Evaluation of the field deployable Loop Flow Analyzer (LFA) for heavy metal determination in water

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Fig. 1. Loop Flow Analyzer

Introduction

The excessive release of heavy metals into environment is a major concern worldwide. They can enter a water supply by industrial and urban waste or can be released from acidic rain into natural water bodies. As most of them are toxic at very low concentrations and tend to bio-accumulate, their determination in natural water is an important environmental task. Because of their trace amounts in environmental samples, very few in-situ measuring techniques are suitable for their determination. The Loop Flow Analyzer (LFA) developed from SYSTEA and modified for the special use of potentiometric sensors provides a useful tool for the in-situ determination of heavy metal ions in water. The LFA analyzer (Fig.1) with the flow-cell specifically designed to mount the standard ISE electrodes from SPU partner is able to manage sequentially and automatically up to four measurements.

The method of standard addition is applied for the determination, adding a concentrated solution with known concentration (INT CAL) to each sample. A buffer solution (ISA buffer) is necessary for accurate measurement with potentiometric sensors, especially at low concentrations. The potentiometric sensors for Pb, Cu, Cd and Zn were developed at the Laboratory of Chemical Sensors of St. Petersburg University (SPU) including membranes based on chalcogenic glass or polymeric thick film.

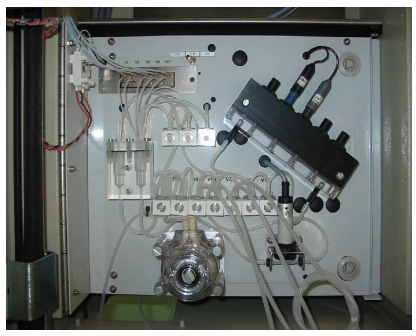

Fig. 2. Prototype LFA hydraulics 7

Fig. 3. Flow cell modified for bulk sensors

Experimental

This work presents the evaluation of the whole LFA system through extensive laboratory experiments. The following operating conditions are carefully tested and optimized: pH of measuring solution, ISA buffer composition, INT CAL concentration, linear working range and sensor contact time.

The chosen evaluation criteria include: system stability / robustness in terms of calibration slope and control sample (CS) concentration; measurement accuracy in terms of control sample concentration; sensitivity in terms of LOD & LOQ as well as sensor production homogeneity.

Results and Discussion

There is a strong impact of ISA solution on the measurement performance calibration slope as well as CS concentration for all target ions. The following buffer substances are tested: NaCl, NaCl+Na-Citrate, Na-Acetate buffer, Li-Nitrate and K-hydrogenphosphate. As shown in Fig. 4 and Fig. 5 the best results are achieved with NaCl+Na-Citrate, for the highest slope of calibration end the best accuracy in terms of control sample, for all four measured ions.

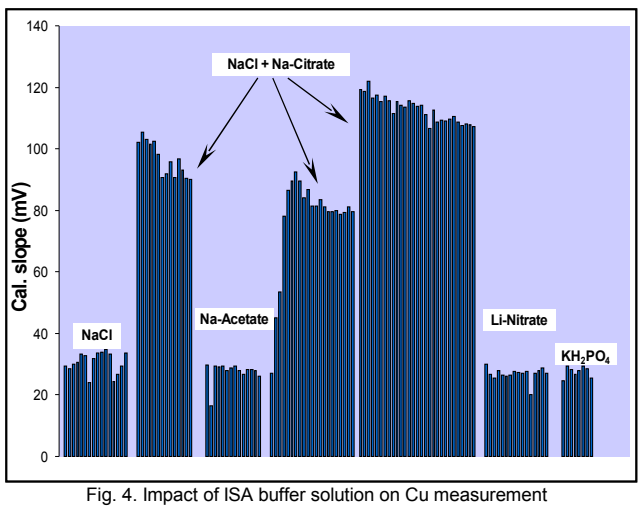

Fig. 4. Impact of ISA buffer solution on Cu measurement

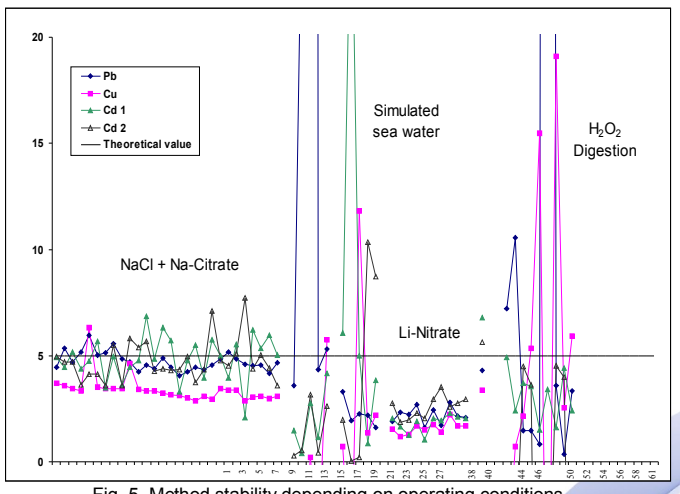

Fig. 5. Method stability depending on operating conditions

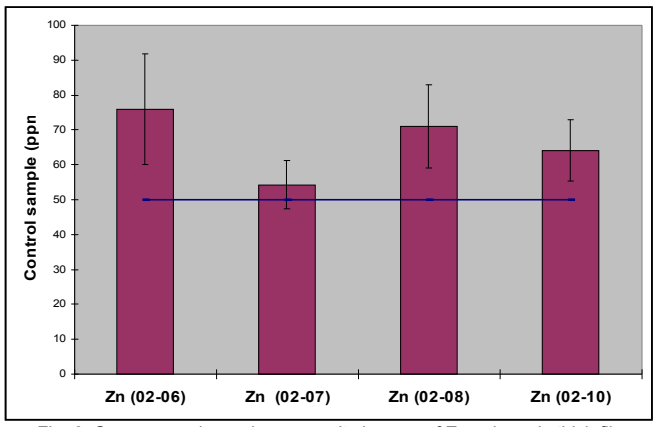

Fig. 6. Sensor membrane homogeneity in case of Zn polymeric thick film

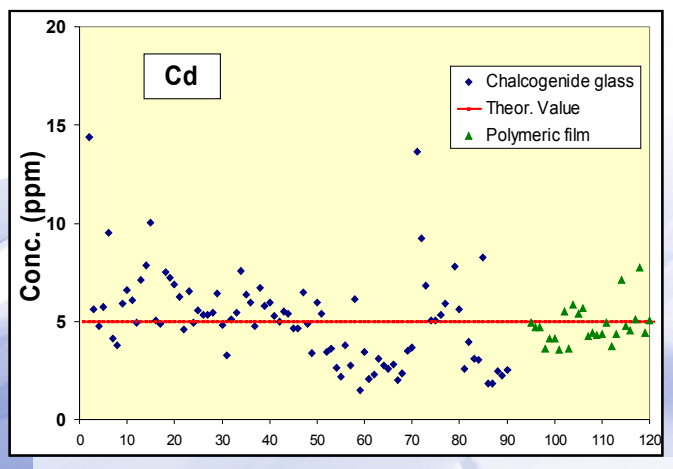

Fig. 7. Accuracy improvement as a concequence of sensor membrane

	Pb	Cu	Cd	Zn
LOD (ppm)	0.3 – 0.6	0.2 – 0.4	0.06 – 0.12	2.5 – 4.0
LOQ (ppm)	0.5 – 0.9	0.3 – 0.7	0.1 – 0.3	3.8 – 8.3

Tab. 8. Sensor's sensitivity in terms of **LOD** (C_{blank} + 3*SD) and **LOQ** (C_{blank} + 10*SD)

Conclusions

- The Loop Flow Analyser (LFA) with the modified flow cell and potentiometric sensors is shown to be a suitable system for on-line analysis of heavy metals in water.
- The sensor performance depends strongly from ISA buffer used. A mixed solution of NaCl/Na-citrate was estimated to provide the optimal stability and accuracy for most metal ions under investigation (Cd, Pb, Cu, Zn), evaluated with pure water standard solutions.
- Acidity (pH) of the sample solutions seems to have an important impact on the measurement accuracy, especially for Cu (chalcogenige glass) and Pb (PVC thick film) sensors. Systematic investigations are ongoing at BOKU laboratory for developing a standard operating procedure to be applied for all kind of samples (different pH).
- The chalcogenide glass sensor for Cu shows very stable calibration slope, but the accuracy (in terms of Control Sample) is need of improvement. The polymeric thick film sensors for Cd and Pb show good stability and accuracy with mixed standard solutions in pure water. For Zn sensors a rather higher statistical spread of mean is estimated. It is a need on improvement of measurement sensitivity (LOD/LOQ) for all targeted metals in order to fit the requirements for surface water quality.
- The evaluation of the whole system through measuring of real water samples (surface, ground and sea water) is in progress at BOKU lab, elucidating the influence of sample matrix on this analysis. Determination of total amount of heavy metals in water samples after digestion, which is one of the goals of WARMER project, is also under investigation.

Aknowledgement

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