommendations and valid approaches to the evaluation of measurement uncertainty for various purposes are well documented in the available literature, EURACHEM/CITAC Guide (www.eurachem.com) [13] and Eurolab Guide 2007 (Measurement Uncertainty revisited, www.eurolab.org) [14].

Measurement by the “differential technique” has not been reported in inductively coupled plasma emission spectrometry, although the differential technique has been widely used for the accurate and precise spectrophotometric determination of major oxides like SiO₂ and Al₂O₃ [15–17] and also for the determination of uranium in samples of diverse matrices of mineralised rocks[6], concentrates and other U rich materials[3,4] over a dynamic range of concentrations from ppm to percentage levels using laser-induced fluorimetry. Application of a differential technique in inductively coupled plasma emission spectrometry at 409.014 nm wavelength, is based on the comparison of net reading or indication of reference ore solutions with a sample of similar but unknown mass fraction of uranium on the same sample weight/dilution basis.

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3 In continuation of our studies on the determination of total concentration of uranium in
4 borehole core samples (without any chemical separation or extraction steps): comparative studies
5 using differential technique in laser-induced fluorimetry (DT-LIF) and ICP-OES [7], this paper
6 describes a reference measurement procedure for the determination of total mass fraction of uranium
7 in mineralized rocks, ores and similar matrices using application of a differential technique in
8 inductively coupled plasma emission spectrometry at 409.014 nm wavelength, based on the
9 comparison of net reading or indication of reference ore solutions with a sample of similar but
10 unknown mass fraction of uranium on the same sample weight/dilution basis.
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20 **Experimental**

21 *Apparatus*

22 **Instrumentation**

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25 The measurement procedure developed [7] at this laboratory was studied and evaluated using the
26 instrument, Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, ULTIMA-2
27 Horiba JY, ICP-OES manual).
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33 **Aqueous standard U₃O₈ (1 mg/ ml) stock solution**

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35 Aqueous standard stock solution of uranyl ion of 1mg/ml was prepared from U₃O₈ or uranyl nitrate,
36 analaR grade (BDH Chemicals Ltd., Poole, England) having 10% HNO₃. The mass fraction of
37 uranium in this stock solution was verified using the method of Davies and Gray [18]. This titration
38 measurement procedure enables uranium to be determined without chemical separation in solutions
39 containing iron, Pu, nitrate and many others foreign ions, which interfere in conventional redox
40 methods. All of the operations needed are carried in one vessel, in the cold. In this measurement
41 procedure, an excess of iron (II) sulphate is employed to reduce U(VI) to U(IV) in a concentrated
42 phosphoric acid solution containing nitric (HNO₃) and sulphamic (NH₂SO₃H) acid. The excess of Fe
43 (II) is subsequently oxidized by nitric acid in the presence of molybdenum (VI) as catalyst. After
44 adding sulphuric acid and diluting the mixture with water, the determination is completed by titration
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with $K_2Cr_2O_7$ solution in the usual manner, using barium- diphenylamine sulphonate as indicator. The coefficient of variation of 200 to 300 mg uranium per aliquot is <0.3%

Reference materials used for method validation and calibration of spectrometer

Reference uranium ore, (CANMET)[19], BL-2a(0.426 g/100g U i.e.,0.502 g/100g U_3O_8 (recommended value for BL-2a pertains to an “as is” basis) and IAEA low-grade uranium ore [8](recommended value for IAEA pertains to for dried sample mass at 110 °C), Torbernite (Australia)—S 1 (0.471 g/100g U_3O_8), Torbernite (Spain)—S 2 (0.313 g/100g U_3O_8), Carnotite (USA)—S 3 (0.418 g/100g U_3O_8), and Uraninite (Australia)—S 4 (0.375 g/100g U_3O_8) were used as measurement standards for calibration of instrument and also for validation purposes i.e.,to check bias,precision of the measurement procedure, digestion procedure, etc. The solutions of powdered uranium ore (0.5 g, 150–200 mesh, IAEA samples were dried at 110 °C and rest others “as is” basis) were prepared as per the procedure described in this publication. All other chemicals were of analytical-reagent grade. Distilled water was used throughout.

Sample solution preparation procedure for rock samples

A sample solution of powdered rock sample (0.5 g, 150–200 mesh) is obtained by repeated evaporation with HF– HNO_3 and then evaporation with HNO_3 to convert to soluble metal nitrates. The sample residue is digested with HNO_3 and boiled for 15–20 min to get a clear solution. If the sample solution is not clear, a few drops of H_2O_2 are added and then boiled vigorously for a further 20–30 min to decompose the excess H_2O_2 . If a little unattacked residue remains, it is filtered off, washed and brought into solution by sintering and fusing with a minimum amount of a mixture of sodium fluoride and potassium pyrosulphate. The melt, after cooling, is dissolved in nitric acid. The two solutions are mixed and made up to 100 ml in a calibrated flask. The final solution is in 10% HNO_3 .

ICP-OES Measurements

ICP-OES measurements were performed after checking the instrument stability by C-Ar test, robustness of plasma and linearity response using aqueous standard U_3O_8 solutions.

ICP-OES instrument stability was checked by performing C-Ar test in first order as well as second order over the entire UV-Visible range of wavelength using 5 % HNO_3 solution: Ar wavelengths at 404.442 nm and 750.387 nm; C wavelengths at 193.026 nm and 247.856 nm. The RSD (%) of 10 replicate measurements for net reading or indication at respective wavelength were found to be 1.23, 1.52, 1.78, and 0.91, respectively (RSD% <3). The RSD of the net reading or indication measured at each wavelength was found to be less than 3% over the entire wavelength range. This indicates the excellent plasma stability in respect of wavelength and line intensity irrespective of its order. Robustness of plasma was checked by considering the intensity ratio of the Mg (II) 280.270 nm and Mg(I) 285.213 nm by using Mg standard solution, 5 $\mu g/ml$ in 3% HNO_3 and found to be 8.35 (>8). This explains the excellent plasma stability condition in respect of excitation and emission. Linearity response of the spectrometer was checked by using aqueous 1, 10 and 100 $\mu g/ml$ standard U_3O_8 solutions, prepared by dilution of the standard 1 mg/ml U_3O_8 maintaining 10% HNO_3 . The optimum plasma emission spectrometer parameters and other operating conditions are given in Table-1.

Results and Discussion

In principle, the application of differential technique in inductively coupled plasma emission spectrometry for the accurate and precise determination of uranium in mineralised rock samples holds good when a linear relationship between net reading or indication and mass fraction of uranium is established. It implies that the system must be free from interferences.

Theory of ICP-OES Measurement

The emission phenomena takes place in a plasma. An atom subjected to a plasma emits characteristic

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3 photons. The number of photons emitted is proportional to the number of atoms of the considered
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5 element. This is the basis of the quantitative analysis.

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7 net reading or indication , $I = K C$ (1)

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9 where, K, is a new constant for the given system and instrument, C, is mass fraction (g/100g) of
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11 uranium which can be traced to the SI unit kg and I, is the net reading or indication.

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14 The above equation can be used to determine the mass fraction of uranium by the application
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16 of a differential technique in ICP-OES by comparing the net intensity of the accurately known
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18 standard with unknown samples in a similar manner on same sample-mass/dilution basis as per the
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20 recommended procedure. This can be considered to be methods that operate in two parts each of
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22 which is a 'direct method'. The two parts of the method can be combined to give:

$$23 \quad I_{\text{std}}/I_{\text{sampl}} = C_{\text{std}}/C_{\text{sampl}} \quad (2)$$

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26 According to the definition recommended in 'JCGM 200:2008 -International vocabulary of
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28 metrology-Basic and general concepts and associated terms (VIM)' [10], the application of
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30 differential technique in ICP-OES [7] can be safely categorized as 'reference measurement
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32 procedure' having high metrological quality (low uncertainty). In this way, the uncertainty (error) in
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34 analysis is confined to the difference in the two concentrations and so is minimized [2-4,6,15]. In the
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36 differential technique, the precision of results is materially improved if a relative rather than absolute
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38 concentration is determined.

39 40 41 42 **Effect of sampling and acidic digestion of ore samples on uncertainty**

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45 As this procedure is intended for determination of total uranium in ores and similar matrices, samples
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47 need to be transformed into a solution before being analysed by ICP-OES procedure. The
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49 contribution of the effect of acidic digestion on total uranium determination was found to be
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51 negligible (Table-2). A 0.5g of powdered ore sample (150-200 mesh) is recommended to minimize
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53 sampling error [2,6].
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Uncertainty in the certified mass fraction in the reference uranium ore samples

IAEA low-grade uranium ores are classified as 'international standard materials' and CANMET-reference uranium ore, BL-2a have been used for the preparation of standard sample solution of uranium. Alternately, suitably diluted solutions from U_3O_8 stock solution in 1.56 mol/L HNO_3 serve as the most suitable measurement standards [4] as per the demonstrated and established ICP-OES measurement procedure [7]. The standard uncertainty in the standard material, such as, IAEA low grade uranium ore samples[8] (in which uranium values are evaluated based on the results of average values using different methods, is triangular distribution[13] (because the values close to the recommended value is more likely than near the bounds). An estimate [13] is made in the form of a maximum range described by a symmetric function using the mean value of average results by different methods [8] (Mean \pm SD, for S 3, it will be 0.418 ± 0.002) and for BL-2a, it will be 0.502 ± 0.0023 % U_3O_8). The uncertainty in reference uranium ore sample is equal to the standard deviation divided by $\sqrt{6}$. In case of S 3 and BL-2a, it will be $0.002 / \sqrt{6} = 0.000816$.

Uncertainty due to differential technique in inductively coupled plasma optical emission spectrometry measurement procedure (“bottom-up” approach):

The flow diagram of inductively coupled plasma optical emission spectrometry analysis is presented in Fig.1 for estimating the uncertainty using the “bottom-up” approach, (as per the steps involved and theory of the application of differential technique in inductively coupled plasma optical emission spectrometry measurement procedure). The uncertainty in analytical measurements arises mainly due to the following factors, 1. Sampling and acidic digestion of samples, 2. ICP-OES instrumental response, 3. Uncertainty due to volumetric operations involved, 4. Uncertainty in the certified concentration in the CRMs/ standard materials, and 5. Uncertainty due to differential ICP-OES procedure of measurement.

Proper use of volumetric glass wares and selection of pipettes for dilution of samples is required for minimization of uncertainty [2]. To remove uncertainties due to systematic bias, all

volumetric operations were carried out using same volumetric glass wares followed by direct comparison of the net reading /indication of samples with those obtained for certified reference ore sample in ICP-OES measurement operations for more accurate and precise results.

In differential ICP-OES procedure of measurement, the whole methodology is checked by the use of reference materials, as appropriate having varied concentration as well as matrix compositions, which are subjected to exactly the same measurement steps as the samples. In differential technique, first, the concentration of uranium in other standard samples is calculated with respect to the response of one standard sample on same sample weight/or dilution basis. The use of different reference standards of accurately known concentration in this recommended 'reference measurement procedure' ensures calibration, control and optimization of the quality of analytical data and also serves as a sound quality assurance/ quality control program in an analytical laboratory. In this way, it is a self-standardized methodology of measurement and guarantees the quality of an analytical result [1,3,4,6] (accuracy, high precision, reliability, comparability and traceability). Application of differential technique in ICP-OES measurement fulfills the essential requirements of both equipment and method calibration as well as is traceable to mass fraction, g/100g, which can be traced to the SI unit kg via international standard comparisons. It is practically true because it cancels the uncertainties to a large extent [2] associated with volumetric operations, measurement of signal and overall uncertainties associated with the method of measurement.

As per Eq. 2, the uncertainty in the measurement result is due to the uncertainty associated with the ratio of net reading /indication (counts) due to reference uranium ore sample solution for calibration of spectrometer and sample solutions plus the uncertainty in the mass fraction of uranium in reference uranium ore . The uranium mass fractions and their uncertainties are presented in Table 3. The combined relative uncertainty $u_{rel}[w(U_3O_8)]$ in the measurement results of samples can be written down as,

$$u_{rel}[w(U_3O_8)] = \left(u_{std}^2 + \{u(I_{std}) - u(I_s)\}^2 \right)^{1/2} \quad (3)$$

If S3 sample has been analysed by ICP-OES as per the measurement procedure, the net reading /indication (counts) was found to be 239377.62 with standard deviation, 3957.24 .The measurement uncertainty is $2(SD)/1.7321$, where SD is the standard deviation[20]. The 2 is referred to as the coverage factor and the 1.732 is the square root of 3 (for three measurements). The net reading /indication found for BI-2a sample is 289426.14 with standard deviation, 5051.50 . The combined relative uncertainty $u_{rel}[w(U_3O_8)]$ in the result of sample having mass fraction of uranium say, 0.502 g/100g U_3O_8 , can be calculated using the Eq. 3 as follows:

$$u_{rel}[w(U_3O_8)] = \left((0.000816/0.418)^2 + \left\{ (4569.29/239377.62) - (5832.80/289426.14) \right\}^2 \right)^{1/2}$$

and is found to be 0.002. Using the recommended coverage factor $k=2$, the relative expanded uncertainty is , 0.004 and 0.4 % respectively. The results are presented in Table-2.

We have demonstrated the application of differential technique in laser-induced fluorimetry [3,4,6] and it has been recommended as a reference measurement procedure for the determination of total uranium content in ores and similar matrices [2]. The method has been applied for the determination of uranium in international standard samples, SY-2, SY-3 and uranium ore, BL-2a, IAEA-low grade uranium ores and borehole core samples. “t”-test for paired data has been applied for comparing the results obtained in the same borehole sample by ICP-OES method with those obtained by using ‘differential technique in laser-induced fluorimetry method’(DT-LIF) as a reference measurement procedure. The results of uranium content compare favorably by two independent techniques [7].

The estimation of measurement uncertainty using the results of replicate analyses (“top-down” approach) in ICP-OES

The standard samples for uranium have been analyzed regularly (25 times) by ICP-OES recommended procedure. The estimation of measurement uncertainty using the results of replicate analyses of these standard samples was performed according to the “top-down” model for individual laboratories [14]. In this case, the combined relative standard uncertainty is simply the combination

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3 of the standard deviation associated with these determinations and the uncertainty in the standard
4 samples value. The estimated relative measurement uncertainty values obtained using the results of
5 replicate analyses (“top-down” approach) in ICP-OES procedure for mass fraction of uranium in low
6 grade uranium ore -IAEA samples, and CANMET-reference uranium ore, are, S1, 0.0015, S2,
7 0.002, S3, 0.002, S4, 0.0015, and BL-2a, 0.001, respectively. Using the recommended coverage
8 factor $k=2$ (this corresponds approximately to the 95% confidence interval), the relative expanded
9 uncertainties for uranium in standard samples are the following: The estimated relative expanded
10 uncertainty values obtained using the results of replicate analyses (“top-down” approach) in ICP-OES
11 for uranium content in standard IAEA samples, and reference uranium ore, BL-2a, are, S1, 0.003
12 g/100g, S2, 0.004 g/100g, S3, 0.004 g/100g, S4, 0.003 g/100g, and 0.002 g/100g, respectively.
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16 The estimated relative measurement uncertainty values by both approaches show high
17 metrological quality of measurement result (low uncertainty) for the determination of total mass
18 fraction of uranium in ores and similar matrices using differential ICP-OES method and are
19 comparable with differential technique in laser-induced fluorimetry [2,4,6]. This differential
20 technique has been developed, tested, evaluated and applied to a large number of borehole core
21 samples in our laboratories and the results are in good agreement with the published data and those
22 obtained by conventional fluorimetry and other methods and are of comparable precision to those
23 obtained by titrimetric assay [7]. The low values of estimated relative measurement uncertainty are
24 attributed because of assumptions of cancelling out the systematic bias to a larger extent in the direct
25 comparison of response (net intensity) of standard with a sample of similar but unknown mass
26 fraction on same sample mass or dilution basis. Bottom-up approach help us to understand the
27 uncertainty components associated with each step of measurement as per the flow diagram of
28 inductively coupled plasma optical emission spectrometry analysis.
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Conclusions

The simplicity, rapidity, freedom from matrix effects, no separation steps, minimum generation of radioactive analytical waste, maximum throughput, and high metrological quality are the significant features of the proposed relative reference measurement procedure. ICP-OES measurement procedure will be useful for the analysis of uranium in ores, certification of reference materials, borehole core assay, and other diverse applications in nuclear fuel cycle.

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Table-1. Operating Parameters of plasma emission spectrometer (ICP-OES ULTIMA-2 Horiba JY)

Forward Power	1000 W
Reflected Power	< 5 W
Type of Generator	Solid state
Frequency	40.68 MHz
Coolant Gas Flow Rate	12.0 L/min
Sample Gas Flow Rate	0.91 L/min
Nebulisation Pressure	2.45 bar
Nebuliser	Concentric Glass
Monochromator	Modified Czerny- Turner
Focal Length	1.0 Meter
Grating grooves	4320 gr/mm
	2400 gr/mm
Order	1 st
1 st order resolution	0.005 nm
Solution uptake	1 ml/min

Table2. Measurement of uncertainty in standard samples using ICP-OES measurement Procedure (“bottom-up” approach)

Sample	w(U ₃ O ₈), g/100g ^a Found	w(U ₃ O ₈), g/100g ^b Recommended	$u_{rel} [w(U_3O_8)]$ Relative combined standard uncertainty value	$U_{rel} [w(U_3O_8)]$ Relative expanded uncertainty value, g/100g
S 1 IAEA	(0.470±0.002)	0.471	0.002	0.004
S 2 IAEA	(0.312±0.001)	0.313	0.003	0.006
S 3 IAEA	(0.416±0.002)	0.418	0.002	0.004
S 4 IAEA	(0.372±0.003)	0.375	0.005	0.010
BI-2a, Canmet	(0.505 ±0.001)	0.502	0.002	0.004

^aThe results are an average of eight determinations ± SD on eight replicates.

^b Results by the following methods were used to evaluate the mass fraction of uranium : S 1 av. Photo: thio, 0.473; dibenzoyl methane, 0.470; vol. cerium sulfate titration, 0.469. S 2 av. Photo: thio, 0.314; arsenazo, 0.313; vol. cerium (IV) sulfate quant., 0.313. S 3 av. Photo: thio, 0.420; dibenzoyl methane, 0.419; arsenazo, 0.415; vol. cerium sulfate titration, 0.417. S 4 av. photo.: thio, 0.377; DBM, 0.376; arsenazo, 0.372; vol.cerium(IV)sulfate quant.:%:0.377

Table 3: Uranium mass fractions and their uncertainties in reference ore samples

description sample	Uranium mass fraction, g/100g	Standard uncertainty, g/100g	Relative standard uncertainty
Uranium S 3	0.418	$(0.002 \text{ g/100g})/\sqrt{6} = 0.000816 \text{ g/100g}$	$0.000816/0.418 = 0.00195$
Uranium BL-2a	0.502	$(0.002 \text{ g/100g})/\sqrt{6} = 0.000816 \text{ g/100g}$	$0.000816/0.502 = 0.00162$

* Sample solution of standard S 3 was used for direct comparison of net intensity in ICP-OES measurement .

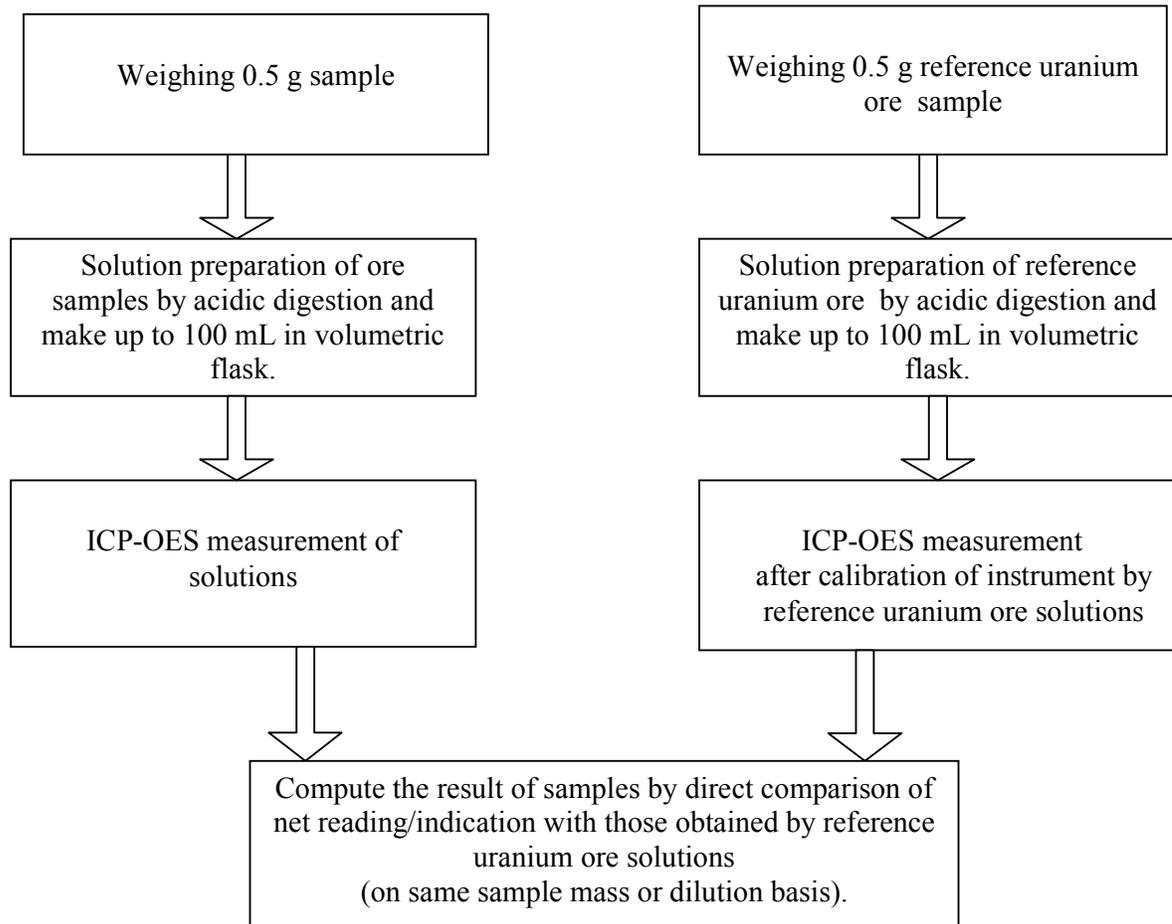


Fig.1. The flow diagram of ICP-OES analysis.

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