

## ANALYTICAL CHEMISTRY CHALLENGES FOR INVESTIGATION OF SEDIMENTS

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### 1 The important role of Quality Assurance in analytical chemistry

The quality and quantity of sediments highly determines the quality and reliability of the generated data. For each analytical method there are always requirements, which need to be fulfilled.

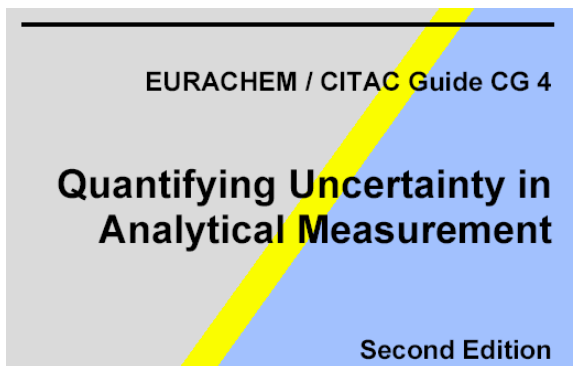
Each individual step of an analysis must be performed at the optimum quality level. The optimum is defined by the needed information. For example, it does not make sense to determine a trace down to a micro gram if the needed information is only percent. The other way around is also true. So before beginning analysis an analytical plan has to be made including all possible steps and takes care of all limiting factors.

In our case the limiting factors were sample quantity and detection limit of the applied analytical methods. With about 5 g of sample for each analysis, the detection limit for elemental analysis -usually referred to as inorganic analysis- by inductively coupled plasma atomic emission spectroscopy could be met. However, for traces of organic contaminants the levels present were too low. This meant, that for each sample an enrichment of organic analyses was necessary and only 5 g of sediment were available for both analyses.

That also meant, that each analysis could not be repeated 3 times ( $n=3$ ), the minimum for reliable data. A repetition of 3 also is the minimum for determining the measurement uncertainty. However, if the analysis is done in agreement with common procedures and that is the frequent use of standards the quality is not much improved but the reliability.

It is always the ultimate goal of the analytical chemist, to provide results to his customer that can be considered to be accurate and reliable. It is much better to provide no data, if they are considered to be bad, instead of providing poor data. This is one important goal of analytical chemistry quality assurance.

Good data always include at least an estimation of measurement uncertainty. A guide with some application is available on the Eurachem home page and also in the ISO/DIN guide 17025.



**Figure 1** Front-page of Eurachem/Citac MU guide

Because each step of an analysis contributes to measurement uncertainty (MU) we should remember the most important steps of an analysis (Fig.2).

- Sampling
- Sample Preparation
- Measurement
- Data Treatment
- Result

**Figure 2** The important steps of an analysis

Sampling contributes by far the most to MU and erroneous data. Caused by this analysis should usually performed by the chemist himself. This is not always possible and the chemist relies on other skilled sample takers. The measurement itself usually contributes only little to MU except when sample quantity plus detection limit are low. This problem can be overcome -at least in parts- by the use of reference material [3].

One common way of QA in water analysis is for example the analysis of dissolved salts in water (Fig. 3).

**Table 3** Data from Water Quality Survey of Lakes ABAYA and CHAMO

Data	from	Water	Quality	Survey	of	Lakes	ABAYA	and	CHAMO
Water temperature		<sup>0</sup> C	21.9	24.3	23.5	23.7	30		25
pH		pH	9.00	9.20	9.06	9.00	9.6		9.19
Electrical Conductivity		µs/cm	1000	1090	1040	1670	1810		1730
Dissolved Oxygen		mg. L <sup>-1</sup>	4.8	6.6	5.4	4.8	6.5		5.4
Chloride ( Cl <sup>-</sup> )		mg. L <sup>-1</sup>	57	58	57.6	113	115		114
Fluoride ( F <sup>-</sup> )		mg. L <sup>-1</sup>	7.2	7.8	7.6	7.8	8.5		8.3
Sodium ( Na <sup>+</sup> )		mg. L <sup>-1</sup>	207	233	215	328	352		337
Potassium ( K <sup>+</sup> )		mg. L <sup>-1</sup>	17.2	19.2	18.5	21.9	22.7		22.2
Calcium ( Ca <sup>2+</sup> )		mg. L <sup>-1</sup>	17	19	18	11	13.3		12.5
Magnesium ( Mg <sup>2+</sup> )		mg. L <sup>-1</sup>	4.5	5.8	5.2	13.5	15		14.7
Hardness ( as CaCO <sub>3</sub> )		mg. L <sup>-1</sup>	103.2	113	107	92	94		92.7

## 2 Inorganic analysis of sediments

Again, the first thing to do is to define the task. Here it is heavy metal analysis as tracers for contamination due to anthropogenic origin and as indicators for a possible contamination in the lakes Abaya and Chamo. It is not necessary to determine all possible metals present in sediments, yet sometimes that can be helpful to trace the elements back to a certain mineral or material.

In this study we have chosen the trace metals As, Cd, Cr, Co, Cu, Pb, and Zn.

In addition to the selected metals the analytical method should fulfill the following technical requirements:

- Fast
- Reliable
  - Reproducible
  - ICP-AES suited at very low sample mass

Inductively coupled plasma atomic emission spectroscopy (ICP AES) is known to be:

- Precise
- Fast
- Sensitive
- Has low susceptibility to interferences

Another advantage is the possibility to select sensitive detection lines offering the chance to use a wide concentration range, without the need to prepare different concentrated solutions.

Sediments are prone to interferences from the matrix and also to sample preparation or dissolution. Matrix interferences are especially bad if the interfering ion is present in high abundance, while the element to determine is present only at very minute concentration. Different matrix elements can be present also at different levels in different sample cores or even in the same core. The digestion step can also contribute to different results (fig.4).

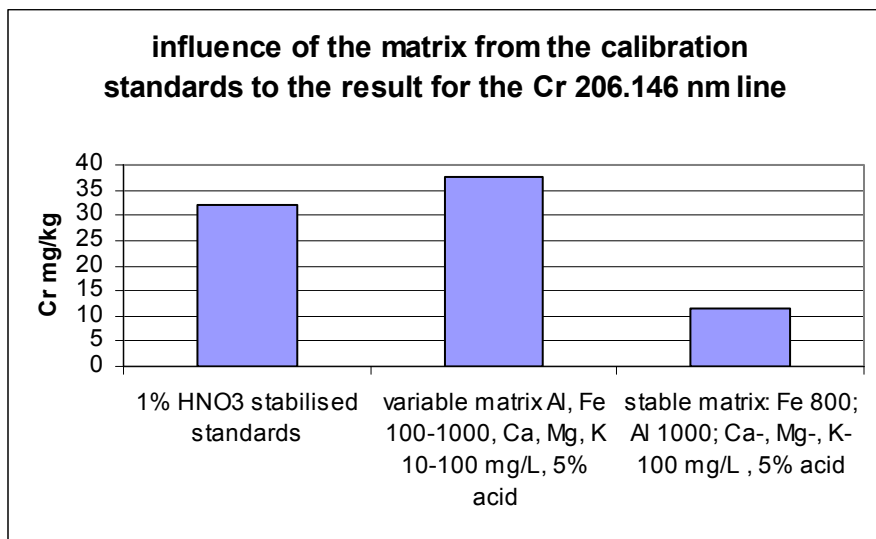


Figure 4 Influence of matrix adjusted sample preparation

One example of a sediment core depth profile is shown in figure 5.

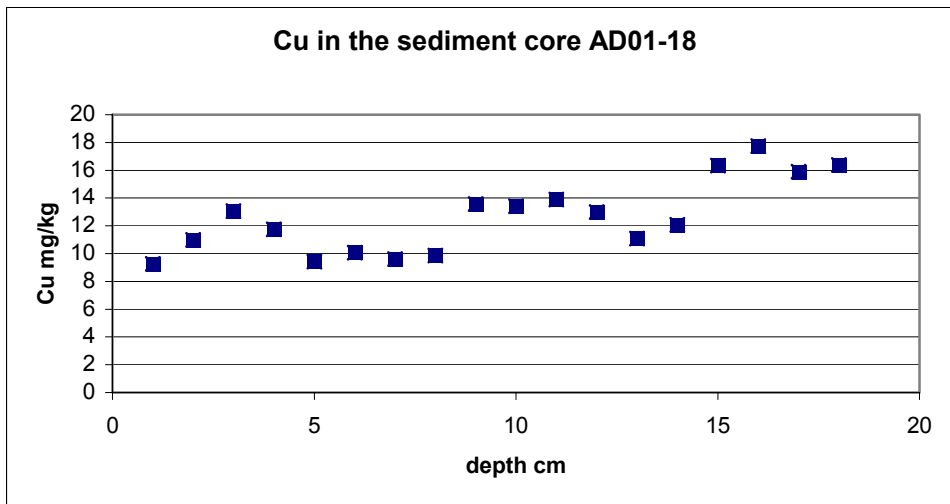


Figure 5 Cu depth profile in a sediment core

### 3 Organic sample analysis

Sediment analysis does not focus on elemental composition but also on “organic” molecules present in the sample. One example presented here is for DDT (fig 6). An insecticide banned in more than 145 countries but still in use in some countries, where Malaria is of major concern.

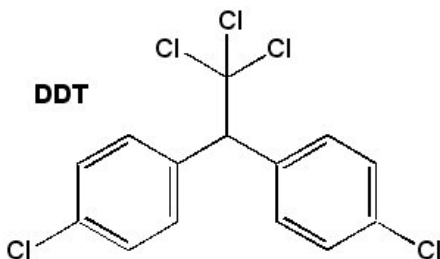


Figure 6 DDT (1,1,1-Trichloro-2,2-bis-(p-chlorophenyl)ethane).

In order to obtain DDT from sediments the sample must not be digested but must be extracted. The most common extraction method is Soxhlet extraction, even though more than 125 years old.

An extraction/depth profile is shown in fig. 7. It is difficult to get reliable and solid data from a sample that is limited in quantity and in concentration of the studied analyze. With one exception all DDT found ranges from 4-8 ppb.

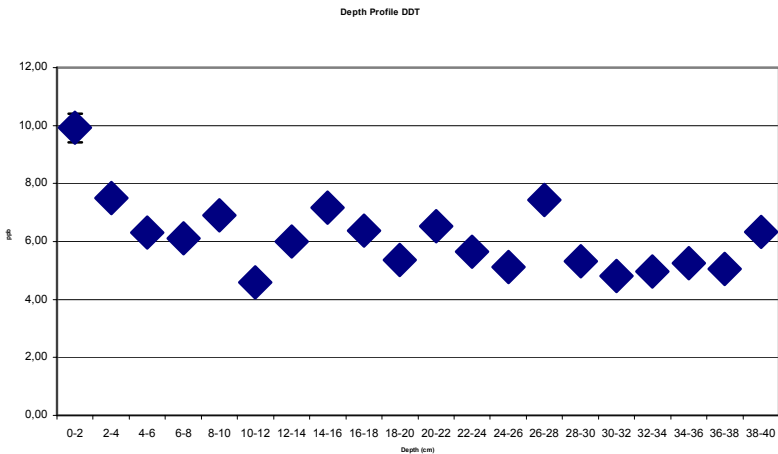


Figure 7 Extraction/depth profile for DDT in a sediment core.

## 4 Conclusion

Results of elemental analysis depend on the matrix. This is mainly due to interfering elements present at different concentrations even in the same sample core.

Digestion and calibration severely influence the results, due to overlapping of spectral detection lines. Ultra trace analysis of DDT etc. is very difficult. It requires a person, a sample clean up and an instrument which is fit for purpose.

## 5 References

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ISO/IEC 17025, October 2001

Quantifying Uncertainty in Analytical Measurement, 2nd Edition (2000) download from <http://www.eurachem.ul.pt/> Eurachem guides

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