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Comments on: The Application of Visible Absorption Spectroscopy to the Analysis of Uranium in Aqueous Solutions

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Abstract

Comments on the application of visible absorption spectroscopy to the analysis of uranium in aqueous solutions are presented. This manuscript is lacking in update of literature survey on the analysis of uranium in aqueous solutions in concentrates. There is nothing new innovation contained in this publication. An update on a comparative analytical performance of their proposed application of visible absorption spectroscopy to the analysis of uranium in aqueous solutions in concentrates with those other reported analytical methods will give a better understanding of the developed analytical protocol. Application of Differential technique in spectrophotometry (DT-spectrophotometry) /laser-/LED-induced fluorimetry (DT-LIF/DT-LED-LIF)/ICP-OES (DT-ICP-OES) has inherent high metrological quality and warrants its introduction as a relative reference measurement procedure.

Keywords: Uranium concentration analysis; Uranyl spectroscopy; Visible absorption spectroscopy; Differential spectrophotometry; Laser fluorimetry; Uranium Concentrates

Comments

I have read this paper [1] and all the cited references in this manuscript. I would like to share some of my observations on this manuscript which may be useful for future research and a meaningful publication.

The authors claim in the abstract of the paper quote “Through assay analysis into an excess of 1 M H_2SO_4 at fixed temperature a technique has been developed for uranium concentration analysis by visible absorption spectroscopy over an assay concentration range of 1.8-13.4 mgU/g. Once implemented for a particular spectrophotometer and set of spectroscopic cells this technique promises to provide more rapid results than a classical method such as Davies-Gray (DG) titration analysis” unquote, the statement quoted in the manuscript appears misleading. This manuscript is lacking in update of literature survey on the analysis of uranium in aqueous solutions in concentrates. Moreover, there is nothing new information contained in this publication. The wellknown Davies and Gray titrimetric method for uranium [2], which permits the accurate determination of uranium in the presence of large quantities of impurities, including several modifications reported in the Davies and Gray’s method [3-5].

In addition to, there are interesting publications on rapid uranium concentration analysis techniques in concentrates, such as, the determination of uranium by high-precision spectrophotometry [6], Differential Spectrophotometric determination of uranium and niobium [7], Differential spectrophotometric method for determination of uranium by measuring absorbance using aqueous uranyl sulfate solutions at 418 nm [8], Determination of uranium in uranium concentrates [9], and application of differential technique in laser-induced fluorimetry for the direct, fast, accurate and precise determination of uranium in samples of diverse matrices of mineralized rocks [10], concentrates and other U-rich materials [11] over a dynamic range of concentrations >0.01% uranium.

The use of a "Differential Technique (DT)" in laser induced fluorimetry (LIF) is different to the standard procedure recommended by the instrument's manufacturer- the Scintrex UA-3 Uranium Analyser (Scintrex Limited, Concord, Ontario, Canada), i.e., two techniques of measurement, first, “measurement by external standard” (calibration graph) and second, “measurement by internal standard” (standard additions). The application of the differential technique in laser-induced fluorimetry is based on comparison of the fluorescence of the standard with a sample of similar but unknown concentration on the same sample weight basis by the use of an appropriate fluorescence enhancing reagent [10]. The theory for selecting the appropriate reference standard concentration to obtain the maximum precision possible in any given analysis has been used in laser induced fluorimetry and has been described in detail [10]. It was very interesting to note that in practice, the accuracy and precision of differential technique (DT) was found to be comparable with those obtained from differential spectrophotometric technique as well as to the classical titrimetry and gravimetric methods. Since differential technique (DT) fulfills the essential requirements of both equipment and method calibration, it is, therefore, a self-standardized methodology by using standards of accurately known concentrations, such as, certified reference materials [10-15]. In principle, laser-induced fluorimetry is an ideal technique for the very accurate determination of uranium by the use of appropriate fluorescence-enhancing reagents and methodology depending upon concentration of uranium and sample matrices [10-15]. The simplicity, rapidity, free from matrix effects, no separation steps, minimum generation of radioactive analytical waste, maximum throughput, cost-effectiveness, accuracy, high precision, comparability and traceability are the significant features of the differential technique [10-15]. In general, Differential technique in spectrophotometry [6-8] /laser fluorimetry [10-15]/ICP-OES [16] has high metrological quality and warrants its introduction as a ‘reference measurement procedure’ [15,16] for determination of total uranium in ores, certification of reference materials, core assay, beneficiation products and other diverse applications in nuclear fuel cycle.

Differential spectrophotometry is based on measuring the absorbance of the test solution against a standard of accurately known concentration instead of a reagent blank or pure solvent. In this way the error in measurement is confined to the difference in the two concentrations and so can be minimized [15]. In the differential technique, the precision of results is materially improved, if a relative rather than absolute concentration is determined. The most important achievement of differential spectrophotometric methods is the gain in precision of results to a level of 0.1-0.5% coefficient of variation, which was equal the precision obtained by classical gravimetric or titrimetric methods, and thus enable the use of easy-to-operate spectrophotometers for the determination of the main components of a given sample with appropriate scale expansion by placing cuvettes containing solutions of suitable concentrations in the cell compartment of the instrument, and adjusting the transmittance scale (in older instruments) with them [17]. A number of papers approach the method in connection with problems of error calculation of spectrophotometric measurements. Hiskey in his papers presented a thorough theoretical and practical description of the differential technique often called transmittance ratio method or precision spectrophotometry, reviewing at the same time the existing practical applications at that time [18,19]. Later a more general view point was presented by Reilley and Crawford about various possibilities of carrying out differential spectrophotometric measurements, which substantially differ from each other [20,21]. A review published by Svehla on the applications of differential spectrophotometry connected mainly with the larger concentrations of metals and organic substances, is commendable [22]. It deals with the principles of various methods of differential spectrophotometry, practical problems connected with the measurements and reviewed analytical applications reported till the period of review. Rapid differential spectrophotometric methods were reported for the determination of high percentages of nickel, uranium, cobalt, aluminium, beryllium, chromium, copper, erbium, manganese, molybdenum, neodymium, niobium, platinum, plutonium, praseodymium, samarium, silver, tantalum, titanium, zirconium, fluoride, cyanide, phosphate, acetazolamide, hydrochlorothiazide and other organic substances. Several comprehensive schemes of analysis detailing so-called ‘rapid methods’ were published generally restricted to the determination of the major elements, of which that of Shapiro and Brannock can be regarded as the most authoritative [23]. In fact, it is the designing of experimental procedure for calibration of instrument as well as the whole methodology for silica determination to bring the final absorbance of the comparison standards in the region of least photometric error. An orthogonal function method has been applied to the differential spectrophotometric determination of acetazolamide and hydrochlorothiazide in tablets [24]. A precision spectrophotometric determination of chromium in chromite ores and ferro-chrome has been reported [25]. The results are in good agreement with, and of comparable precision to, published data and to those obtained by titrimetric assay.

Conclusion

Differential Technique in spectrophotometry(DT-Spectrophotometry)/laser-induced fluorimetry/LED fluorimetry (DT-LIF/DT-LED-LIF) and in inductively coupled plasma emission spectrometry (DT-ICP-OES) has emerged as a technique with traceability and warrants its introduction as a relative reference measurement procedure. Over the years, the application of differential technique will continue to grow for more reliable measurement of uranium in rocks, minerals, and concentrates with higher productivity to fulfill the mission and mandate in uranium processing industries.

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