



## **Determination of dioxins in mineral feed, trace elements, premixtures and compound feed:**

### **Recommendation for extraction procedures**

Extraction procedures for determination of dioxins and dioxin-like PCBs in products of mineral origin, premixtures or compound feed containing products of mineral origin or trace elements vary widely. They comprise methods using different organic solvents of varying polarity, different techniques (e.g. Soxhlet or ASE), different approaches to moisten dried products before extraction and different approaches to digest mineral products with HCl before extraction, if applied at all. It has been shown that recoveries of internal standards and dioxin results can vary considerably depending on the extraction procedure. This can cause severe problems if an analytical result has to be compared with maximum levels as fixed for feedingstuffs. Therefore, harmonizing extraction procedures for mineral feeds is of high priority for the Commission.

Some minerals show exothermal reactions when treated with HCl. Application of external heat or exothermal reactions producing high temperatures might raise the question of formation of dioxins from precursors, in particular if possible catalysts (such as copper) are present. The issue of dioxin formation as result of high temperature during extraction can be avoided (i) by use of an ice bath if exothermal reactions occur and (ii) by not using quite extreme digestion conditions such as boiling with concentrated acids under reflux.

The CRL for Dioxins and PCBs organized two interlaboratory studies on extraction techniques in 2006 and 2007 for sepiolite, fullers earth and manganese oxide. Results of these comprehensive studies on extraction techniques of sepiolite, mineral clay and oxides of trace elements were also presented at the Dioxin Conference (International Symposium on Halogenated Persistent Organic Pollutants (POPs)) in 2007 and 2008.



### **1. Conclusions for mineral feeds such as clays (except oxides of trace elements) and compound feeds**

For the extraction of mineral feeds such as clays and compound feeds, toluene and other non-polar solvents used alone are not suitable for extraction. A mixture of polar and non-polar organic solvents must be used for extraction regardless whether pressurized liquid extraction, Soxhlet or any equivalent extraction procedure is used. Oxides of trace elements shall be treated separately.

### **2. Conclusions for oxides of trace elements**

For extraction of oxides of trace elements, toluene is more suitable than a mixture of polar and non-polar organic solvents regardless whether pressurized liquid extraction, Soxhlet or any equivalent extraction procedure is used.

### **3. Pretreatment with hydrochloric acid**

For both of the above mentioned groups of mineral feeds (mineral feeds such as clays and compound feeds and oxides of trace elements) no significant difference between extraction without pretreatment and pretreatment with 0.3 M HCl was observed. Higher concentrations than 0.3 M HCl do not reflect physiological conditions and therefore the higher dioxin extraction obtained by HCl > 0.3 M is not relevant. As a result, pretreatment with HCl is not required for mineral feeds, compound feeds and trace elements as feed additives.

### **4. Samples with unknown or problematic composition**

The laboratories analyzing these samples should, wherever possible, have access to all relevant data on sample composition (premixtures, compound feed) to avoid choosing an inappropriate extraction solvent.

For an unknown premixture or mixture with problematic composition, it is recommended to combine two extraction steps, e.g. first with toluene and then with toluene / polar solvent mixture.



## Summarizing conclusions

- For mineral feeds such as clays (except oxides of trace elements) and compound feeds, a mixture of toluene and polar solvents (e.g. ethanol, acetone, isopropanol; in substantial proportion) is the best extraction medium
- For oxides of trace elements, toluene is the most suitable solvent.
- There is no need to pretreat samples with HCl.
- For an unknown premixture or compound feed or a premixture or compound feed with problematic composition, it is recommended to combine two extraction steps, e.g. first with toluene and then with a toluene / polar solvent mixture.

Participants of the workshop on November 5<sup>th</sup> and 6<sup>th</sup>, 2007, concluded that the following aspects should be addressed in the **future work programmes**:

- Use of different polar solvent / toluene mixtures using different kind of polar solvents and different proportions of the solvents;
- Use of different extraction procedures and adjustments, e.g. number of PLE cycles, cycles for Soxhlet extraction and use of "hot" Twisselmann extraction;
- Addition of water (e.g. up to 20 %) to dried samples and homogenization before extraction;
- The extension of the study on bioavailability performed by SIPH Brussels is supported to cover higher members of the food chain;
- Inclusion of supercritical fluid extraction (SFE) as extraction technique.

These observations, conclusions and recommendations were formally adopted at the CRL/NRL workshop on November 5<sup>th</sup>, 2007 in Freiburg.

Dr. Rainer Malisch

Freiburg, December 10<sup>th</sup>, 2007