P44: AN INTEGRATED EVALUATION APPROACH FOR METRIC COMPARISON OF ANALYTICAL TECHNIQUES, BASED ON DIVERSE REQUIREMENTS. APPLICATION IN SELECTION OF SUITABLE TECHNIQUE FOR AMMONIUM DETERMINATION IN POTABLE AND RECYCLED HYGIENE WATER, TO BE USED IN MANNED SPACE MISSIONS

Zachariadis G.[1)*], Giakisikli G.[1)], Trikas E.[1)], Anthemidis A.[1)], Karapantsios T.[2)]

[1]Lab. of Analytical Chemistry and [2]Lab. of General and Inorganic Chemical Technology, Department of Chemistry. Aristotle University of Thessaloniki, Greece- zacharia@chem.auth.gr

Abstract – Water is a basic human need and is provided to the crew of International Space Station (ISS) from the water storage/transfer systems that are placed in there. Except of the direct regular supply of drinking water, the development of proper water recycling systems is equally critical as the employment of reliable automatic water quality monitoring systems. A fully automated on-line analyzer for ammonium determination in consumed drinking water and/or recycled hygiene water produced on board the ISS is needed according to ESA requirements. In this work, a trade-off methodology similar to a weighted-point method, was developed to evaluate appropriate analytical systems, adaptable to space flight requirements. The developed scoring methodology for the assessment of the suitability of the techniques, was based on scales and weighting factors for various applied criteria, like analytical performance (e.g. LOD, LOQ, accuracy, repeatability), adaptation to space flight conditions (e.g. microgravity applicability, volume/mass of the analyzer, solutions consumption, wastes production etc.), safety criteria (e.g. use of hazardous materials/reagents, pressure, heating, flammability), etc. as provided by the manufacturers or in literature. The evaluation approach offers a somehow arbitrary in metrics but still reasonable and countable discrimination between analytical techniques. This evaluation method is a first-time metrological contribution to the frequently appearing issue to select between available techniques taking into account diverse requirements. The proposed approach may be applicable also to evaluation needs for specific analytical techniques/methods, in order to be employed for various other customized purposes. In this particular case, among several technologies which were investigated, sequential injection systems meets the specifications for on-line monitoring in space conditions as it is an integrated flow manifold with small dimensions operating in a totally closed loop preventing any contact or release of the fluids/gases inside the space environment. Also, an appropriate ammonium ion selective electrode with real-time potassium compensation may be used as an alternative solution.

Keywords: analytical techniques; metric comparison; trade off methodology; ammonium determination; international space station;

1. INTRODUCTION

There are numerous published automated flow methods for ammonium/ammonia determination in the literature. The flow systems, which are commonly used for ammonium determination, are categorized as follows: segmented flow analysis (SFA), flow injection analysis (FIA) [1], sequential injection analysis (SIA) [2], multisyringe flow injection analysis (MSFIA) [3], multicommutated flow injection analysis (MCFIA) [4] and multipumping flow injection analysis (MPFIA) [5] with or without a gas diffusion (GD) unit. Among them, only few meet the requirements for proper operation in space conditions. An analyzer, first of all, must be microgravity compatible, operating in a fully automated mode for a long period, even months, without any human intervention. The low consumption of sample and reagent solutions is very important to produce low wastes, considering, not only the limited room-space in the ISS or a space shuttle, but also the weight. In addition, special care should be taken into a totally closed loop system, so no leaking of fluids or release of any gas should ever happen into the orbiter due to the isolated environment of the station. Finally, the use of low toxicity reagents and minimum flammable materials is very important to ensure the safety of the crew and the whole station as well.

The requirements for the developed method are defined in the Statement of Work: ESA Express Procurement EXPRO On-Line Ammonium Analyzer for water recycling systems. The limit of detection shall be 0.05 mg L^{-1} NH_4^+, the limit of quantification shall be 0.1 mg L^{-1} NH_4^+ and the dynamic measurement range shall be defined between 0.1 mg L^{-1} and 50 mg L^{-1} NH_4^+. The precision shall be at a value of standard deviation of ± 0.05 mg L^{-1}, while the accuracy shall be at an error level of 0.05 mg L^{-1}. In case of the space adaptation criteria, the volume of the on-line ammonium analyzer shall be under 516x440x253 mm^3 (based on the ISS Locker), while its mass shall be under 27 Kg. In addition, the consumed sample volume shall be minimal and the amount of waste generated during analysis shall be as low as possible, allowing safe disposal. Considering the power consumption and the current intensity, they shall be under 300W and 116-126V DC, respectively. Regarding the safety criteria, the analyzer shall be automatic, tolerant to failures due to operations and maintenance and shall consist of a minimum of flammable material; wastes shall be stored for a safe disposal; no release of hazardous or toxic materials will occur.

2. EXPERIMENTAL

2.1. Trade off studies

In accordance with the ESA standard procedures, trade-off studies shall evaluate the candidate concepts for a mission candidate technique. Therefore, to evaluate and select the most appropriate of them, a trade-off methodology has been developed taking into account the detection / quantification requirements (LOD, LOQ, accuracy, repeatability, etc.) and critical items regarding the adaptation to space (microgravity applicability, volume/mass of the analyzer, solutions consumption, wastes production) as well as safety criteria (use of hazardous materials/reagents, pressure, heating, flammability).

Every criterion was scored based on defined scale/levels of each one with a specific weighting factor (WF). Each particular weighting factor has been attributed to every criterion taking into consideration the significance of the specific parameter. For instance, parameters that could affect the crews' wellbeing, such as maintenance and safety issues, were evaluated as of higher importance (x10 WF) compared with others that are subject to design adaptation and could be optimized, like volume of the analyzer (x5 WF) and power consumption (x4 WF). In addition, since the concept of the WF refers mainly to the criteria, in order to distinguish between the examined methods, a scale was required to be established for each criterion in order to provide a reliable assigned value for each one. The scale of the criteria is based on numeric features. The score of each criterion for every method was given as the result of a value (into the range of scale) x weighting factor.

3. RESULTS AND DISCUSSION

The scale selected for the limit of detection contained four different levels, valued from 0 to 5 points with 10x weighting factor. A high weighting factor (10x) was adopted because the criterion of the detection limit is considered to be very critical for the selection of the appropriate technology and it plays a decisive role among other criteria of the analytical performance. The scale selected for the limit of quantification contained four different levels, valued from 0 to 5 points with 9x weighting factor. The high weighting factor of 9x was adopted because the criterion of the limit of quantification is considered to be critical for the selection of the most appropriate methodology for ammonium/ ammonia determination on board the ISS, since it practically corresponds to the lower concentration in the calibration curve. Considering the dynamic measurement range, the graduated range selected, contained six different scale levels, valued from 0 to 5 points with 3x weighting factor. The low weighting factor of 3x was chosen because even for techniques with short dynamic range, it is technically possible to be used after proper automated dilution of the sample. The scale selected for the precision contained 7 different levels, valued from 0 to 10 points with 4x weighting factor. The relatively low weighting factor of 4x is attributed to the fact that a typical automated method has small RSDs (<5%) which are satisfactory for on-line chemical analysis. In case of the accuracy, the graduated range contained 3 different scales, valued from 0 to 5 points with 6x weighting factor. The weighting factor of 6x was adopted because although the criterion of the accuracy is of high importance for the selection of the appropriate technology, it is not equally important in this case as for instance the detection or quantitation limit.

Regarding the space adaptation criteria, the scale selected for the volume of the analyzer contained six different scales, valued from 0 to 5 points with 5x weighting factor. A medium weighting factor of 5x is attributed to the fact that the criterion of the volume of the analyzer is subjected to optimization of space adaptation technology. The scale range selected for the mass of the analyzer contained six different scales, valued from 0 to 5 points with 5x weighting factor. A weighting factor of 5x was adopted because, although the criterion of the mass of the analyzer is important for the adaptation of the appropriate technology on board the ISS, the final mass of the analyzer can be optimized further by the manufacturers in order to fulfill the requirement of the total 27 kg (including the reagents and wastes). The scale selected for the sample volume needed for the analysis of the sample contained five different scales, valued from 0 to 5 points with 5x weighting factor. The required sample volume is strongly related to the analytical technique but it is subjected to miniaturization and optimization for space adaptation, so the medium weighting factor of 5x was adopted. The scale selected for the sample volume needed for the analysis of the sample contained five different scales, valued from 0 to 5 points with 5x weighting factor. The medium weighting factor of 5x was adopted because the wastes volume is a key point to the selection of the appropriate technology to be employed on board the ISS. The scale selected for the power consumption needed for the analysis of the sample contained four different scales, valued from 0 to 3 points with 4x weighting factor. The criterion of the power consumption is subject to optimization of space adaptation technology, so the relatively low weighting factor of 4x was adopted. The scale range selected for the maintenance of the analyzer contained three different levels, valued from 0 to 5 points with a 10x weighting factor. The high weighting factor (10x) was adopted because the criterion of the maintenance (MNT) is considered to be very critical for the selection of the most suitable technology that can be easily used in zero-gravity conditions with the least possible care and human interference.

Finally, the scale selected for the safety issues (hazardous reagents / wastes) that are used during the analysis contained levels, were valued from 0 to 5 points with 10x weighting factor. The high weighting factor (10x) was adopted because the criterion of the safety issues - hazardous reagents / wastes (SAF) is a key point for the selection of the appropriate technology in order to be applicable in space, on board the ISS, without calling into question the safety of the crew.

Table 1 shows all the examined parameters for the automated flow methods together with the score of each parameter as well as the total score of a method (given as an example).

Table 1. Trade off methodology.

Group	Trade off criteria	Scale/ Levels	Weight	example of criteria score
Analytical Performance	Limit of Detection (LOD)	0-5	10	50
	Limit of Quantitation (LOQ)	0-5	9	45
	Dynamic measurement range	0-5	3	12
	Selectivity / interferences	0-2	5	5
	Precision (RSD)	0-10	4	24
	Accuracy (as relative error)	0-5	6	18
Adaption Characteristics	Capability for Off-Line analysis	0-5	8	40
	Volume of the analyzer	0-5	5	10
	Mass of the analyzer	0-5	5	10
	Sample volume	0-5	5	25
	Wastes Volume	0-5	5	10
	Power consumption	0-3	4	8
	Votalge or Current Intensity	Pass/Fail	Pass/Fail	Pass
	Compatibility with microgravity	Pass/Fail	Pass/Fail	Pass
	Maintenance	0-5	5	50
Safety Criteria	Safety issues Hazardous Reagents / Wastes	0-5	6	30
	Heating/Flame/ Pressure/Gas	0-2	6	6
	Total analyzer score			343

3. CONCLUSIONS

A trade off methodology has been developed for the evaluation of flow analytical methods for ammonium/ammonia determination in terms of the ISS requirements for proper operation in space conditions. Special attention shall be given to the preliminary demonstration of the ability of the analysis techniques to meet detection and quantification requirements (threshold, accuracy, repeatability, etc.). Great attention has been given in the space adaptation of the systems with a view to their easy and effective implementation at conditions of zero-gravity. In addition, special care has been given in the proper management of the reagents and hazardous materials that will reduce the amount of the materials and hazardous waste, and will not cause any sort of problems to the analyzer operators.

The trade off studies have showed that the ideal analyzer should be an automated and miniaturized integrated system with a low volume and mass, so that it could fit in a place of defined dimensions. It should be an easy-to-use system which allows for an automatic handling of the solutions without any human intervention, avoiding any potential errors, regarding overpressure or overheating of the system. In addition, it should use low volumes of sample/reagents solutions resulting in low production of wastes, considering not only the restricted space inside the ISS, but also the weight. Finally, it has been showed that the operation of the whole procedure in a totally "closed loop" makes it microgravity applicable and prevents problems like leakage or gas elimination, which could create a negative or even fatal environment inside the limited and isolated space station or space shuttle.

ACKNOWLEDGMENTS

The authors would like to thank European Space Agency for its financial support through the project "On-Line Ammonium Analyzer for water recycling systems, Contract No 4000113078/14/NL/SFe".

REFERENCES

[1] Y. Zhu, D. Yuan, Y. Huang, J. Ma, S. Feng and K. Lin, "A modified method for on-line determination of trace ammonium in seawater with a long-path liquid waveguide capillary cell and spectrophotometric detection", Marine Chemistry 162 (2014) pp. 114–121.

[2] R. A. Segundo, R. B. R. Mesquita, M. T. S. O. B. Ferreira, C. F. C. P. Teixeira, A. A. Bordalo and A. O. S. S. Rangel, "Development of a sequential injection gas diffusion system for the determination of ammonium in transitional and coastal waters", Anal. Methods 3(2011) pp. 2049-2055.

[3] C. Henrıquez, B. Horstkotte and V. Cerdà, "Conductometric determination of ammonium by a multisyringe flow injection system applying gas diffusion", Intern. J. Environ. Anal. Chem. 93 (2013) pp. 1236-1252.

[4] S. M. Oliveira, T. I. M. S. Lopes, I. V. Toth, A. O. S. S. Rangel, "Determination of ammonium in marine waters using a gas diffusion multicommuted flow injection system with in-line prevention of metal hydroxides precipitation", J. Environ. Monit. 11(2009) pp. 228–234.

[5] C. Henríquez, B. Horstkotte and V. Cerdà, "A highlyreproduciblesolenoidmicropumpsystemf ortheanalysis of total inorganic carbon and ammonium using gas-diffusion with conductimetric detection", Talanta 118(2014) pp. 186–194.