Comments on: Simultaneous Separation and Preconcentration of Rare Earth Elements on Activated Carbon for its Determination by ICP-OES in Beneficiation Products

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Abstract

Comments on simultaneous separation and preconcentration of rare earth elements on activated carbon/charcoal for its determination by ICP-OES in beneficiation products and different geological matrices has been presented. The manuscript published on beneficiation products is lacking in any innovation, originality or novelty over the earlier published paper titled "Determination of Rare earth elements in different geological matrices by ICP-AES after solid phase micro extraction on activated charcoal" by Murty, Mohanta and Radhamani published in the journal, Atomic Spectroscopy. There is a repetition of the "The unique feature of the method" in the above cited manuscript and also in his earlier publication titled "A single stage simultaneous separation and preconcentration of rare earth elements on activated carbon for its determination by ICP-OES after wet ashing–application to soil samples by Chakrapani, Mahanta, Hanuman, Srivastava published in the journal "Exploration and Research for Atomic Minerals on bromoheavies. Moreover, there are contradictory and misleading statements /findings on the role of AC as adsorbent, amount of AC and desorption of REEs from AC in the published papers by Chakrapani et al. [1] and other authors from AMD laboratories. The findings have previously published elsewhere without proper cross referencing /justification in manuscripts. The desorption of REEs from AC simply by treating AC with 3.2 M HNO₃ is the best analytical protocol, thus avoiding the tedious and time consuming operation of ashing AC. Moreover, regenerated AC can be re-used for further experiments. Dry-ashing of the charcoal pellet is the alternate option and can be completed in 1 hr. Wet-ashing of charcoal pellet with HNO₃ and HClO₄ involves toxic acids fuming, is a health hazard and may lead to serious explosions. Separation of rare earth metals through biosorption using low cost biomaterials or modified AC will continue to remain a greatest challenge.

Keywords: Rare earth elements; Preconcentration; Separation; Activated carbon; ICP-OES; Beneficiation products; Geological materials

Comments

I have read the above published paper [1], all the cited papers in references and available published literature on the above subject very carefully. This manuscript [1] is lacking in any originality, innovation or novelty over the earlier published paper cited in the manuscript titled "Determination of Rare earth elements in different geological matrices by ICP-AES after solid phase micro extraction on activated charcoal, published [2] in the journal, Atomic Spectroscopy.

I would like to reproduce from this publication [2] abstract section, Page no. 65 quote "The novelty of the method lies in the fact that REEs are adsorbed on activated charcoal as their fluoride complexes. The present method has very wide dynamic range of applicability for a variety of geological samples" unquote. The author, Chakrapani has published a number of papers with the same reagent system, AC as preconcentrate/separator for REEs without any significant improvements over publication [2] cited as Reference no. 16 in the published paper [1].

Author, Chakrapani et al. published a paper [3] titled "A single stage simultaneous separation and preconcentration of rare earth elements on activated carbon for its determination by ICP-OES after wet ashing –application to soil samples, published in ERFAM. The unique feature of the method is the same using the reagent system- Activated carbon. The same feature of the method has been described in the publication by Chakrapani [4] on Page 449, Section 3 vide his publication in Journal of Applied Geochemistry and also in his publication titled [5] "Determination of rare earth elements in uraninite samples by ICP-OES after solid phase extraction on activated carbon" by Mahanta, Chakrapani and Radhamani published in Atomic Spectroscopy. Both these publications of the senior corresponding author, Chakrapani have neither been cited or nor there is any discussion in the references related with Solid phase extraction on AC for REEs determination in the above cited JICS paper [1] by the authors Chakrapani et al. published a paper [5] titled Simultaneous separation of rare earth elements from geological samples based on preconcentration on activated carbon and its determination by ICP-OES published in ERFAM. In this paper [5], REEs are selectively sorbed onto AC at pH 6 ± 1, in presence of complexing agent,
triethanolamine, used to prevent precipitation by various interfering elements. The effects of various parameters for quantitative sorption of REEs on AC are discussed. The REEs are desorbed from AC simply by treating AC with 3.2 M HNO₃, thus avoiding the tedious and time consuming operation of ashing AC. The author, Mohanta et al. published a paper [6] titled ‘Determination of Rare Earth Elements in Uraninite Samples by ICP-OES After Solid Phase Extraction on Activated Carbon’ published in Atomic Spectroscopy. The REEs have been recovered from AC by igniting into ashes.

Moreover, in the publication by Chakrapani [4] in Journal of Applied Geochemistry, the main reference on AC by Murty et al. [2], Atomic Spectroscopy is missing. The authors have suppressed the already reported and published information. Such activities of a senior author are unscientific and highly misleading. It constitutes plagiarism, misconduct and is a gross violation of the ethical guidelines by the authors for their scientific publications.

As stated in the manuscript [1] “The most common physical method for mineral separation is the gravity separation using heavy liquid like bromoform, which is generally used to separate ferromagnesian minerals from quartz and feldspar. Thus, bromoform separated heavier fractions are normally free from quartz and other silicate minerals and contains refractory mineral phases”. The information on bromoheavies as beneficiation product is same as reported by Chakrapani and the same has already published vide his publication [7] titled “A rapid sample decomposition procedure forbromo-heavies containing ferugenerous material: determination of REEs and thorium by ICP-AES” by Khorge, Chakrapani, Murugesan, Exploration and Research for Atomic Minerals. They have applied on samples containing very high concentration of REEs. In the present paper [1], authors have applied to beneficication product, the bromoheavies containing low concentration of REEs. This statement of the authors is highly contradictory and misleading.

There is a contradiction on the optimal parameters such as amount of AC and contact time in different publications. For the same reagent system, amount of AC differed from 0.2 g to 1.0 g and contact time from 1 hr [1], 4 hr [2] and overnight [8]. As on date, the basic informations on adsorption capacity of AC, thermodynamic parameters and modeling are missing for such reagent system. The adsorption capacity is an important factor, because it determines how much sorbent is required to quantitatively concentrate the analytes from a given solution. From the available literature [9], there is a decrease in adsorption of uranium on AC in the presence of fluoride, nitrate, thioulsphate and oxolate ions can be attributed to weak adsorption of the anionic complexes. Qadeer et al. [10], published their studies on surface characterization and thermodynamics of adsorption of Sr²⁺, Ce³⁺, Sm³⁺, Gd³⁺, Th⁴⁺, UO²⁺ on activated charcoal from aqueous solution. In view of the solubility products values of REEs fluorides [10] and the conditions used by the authors (3-4 M HF medium) for adsorption of REEs on AC needs further investigations on the role of AC. There is no characterization of AC and REEs sorbed-AC by the authors for their claim. In the cited manuscript [1], authors have recommended wet-ashing, quote “The REEs are desorbed quantitatively from activated carbon, by completely oxidising and solubilizing AC by wet digestion (HNO₃ and HClO₄ treatment). Thus the time consuming and tedious method of ignition of charcoal to ashes is avoided, to increase the sample throughput in geochemical exploration studies” unquote. This statement of the authors is absolutely wrong and highly misleading.

Murty et al. [2,6] and Kumar et al. [8] have recommended dry-ashing of the charcoal pellet in a furnace. In my opinion, the desorption of REEs from AC simply by treating AC with 3.2 M HNO₃ is the best analytical protocol, thus avoiding the tedious and time consuming operation of ashing AC. Moreover, regenerated AC can be re-used for further experiments. Dry-ashing of the charcoal pellet is the alternate option and can be completed in 1 hr. Wet-ashing of charcoal pellet with HNO₃ and HClO₄ involves toxic acids fuming, is a health hazard and may lead to serious explosions. dry-ashing of the charcoal pellet is the best option and can be completed in 1 hr. As far as possible, toxic acids fuming should be avoided and is a health hazard. Perchloric acid (HClO₄) is an extremely reactive liquid. It is clearly stated in ASTM document [11], Designation: C 25-06, Section: Procedure: Warning, page no. 6. quote “When using HClO₄ there are precautions to be followed which, if unheeded, may lead to serious explosions. Contact of the hot concentrated acid with organic matter (AC in this case) must be absolutely avoided. Any organic matter in the sample must first be destroyed by the addition of nitric acid (HNO₃) to the sample prior to fuming with HClO₄” unquote. If proper care is not taken, wet-ashing treatment of charcoal pellet with HNO₃ and HClO₄ may result in a blast.

Activated carbon (Merck make, Germany) is not a low cost material [12-14]. Activated carbon adsorption is a well known method for the removal of heavy metals, but the high cost of activated carbon restricts its large scale use for separation/preconcentration. Activated carbon can be manufactured [14] from any material having high carbon content and low inorganic contents such as sawdust, coal, nutshell, lignite, peat, agricultural wastes and some polymers. Oxalate precipitation method is a well-established method for the separation of REEs [15]. Recovery/separation/preconcentration of rare earth metals through biosorption using low cost biomaterials [16] or modified AC [17] will continue to remain a greatest challenge.

Conclusion

In my opinion, any methodology developed should be investigated thoroughly for its real applications in diverse matrices. The desorption of REEs from AC simply by treating AC with 3.2 M HNO₃ is the best analytical protocol, thus avoiding the tedious and time consuming operation of ashing AC. Moreover, regenerated AC can be re-used for further experiments. Dry-ashing of the charcoal pellet is the alternate option and can be completed in 1 hr. Wet-ashing of charcoal pellet with HNO₃ and HClO₄ involves toxic acids fuming, is a health hazard and may lead to serious explosions. Oxalate precipitation method is a well established method for the separation of REEs. Recovery/ separation/preconcentration of rare earth metals through biosorption using low cost biomaterials or modified AC will continue to remain a greatest challenge.

References

1. Hanuman VV, Chakrapani G (2013) Simultaneous separation and preconcentration of rare earth elements on activated carbon for its determination by ICP-OES in beneficiation products. J Indian Chem Soc 90: 1919.
2. Murty DSR, Mohanta PL, Radhamani R (2002) Determination of rare earth elements in different geological matrices by ICP-AES after solid phase micro extraction on activated charcoal. Atomic Spectroscopy 23: 65-74.
3. Chakrapani G, Mahanta PL, Hanuman VV, Srivastava PK (2007) A single stage simultaneous separation and pre concentration of rare earth elements on activated carbon for its determination by ICP-OES after wet
ashing Application to soil samples. Exploration and Research for Atomic Minerals 17: 53-61.

4. Chakrapani G (2012) Development of novel flux for effective sample decomposition of refractory samples and field oriented pre-concentration methods for the determination of twenty nine trace and ultra trace elements in a variety of geological samples by flame and plasma techniques for application to geochemical exploration of uranium. Journal of Applied Geochemistry 14: 447-452.

5. Chakrapani G, Jain SK, Srivastava PK (2007) Simultaneous separation of rare earth elements from geological samples based on preconcentration on activated carbon and its determination by ICP-OES. Exploration and Research for Atomic Minerals 17: 62-69.

6. Mahanta PL, Chakrapani G, Radhamani R (2010) Determination of rare earth elements in uraninite samples by ICP-OES after solid phase extraction on activated carbon. Atomic Spectroscopy 31: 21-26.

7. Khorge CR, Chakrapani G, Murugesan P (2013) A Rapid Sample Decomposition Procedure for Bromo-Heavies Containing Ferruginous Material: Determination of Rees And Thorium By ICP-AES. Exploration and Research for Atomic Minerals 23: 1.

8. Kumar A, Sunilkumar B, Lalithambal R, Chowdary GS (2007) Determination of rare earth elements and yttrium in rock samples by Inductively coupled plasma optical emission spectrometry. Exploration and Research for Atomic Minerals 17: 70.

9. Qadeer R, Hanif J, Saleem M, Afzal M (1993) Surface characterization and thermodynamics of adsorption of Sr2+, Ce3+, Sm3+, Gd3+, Tb4+, UO22+ on activated charcoal from aqueous solution. Colloid and Polymer Science 271: 83-90.

10. Hisako I, Hiromitsu H, Masashi T, Yasuo S, Yasukazu A (1984) Determination of Solubility Products of Rare Earth Fluorides by Fluoride Ion-selective Electrode Bull. Chem Soc Jpn 57: 1689.

11. Standard Test Methods for Chemical Analysis of Limestone, Quicklime and Hydrated Lime.

12. Berrima B, Mattar W, Mortha G, Boufi S, Aloui El L (2015) Adsorption of heavy metals on charcoal from lignin. Cellulose Chemistry and Technology 5: 701-709.

13. Activated Carbon. Learning Center. Technical Bulletins. AL-143.

14. Bansal DC, Donnet JB, Stoeckli HF (1998) Active Carbon. Marcel Dekker, New York, USA.

15. Patent US3420861 - Efficient preparation of rare-earth metal oxalate.

16. Das N, Das D (2013) Recovery of rare earth metals through biosorption: An overview. Journal of Rare Earths 31: 933-943.

17. Liang P, Liu Y, Gu Li (2005) Determination of trace rare earth elements by inductively coupled plasma atomic emission spectrometry after preconcentration with multiwalled carbon nanotubes. Spectrochimica Acta Part B 60: 125-129.