Testing sample stability in short-term isochronous stability studies for EU-wide monitoring surveys of polar organic contaminants in water

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The article introduces the European Union (EU)-wide monitoring concept as run by the European Commission's Joint Research Centre (JRC) and specifically addresses the issue of stability tests for environmental specimen and samples using the so-called isochronous stability-test design. We briefly describe the underlying statistical concept and apply it to water samples being collected in the context of the JRC's EU-wide environmental monitoring activities.

The stability of spiked tap-water and river-water samples and their containers was assessed at 4°C, 20°C and 40°C using ibuprofen, gemfibrozil, ketoprofen, diclofenac, bezafibrate, naproxen, perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorooctane sulfonate (PFOS), carbamzepine, sulfamethoxazole, terbutylazine and triclosan as test substances in two different stability-testing schemes.

The stability of the samples decreased as expected with an increase in the storage temperature. Uncertainty contributions were calculated and it was concluded that this type of sample remains stable for ca. 6 weeks if stored at 4°C.

Keywords: Environmental monitoring; Ibuprofen; Isochronous study; Monitoring survey; Polar organic contaminant; Spiked sample; Stability test; Storage temperature; Uncertainty contribution; Water sample

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1. Introduction

Investigation of the fate and the pathways of environmental pollutants is an integral part of all policies dealing with the management of environmental resources and activities affecting environmental quality. In the past three decades, Europe has developed a large amount of environmentally related legislation, much of which leads directly or indirectly to the introduction of more or less stringent limit values for conventional pollutants. When it comes to new or less investigated environmental pollutants, which are not subject to any explicit environmental regulations, the knowledge base is very poor. However, this information is needed to decide whether a given substance, which is detected in the environment after deliberate or accidental release, poses an emerging risk or not. In other words, one

 0165-9936/$ - see front matter © 2012 Elsevier Ltd. All rights reserved. doi:http://dx.doi.org/10.1016/j.trac.2012.04.001

enters a vicious circle of substances not being regulated because of a lack of information regarding their occurrence in the environment and their unknown environmental fate because they are not monitored in the context of environmental regulations.

For this purpose, European Union (EU)-wide monitoring exercises following a non-probabilistic approach have been shown to be a viable way to arrive quickly at a representative data set of known quality [1,2]. The logistics of these exercises follow a mechanism similar to the centralized dispatch of proficiency testing (PT) schemes or certification exercises involving the shipment of a series of test specimens or samples to laboratories in a way that the transportation does not affect sample stability.

Fig. 1 gives an overview on this activity, which foresees the centrally coordinated collection of samples from European sampling stations, many of which are monitored in the context of national or regional monitoring activities. This has the advantage that the sampling stations are well documented, frequently visited and hence easily accessible in a cost-effective manner.

Following precise instructions, the samples are then dispatched to a sample-collection point or specimen bank, where samples and relevant information are carefully documented. The samples are next forwarded to the competent laboratories, which must have proved and documented measurement capability and expertise for the substance being investigated, and which are analyzing the whole sample pool under repeatability conditions (i.e. in one single analytical run). This is crucial to overcome day-to-day measurement variability or other within-laboratory effects, which may increase the uncertainty of the measurement result. The main advantage of this approach is that it overcomes all problems related to data comparability and necessarily costly mechanism of quality assurance and quality control (QA/QC) [e.g., PT schemes or the use of certified reference materials (CRMs)].

One must also bear in mind that these EU-wide campaigns are organized by the Joint Research Centre (JRC) of the European Commission (EC) to anticipate and to identify emerging issues around new and less-investigated substances, thus following up other activities being carried out e.g., by the NORMAN Network [3]. The necessary knowledge for the preparation of suitable matrix reference materials, which are necessary for any QA/QC activity, is hence not usually available and would be too lengthy and costly. The laboratories chosen usually have a high degree of automation for their analytical procedures, which also increases the repeatability of the methods and decreases the cost per analysis.

Upon completion of the analytical work, the data and relevant background information regarding the analytical method is then compiled under the lead of the JRC. It is obvious that this procedure can deliver reliable information only if the dispatched samples remain stable until the moment of analysis. Hence, the correct investigation of short-term sample stability is of paramount importance.

The necessary experimental investigation of test-specimen and sample stability has a long tradition, in particular in the field of environmental specimen banking, materials for PT schemes or CRM production [4–6]. Various approaches and statistical designs to assess sample stability and to quantify its contribution to the uncertainty of the overall analytical result have been developed [7]. Probably the most robust design, delivering not only qualitative statements about sample stability, but also leading to the quantitative uncertainty statement and establishment of a shelf life and expiry date for samples, was achieved with the introduction by the so-called isochronous testing design in the late 1990s by Lamberty and co-workers [6]. However, most applications relate to the investigation of the long-term stability of environmental samples, and only very few examples address the issue of short-term stability of environmental or biological samples during transport, shipment to the moment of analysis {e.g., [8–10]}. For this reason, in this article, we propose to apply the isochronous stability-test design to investigate the short-term stability of water samples used in the aforementioned EU-wide monitoring mechanisms.

2. Theoretical considerations

2.1. Types of stability test

The basic purpose of stability tests is to investigate the influence of storage conditions on the stability of an analyte itself, its matrix or the combination of the two aspects. With the introduction of the concept of quantifying uncertainty contributions to the overall analytical result, the sheer qualitative statement whether a sample is stable for a given period or not no longer suffices. A quantitative statement in the form of an expiry date is needed.

In this context, Van der Veen et al. [11] described two fundamentally different types of (in)stability of an analytical sample, test specimen or reference material and the respective scope of a stability study:

(1) long-term stability of the sample (e.g., shelf life), which is the more important the longer a material/sample has to be stored (e.g., in the case of CRMs, retained samples or environmental specimen banking); and,
(2) short-term stability (e.g., stability of the sample under ''transport conditions'').

While the first kind of stability study is well known (e.g., usually implemented in certification projects), the second kind of stability study is less common. Clearly, in the above context, particularly when it comes to the investigation of ''fresh'', not stabilized, samples in environmental monitoring, knowledge of short-term stability is pivotal, as it has considerable impact on the logistical framework of the monitoring exercise, because the behavior of the sample