International Journal of Applied Science-Research and Review
ISSN: 2394-9988

Open Access Mini Review

Application of Differential Technique: A Self-Standardized and an Absolute Methodology: Brief Communication

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ABSTRACT

Application of differential technique is based on the comparison of the signal response of the standard with a sample of similar but unknown concentration on same sample-weight basis. Under the conditions for the use of the differential technique, in which the instrumental signal response of the unknown concentration in the sample cuvette is matched with that of the standard of accurately known concentration using a suitable reagent, which amount to a titration. In this way, accuracy and precision of the application of the differential technique in laser-induced fluorimetry/pulsed LED-fluorimetry were found to be comparable with differential spectrophotometric technique as well as to classical titrimetric and gravimetric methods. By analogy of differential technique with titrimetry, thus give rise to an absolute methodology based on the use of at least three independent analytical chemical standards or certified reference materials. Application of differential technique may prove valuable absolute methods in other fields of applications of fluorimetry and other sensitive techniques.

Keywords: Differential technique; Laser-induced fluorimetry; Pulsed LED-fluorimetry; Self-standardized; Absolute methodology

INTRODUCTION

Achieving reliable measurement data is the greatest challenge of the decades to the analytical chemists [1,2]. There are three methods of measurement in an instrumental technique namely, 1) Calibration method, 2) Method of standard additions and 3) Differential technique. All these methods have significant bearing on the reliability, cost, traceability and comparability of measurement data. The applications of all these methods hold good when a linear relationship between signal response and concentration of analyte is established. Truely, if proper care is not taken, results obtained will depend on the vagaries of the analyst.

There is a need to adopt such simple practical approach which can provide an analytical data support capable of fulfilling the stated and implied needs as well as the essential requirements of quality in totality. In this brief technical report, an overview of the salient features of differential technique *vis-a-vis* available approaches of measurement of data by absolute methods reported till date in analytical chemistry is presented [3].

Received:	29-January-2024	**Manuscript No:**	IPIAS-24-18988
Editor assigned:	01-February-2024	**PreQC No:**	IPIAS-24-18988 (PQ)
Reviewed:	15-February-2024	**QC No:**	IPIAS-24-18988
Revised:	23-February-2024	**Manuscript No:**	IPIAS-24-18988 (R)
Published:	01-March-2024	**DOI:**	10.36648/2394-9988-11.1.056

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Citation: Rathore DPS (2024) Application of Differential Technique: A Self-Standardized and an Absolute Methodology: Brief Communication. Int J Appl Sci Res Rev 11:056.

LITERATURE REVIEW

Calibration method

In calibration method, to establish the calibration graph using pure diluted working standard solutions it is assumed that there is no matrix effects *i.e.,* reduction or enhancement of signal by other matrix component accompanying the analyte of interest in the sample taken for analysis [4]. Calibration method is generally applied in spectrophotometric determinations after the isolation of analyte of interest from the accompanying matrix under the conditions by using selective reagents, adjusting pH conditions, use of masking agents, separations (if any) using solvent extraction, etc. The system should be free from matrix effects. Moreover, calibration method is based on two assumptions: 1) The errors in the calibration experiment occur only in the instrumental response plotted on vertical Y-axis, 2) The magnitude of errors in vertical Y-axis values is independent of the analyte concentration.

Both these assumptions have their limitations. In case of first assumption, the stock solution of standards of analyte of interest can be made up with an error of ca. 0.1% or better. While errors associated with the working standard solutions used for plotting of calibration graph may vary appreciably. The errors in the working standard solutions (diluted solutions) will depend on the type of glass wares (pipettes, volumetric flasks) used for dilutions, acidity, concentration levels and on storing/aging etc. The second assumption is often unlikely to be true because the relative errors in measurement are constant while the absolute errors will increase as the analyte concentration increases. The total errors in the determination of analyte thus depends on the precision of the method as well as on the number of steps involved. Direct methods having high precision and involving minimum steps are more desirable to obtain the reliable analytical data.

The method of standard additions

The method of standard additions is a fundamental method for analyte determination because it minimizes errors produced by composition and physical properties of sample solution (without any separation of analyte of interest from the accompanying matrix) [5,6]. Truely, it is a simple means of verifying analytical values obtained by analytical working curves without the need for using another analytical instrumental method as a reference method. In fact, it is a self-calibration or auto-standardization method and is well documented in the literature.

Differential Technique (DT)

Differential Technique (DT) is based on the comparison of the signal response of the accurately known standard with a sample of similar but unknown concentration on same sample weight or dilution basis [7,8]. The application of differential technique holds good when a linear relationship between the analyte response and concentration is established. The system must be free from interference effects.

Truely, the concept of classical titrimetry has changed with the advancement in electronics, instrumentation and automation [9-13]. New approaches of titrimetry have emerged, which give excellent precision and efficiency in comparison with classical titrimetry even at micro-litre volume level. Various reagents in highly precise micro-litre aliquots can be delivered in the reaction chamber (equipped with conductometric, potentiometric, fluorimetric and spectrophotometric sensors) from pneumatically pressurized reservoirs fitted with inexpensive high-speed valves in the liquid delivery lines controlled by microcomputers [14-18].

DISCUSSION

More recently, we have established and demonstrated the application of differential technique in laser-induced fluorimetry for the direct, fast, accurate and precise determination of uranium in samples of diverse matrices of mineralised rocks, concentrates and other U-rich materials over a dynamic range of concentrations from ppm to percentage levels. By taking advantage of high sensitivity of the laser/LED fluorimetry technique, the procedure of elimination of interference by simple dilution of the sample solution using push-button pipettes has the distinct advantage of being quick and very simple to perform because it does not require any chemical preparation or extraction. Application of differential technique fulfills the essential requirements of both equipment and method calibration; it is therefore, a self-standardized and an absolute methodology by using at least three independent standards of accurately known concentrations such as, certified reference materials.

Under the conditions for the use of differential technique, in which the analyte signal response of the unknown concentration in the cuvette is matched with that of the signal response of the standard of accurately known concentration (mean signal response from at least three independent accurately known standards), which amount to a titration. In this way, accuracy and precision of differential technique were found to be comparable with differential spectrophotometric technique as well as to classical titrimetric and gravimetric methods. By analogy of differential technique with titrimetry, thus give rise to an absolute methodology based on the use of analytical chemical standards or certified reference materials. The use of certified reference materials as standards ensures calibration, control and optimization of the quality of analytical data. The use of at least three independent standards of accurately known concentration in differential technique further minimises the total errors associated with dilution steps, measurement of signal, overall errors associated with the method of measurement. Differential technique is more likely like applying the 'method of least squares' indirectly while obtaining the more reliable common factor of slope. Differential technique using reference standards guarantees the quality of an analytical result (accuracy, high precision,

reliability, comparability and traceability). It is a self-standardized and an absolute methodology of measurement.

Choice of certified reference standards for differential technique should be made cautiously. The reported recommended/certified value of an analyte in reference standard should be based on the evaluation of analytical values obtained by using primary methods or documented standard methods. Alternatively, independent three stock solutions prepared in minimum 10% acidity from spec-pure elemental powder or compound, serve as the most suitable reference standards comparable with and fulfilling all the criteria essential for certified reference materials for such applications similar to wet chemical analysis. In wet chemical procedures, standard elemental/analyte stock solutions are prepared from primary standards; here arbiter of accuracy is considered to be the chemical purity of standard reagent and the accuracy of the analytical balance. Precision engineering, micro and nano technology requires standards of physical and chemical measurements with highest accuracy, comparability and traceability to international measurement system. Otherwise, the errors inherited (if any) to these certified reference materials will be transmitted to other measurement data by using modern analytical techniques as well as in the preparation/certification of other certified reference materials and so on, if proper checks are not implemented. The commentary article further documents the unique potentiality of differential technique discussed in depth [19].

Recent advances in narrow and broad-band LED light sources from the far UV to the NIR wavelength regions have also opened up the flexibility for additional designs, electronics and instrumentation. With the addition of new fluorescence reagents or probes, advancements in the technologies have continued in high performance qualification, portable instrumentation and appear promising in future [20]. With LED in the visible range (400 nm) replacing laser (337 nm) in the UV range, the tolerance levels of many associated interfering elements improved almost 10 times in this new LED-based technique. Tolerance to pre-filters like Fe (III) has been found to be high (10 fold increase as compared to laser-induced fluorimetry). Same is the case with post filters like Mn, Cu, Cr etc. It was found that the tolerance to many ions have been enhanced at least 10 times in LED fluorimetry in comparison to laser-induced fluorimetry. Several innovations were added to the instrument to make it more reliable, more versatile and easier to operate than the nitrogen laser fluorimeter. The excitation source was a bank of pulsed LED's emitting at 400 nm, Model LF-2 [21].

The application of differential technique may prove valuable absolute methods in other fields of applications using new reagent systems/portable instrumentation in the areas of clinical pathology, clinical toxicology, biochemistry, medical research, pharmaceutical industry, inorganic analysis and other related diverse applications.

CONCLUSION

In the author's opinion, differential technique is a simple practical approach for an absolute method of measurement and warrants its introduction in other areas of applications. It may be helpful in designing and development of microchemielectronic devices coupled with flow-injection. The application of differential technique may prove valuable absolute methods in other fields of applications of fluorimetry and also in other modern instrumental techniques (which need micro-litre sample volume and measurement at nano gram level) in the areas of clinical pathology, clinical toxicology, biochemistry, medical research, pharmaceutical industry, inorganic analysis and other related diverse applications.

CONFLICT OF INTEREST

There is no conflict of interest to declare.

FUNDING

There is no funding.

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