Reliable determination of element contents in heterogeneous waste fractions

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Abstract

Recently a particle based procedure has been developed to characterize chlorine content in heterogeneous waste fractions by sorting analysis and fractionated chemical analysis. The procedure generates reliable results including variances within a few hours. At the same time the development of mobile RFA analysis allows on-site analytical characterization. The combination of sorting analysis and RFA elemental characterization may offer the opportunity for an on-site multiple elements characterization within a short period of time.

For testing those opportunities a RDF has been characterized not only by sorting but also by RFA analysis. The results show that the elements lead, cadmium, antimony, chromium and zinc are distributed extremely heterogeneous as known for the element chlorine. For every single element different “levels of preferred concentrations” occur. Therefore the result of a chemical analysis is strongly depending on the number of high load contributors reaching the sample and their particle weight.

Based on statistical demands the necessary sample size can be calculated. For every single element a different sample size is needed. On the other hand for a defined sample size the reliability of evidence varies from element to element.

The attempt to achieve a fast and reliable on-site-analysis can only deliver a screening. Producing reliable results either need an extremely high number of single “shots” or very small particle sizes. The mobile RFA may ideally be used in cases where huge load contributors have to be identified in order to get separated.

Inhaltsangabe

Die sortieranalytisch unterstützte Bestimmung des Chlorgehaltes von Abfällen ermöglicht eine schnelle Bestimmung unter Angabe des Vertrauensbereiches. In Verbindung mit tragbaren RFA-Schnellanalysatoren ergibt sich ggf. die Möglichkeit, innerhalb weniger Stunden für 30 chemische Elemente Gehalte und Vertrauensbereiche zu ermitteln.

Die Vorgehensweise ist an einem gut definierten Ersatzbrennstoff erprobt worden. Im Ergebnis zeigt sich, dass die Elemente Blei, Cadmium, Antimon, Chrom und Zink ähnlich heterogen verteilt vorliegen wie das Element Chlor. Für jedes Element sind verschiedene „Konzentrationsfenster“ unterscheidbar. Ein gemessener Analysenwert hängt damit entscheidend davon ab, wie viele Artikel aus den jeweiligen Konzentrationsfenstern in der Analysenprobe vorhanden sind und wie schwer die Artikel sind.

Aus der Stückzahlhäufigkeit der jeweiligen Frachtträger kann auf die erforderliche Probenmasse zurückgeschlossen werden. Dabei zeigt sich, dass zur Erreichung vergleichbarer Aussagesicherheiten für jedes Element eine spezifische Probenmasse erforderlich ist. Im Umkehrschluss ergibt sich für eine definierte Probenmasse elementspezifisch eine unterschiedliche Aussagesicherheit.

Der Zielsetzung einer Vor-Ort-Analytik mit der mobilen RFA kann im Rahmen einer orientierenden Analyse entsprochen werden. Eine exakte Analyse benötigt entweder eine extrem hohe Zahl an Messpunkten oder aber die Zerkleinerung des Materials auf sehr kleine Korngrößen. Die mobile RFA findet ihr Einsatzgebiet in erster Linie bei der Identifikation einzelner großer Frachtträger. Hier leistet sie sehr wertvolle Dienste.

Keywords

Elementgehalte; Heterogene Abfälle; Aussagesicherheit; Sortieranalysen; RFA-Schnellanalysatoren; Vor-Ort-Analysen; Qualitätssicherung; Inputkontrolle; Mindestprobenmasse

Element Contents; heterogeneous wastes; reliability; sorting analysis; mobile RFA analysis; on-site-analysis; quality assurance; input control; sample size definition

1 Introduction

Within the last years a particle based procedure has been developed to characterize heterogeneous waste fractions by sorting analysis which has been presented and published in scientific literature [KETELHUT 2006, KETELHUT 2008]. It has been shown that for characterization of elemental contents the results are determined by three factors:

- The portion of “load contributors” in the sample
- The ratio of average particle weights of load contributors and all particles
- The difference between element concentration in load contributors and background

Using this procedure the determination of the chlorine content in heterogeneous wastes can be done very fast and efficiently compared to chemical analysis. In addition the statistical framework like average, mode, mean and standard deviation can be defined precisely. This clearly exceeds the actual standards followed in chemical analysis.

At the same time the development of mobile RFA analysis has reached a level that the market offers on-site analytical characterization within a few seconds. The combination of sorting analysis and RFA elemental characterization may offer the opportunity for an on-site multiple elements characterization.

For testing those opportunities a RDF has been characterized not only by sorting analysis but also by RFA analysis. The results are presented here.

2 Sorting Analysis

A well known RDF with a d_{95} < 50 mm has been sampled by 15 single samples of 2 liters each for a whole day of production. During sorting analysis the material was separated into the fractions:

- Ferrous-Metal
- Non-ferrous Metal
- Minerals
- Organics (paper, cardboard, wood, biomass)
- Non-halogenated Ppolymers (NFT)
- Halogenated Polymers (Chlorine Load Contributors, FT)
- Fine Grain < 15 mm

The diversification of plastic for chlorine content was done by “Beilstein-testing”.

From the sorted fractions particle-mass distributions were developed by single parts weighing. Based on these distributions the mass contents of the fractions can be calculated using the statistically defined particle portion distributions.

The sample showed the following characteristics:

080910 X-Ray testing	Weight [g]	No. of Parts in Sample	Average Weight [g]	Percentage of No	Percentage of Mass > 15 mm	Percentage of Mass total	Percentage of Mass stat.	Cl Conc.	Cl Load	Percentage Cl-Load
Ferrous Metal	0,0	0	0,0	0,1%	0,0%	0,0%	0,0%			
Non-ferrous Metal	51,8	109	0,5	3,8%	2,5%	1,5%	1,9%			
Minerals	52	13	4,0	0,4%	2,5%	1,5%	1,5%			
Organics	701	993	0,7	34,3%	33,5%	20,6%	20,7%	0,3%	0,1%	4,1%
Polymers halogen.	234	147	1,6	5,1%	11,2%	6,9%	6,5%	19,8%	1,3%	81,0%
Polymers non hal.	1.052	1.629	0,65	56,3%	50,3%	30,9%	30,7%	0,4%	0,1%	6,8%
Sum sorted	2.090	2.891	0,72	100,0%	100,0%	61,4%	61,3%	2,4%	1,5%	91,9%
< 15 mm	1.315					38,6%	38,6%	0,3%	0,1%	8,1%
Total	3.405					100,0%	100,0%	1,6%	1,6%	100,0%

The chlorine content of the sample can be prognosticated as a cumulative frequency distribution using the chlorine contents gained from fractionated analyses in the past and the mass contents of the fractions based on the results of the actual sorting analysis.

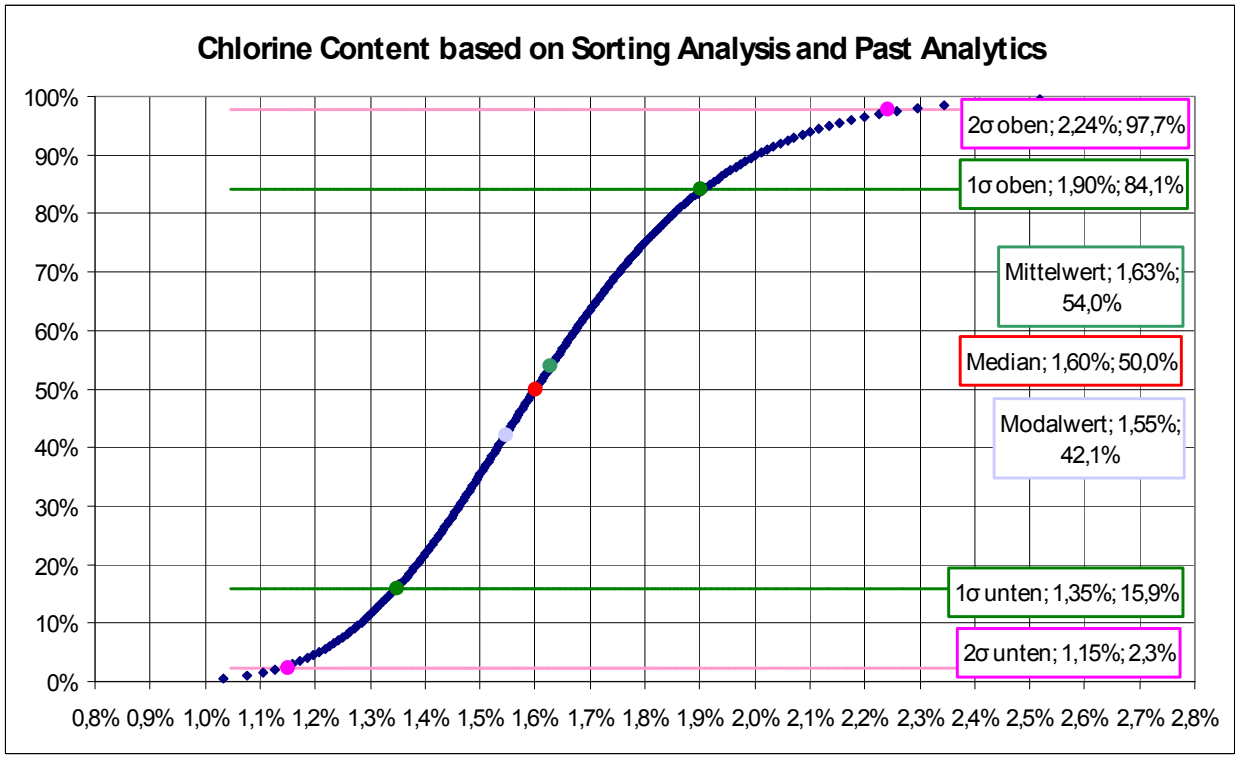

Figure 1: prognosis of the chlorine content

3 RF-Testing

The RF-Analysis was done by Mr. Stefan Rutsch from UBeRU (Rutsch Environmental Consulting) with a RF Spectrum Analyzer of the series XL3t 900 of Thermo – NITON which is marketed in Middle Europe by AnalytiCON Instruments GmbH.

From the organic fraction and from both of the plastic fractions a certain number of single particles were analyzed by RFA and weighted. The fine grain was analyzed by multiple “shots” on the whole fraction’s surface.

In total 299 Analyses were conducted.

- Organics 53 particles
- Non-halogenated plastics 85 particles
- Halogenated plastics 131 particles
- Fine Grain < 15 mm 30 shots one fraction’s surface

The measured number of particles did not correspond to the particles portions. Both of the metal fractions as well as the Minerals were not analyzed.

3.1 Results Chlorine

Chlorine was found in 287 out of the total of 299 single analyses.

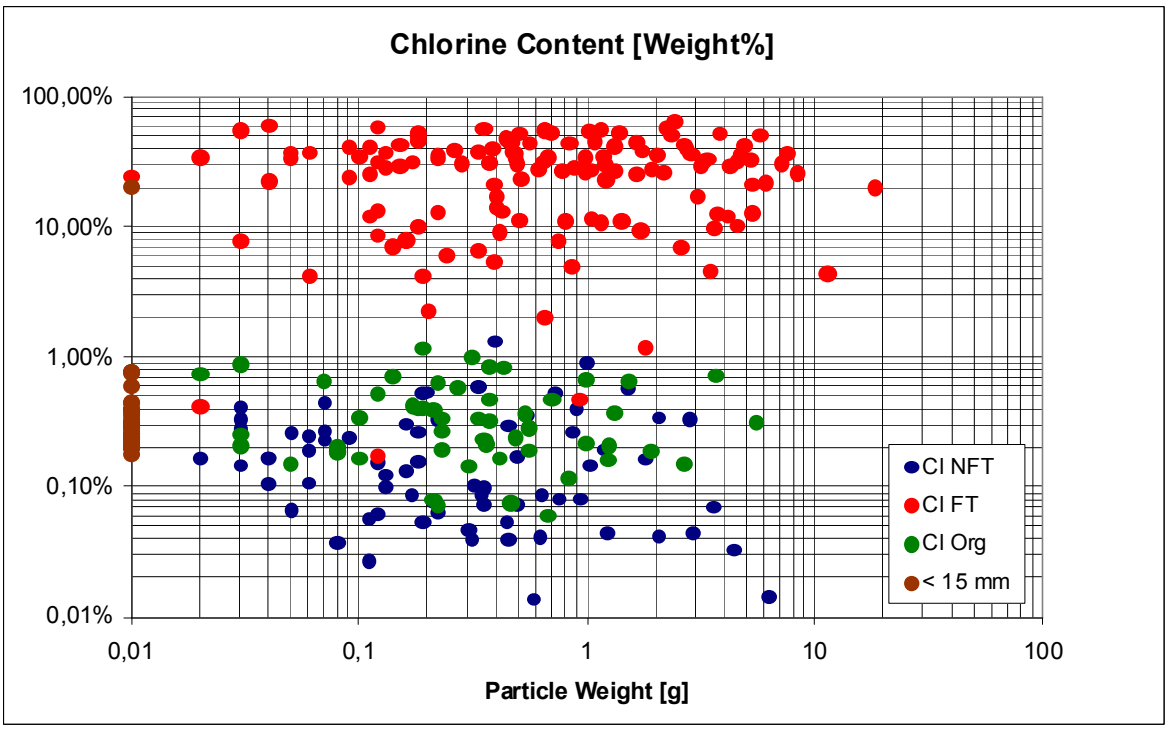

Figure 2: overview results for chlorine

Compiled as a cumulative frequency distribution the values look like this:

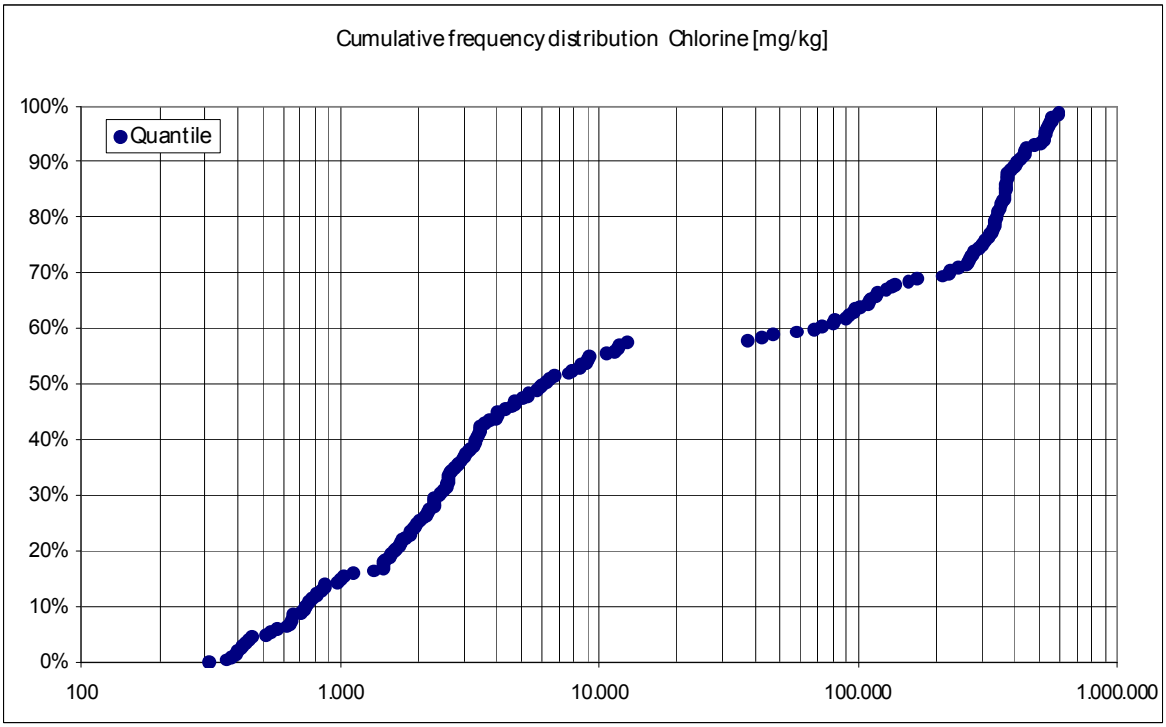

Figure 1: chlorine results as cumulative frequency distribution

It is obvious that the element chlorine is distributed in the very heterogeneous way. Especially striking is the gap between 2% and 4% chlorine content (20,000 and 40,000 mg/ kg). On this gap the differentiation between load contributors and background is based. The detailed analysis reveals that behind the found distribution four single distributions might be hidden:

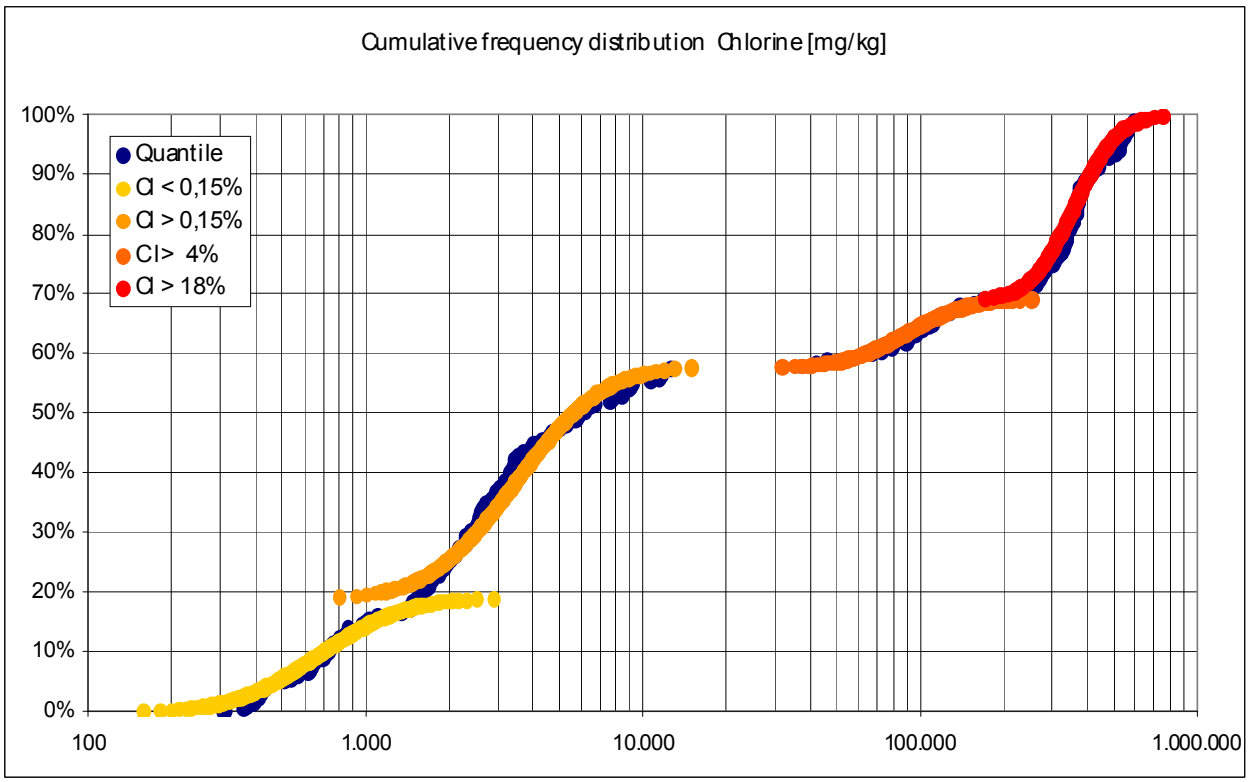

Figure 3: approximation of the distribution of chlorine values by four single distributions

Chlorine values > 18% are found in the halogenated plastics. A single value of 22% was also in the measurement in the fine grain <15 mm. The average of the single distribution is around 37.4%. The expected value for the occurrence of highly chlorinated articles is about 3.5%. It is likely to be PVC.

The orange curve approximates chlorine concentrations from 4 to 18%. It shows a relatively broad spectrum. The average chlorine content is close to 10%. Even these particles are found exclusively in the group of halogenated polymers. The frequency of occurrence of these particles is in the order of 1.3%. Several halogenated rubber products can be found here.

The chlorine levels below 2% can also be divided into two groups. The boundary concentration is in this case 0.15% respectively 1,500 mg/kg. Values below 1,500 mg/kg are mainly found in non-halogenated plastics and in some organic particles. Most results for the fine grain and a variety of measurements of organic particles are located in the range 0.15 to 0.8% chlorine. The mean of this distribution is approximately 0.4%.

For a reliable analytical testing (+/- 20% deviation from the true value) it is recommended reach a sample size that ensures to have at least 100 different load contributors in the analytical sample. If this number is significantly under-run the measurement is very much influenced by the stochastic weight of load contributors in the sample. For this RDF a sample for chlorine testing should comprise at least 7,500 articles > 15 mm.

3.2 Results Lead

67 out of 299 analyses show results for lead.

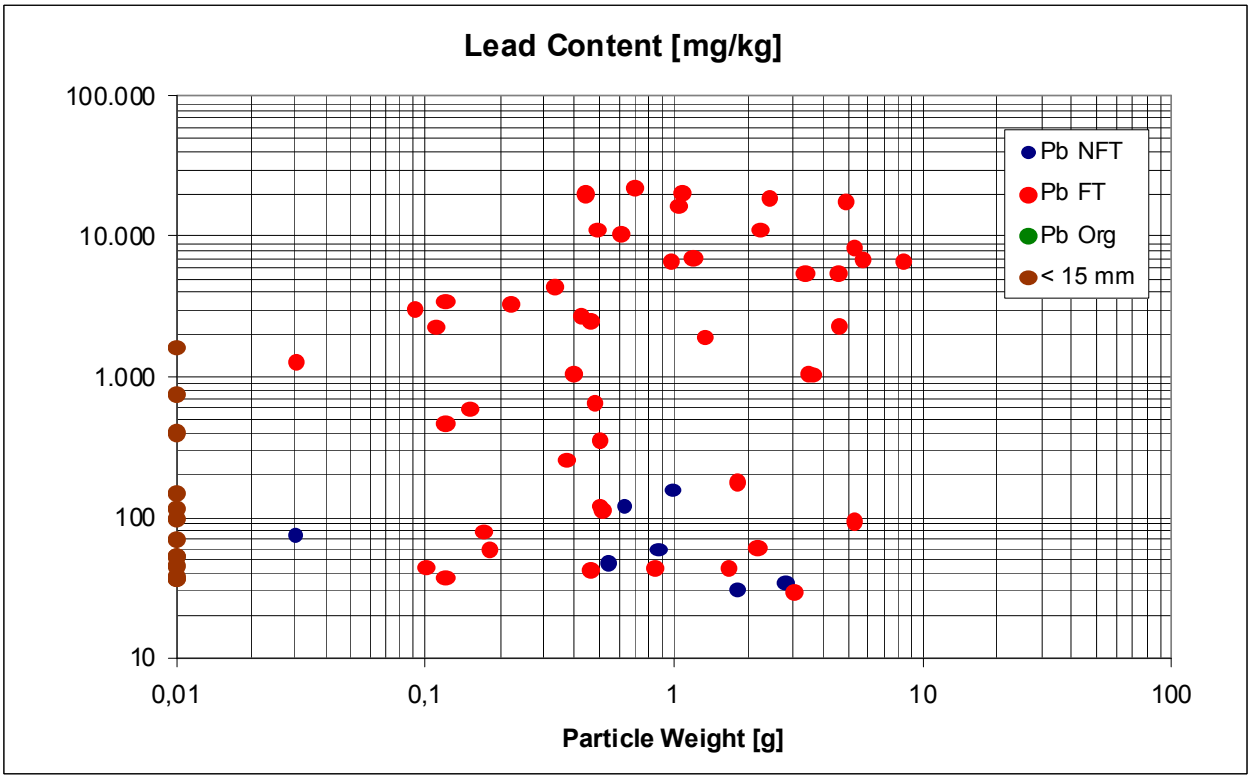

Figure 4: overview results for lead

Even the results for lead seem to belong to different uses resulting in distinguishable distributions. Lower concentrations are around 70 and up to 200 mg/kg. They are found in plastics and in the fine grain. Lead contents above 200 mg/kg are mainly found in halogenated polymers, which is not a surprise as lead compound are used as standard stabilizers in PVC. In addition three out of thirty shots on the fine grain delivered values above 200 mg/kg,

Around 1.2% of all articles have a lead content of > 200 mg/kg, so a reliable sample should at least cover 8,500 articles.

3.3 Results Cadmium

Based on a detection limit of 10 mg/kg cadmium was detectable in 44 measurements.

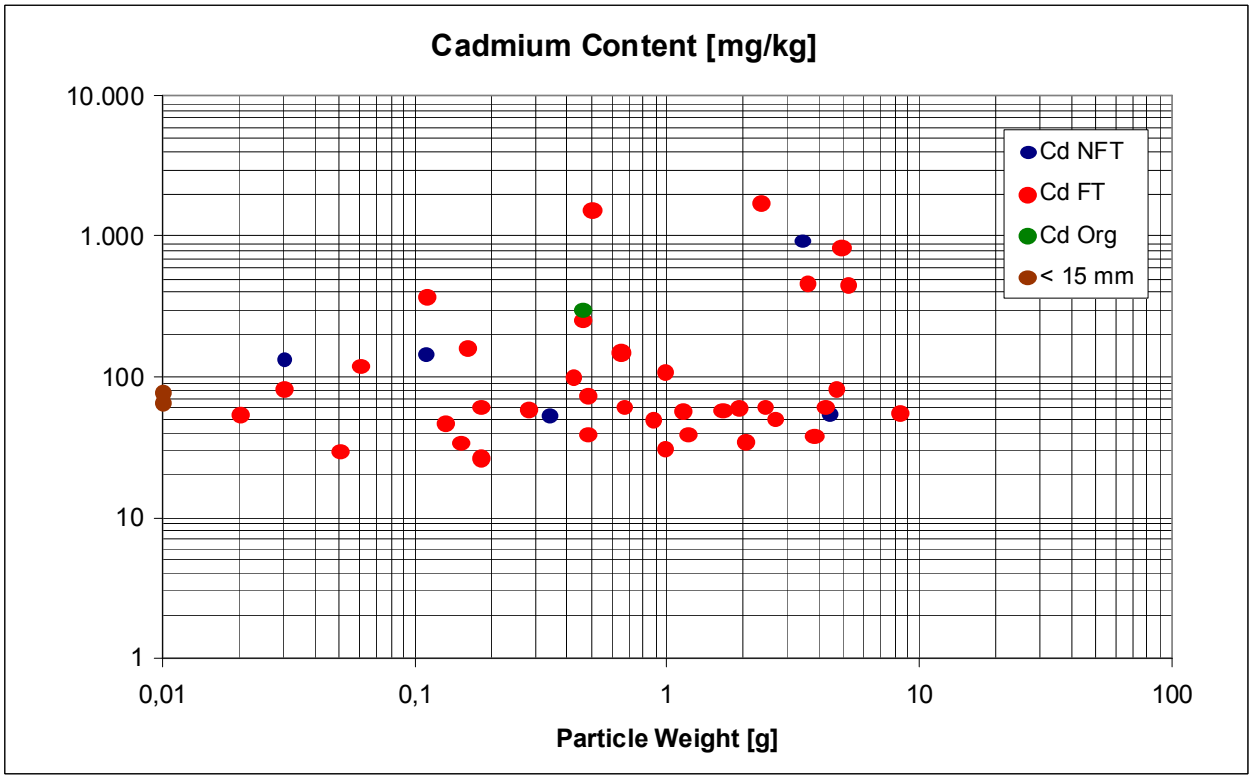

Figure 5: overview results for cadmium

Results < 80 mg/kg comprise 26 out of 44 positive results. 22 out of these were found in halogenated polymers. The average cadmium content is around 50 mg/kg. In the range up to 160 mg/kg six halogenated and two non halogenated polymers showed results.

The range form 160 up to 500 mg/kg covers 5 values. Apart of 4 findings in halogenated polymers an organic particle showed this kind of high cadmium concentration. Concentrations above of 500 mg/kg were found in further four articles. Again three out of the four were halogenated plastics.

Cadmium concentrations above 500 mg/kg are very seldom. In order to ensure the presence of around 100 particles of this type a sample should not contain less than 13,000 articles > 15 mm.

In small samples the presence of particle with a high cadmium load can significantly influence the analytical result.

Cadmium has been used for pigmentation and as an additive for PVC. Despite the decreased use in Europe it can still be found in waste fractions.

3.4 Results antimony

The element antimony was detectable in 61 out of 299 analyses.

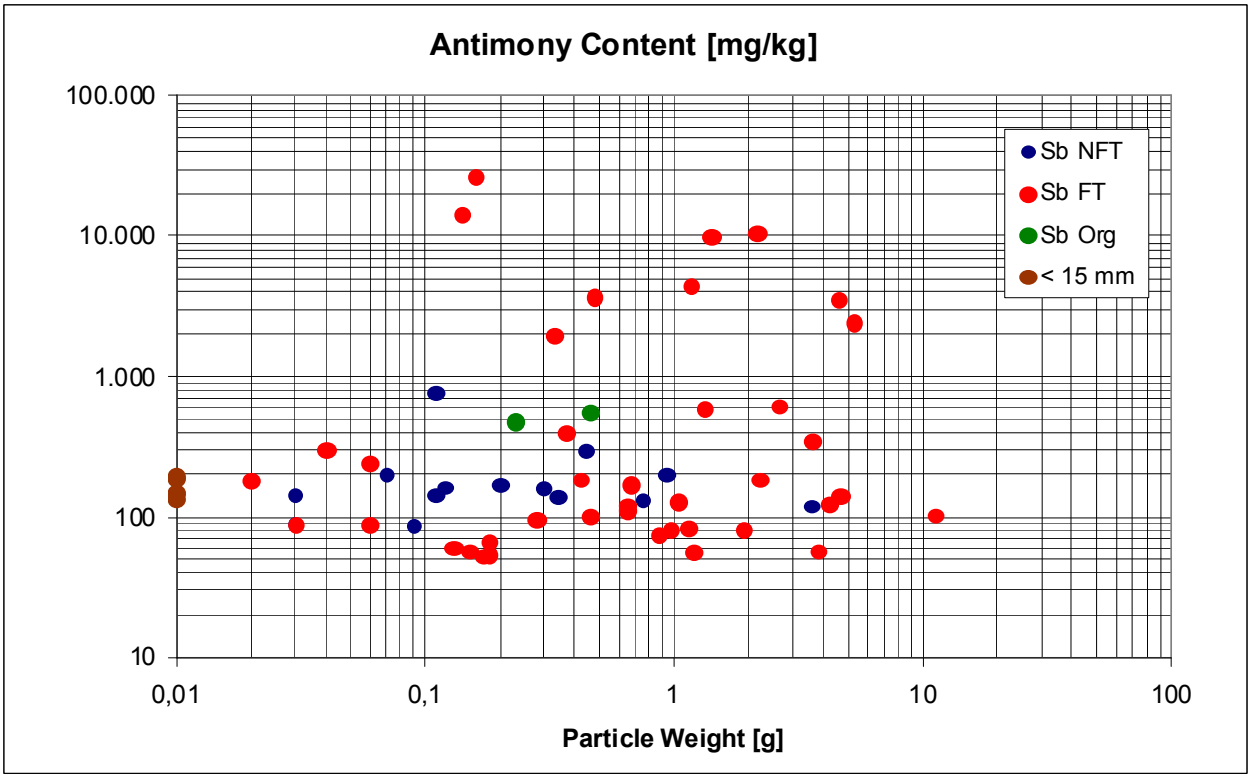

Figure 6: overview results for antimony

Two third of the measured results are related to concentration below 200 mg/kg. They belong to all fractions except the organic fraction. 20% of the values are located between 200 and 800 mg/kg. Here apart of the polymer fraction two organic articles appeared to contribute some antimony load.

The region above 800 mg/kg was only reached from halogenated polymers. Very likely this arises from the use of antimony trioxide as flame retardant, where either polybrominated compounds or even PVC have a synergistic function.

Only three out of one thousand articles contain antimony in such high concentrations. This is why especially for antimony very huge sample sizes are needed. In this case it is recommended to go for a sample size of > 32,000 articles > 15 mm.

It is very likely, that the reported difficulties to generate reproducible results in antimony testing [FLAMME 2009] have to do with these rare parts providing a very high antimony load.

3.5 Results chromium

For chromium we revealed 110 analyses above the detection limit.

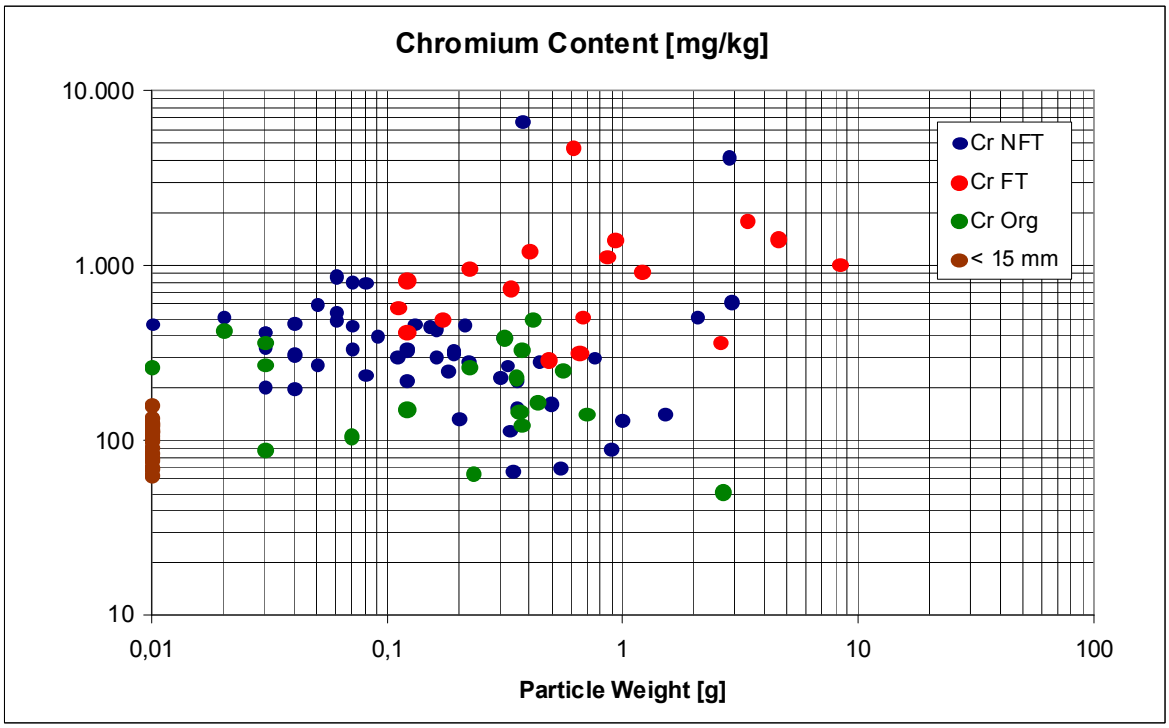

Figure 7: overview results for chromium

Obiously these results belong to different application of the element.

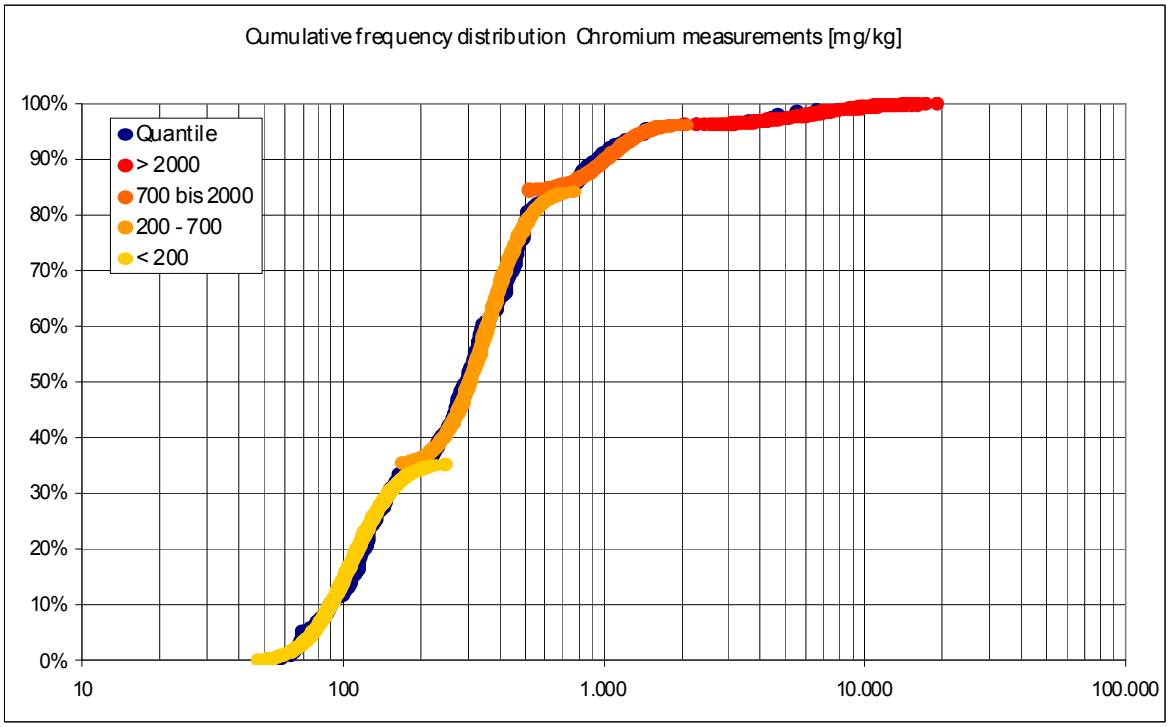

Figure 8: approximation of the distribution of chromium values by four single distributions

Around 30% of the results show values below 200 mg/kg. They belong to organic particles and non-halogenated polymers. Almost 63% of the values fit in the region between 200 and 700 mg/kg. Here we find a comparable amount of organic particles and a huge quantity of non-halogenated polymers.

Concentrations above 700 mg/kg are only found in polymers. Halogenated polymers do not attract specific attention.

The expected value for the quantity is around 5%, so a 5,000 piece sample will be large enough for the delivery of reliable results.

High concentrations may indicate the use of chromium pigments.

3.6 Results zinc

With respect to zinc 60% of all measurements led to results.

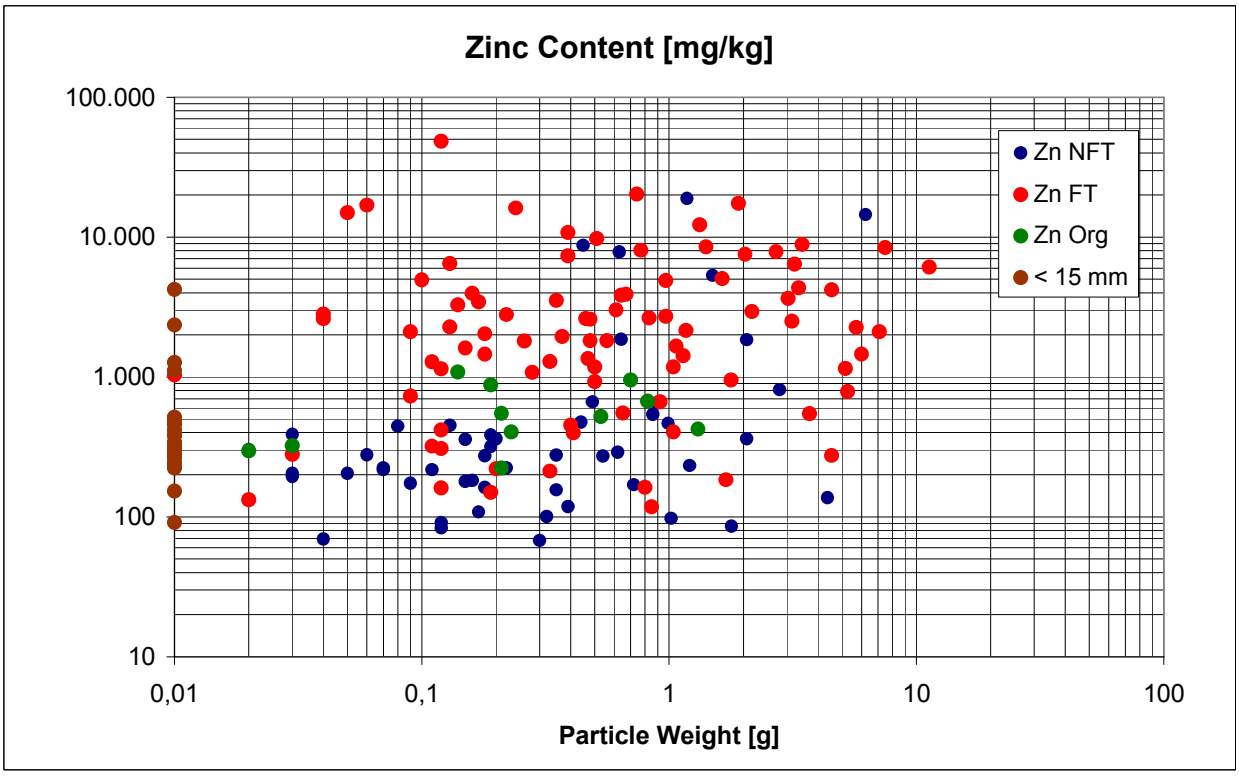

Figure 9: overview results for zinc

The cumulative density distribution allows the conclusion that the values belong to three different distributions.

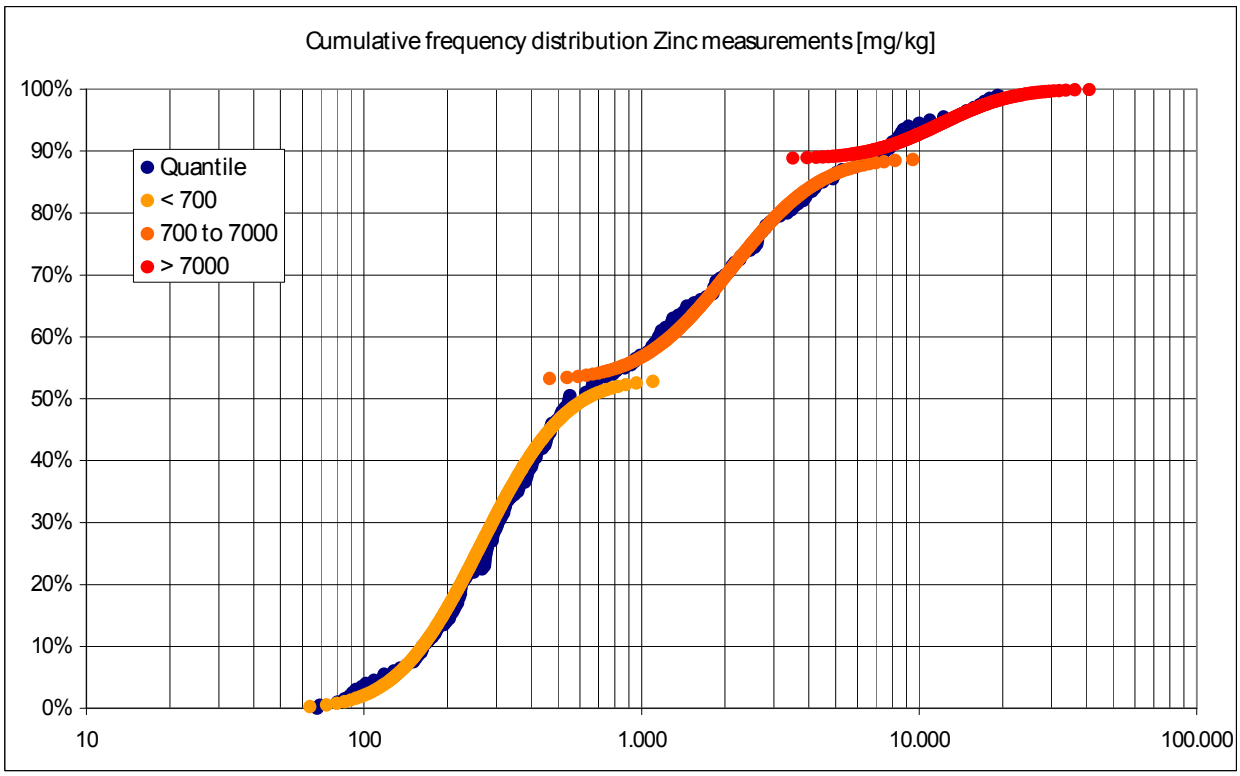

Figure 10: approximation of the distribution of zinc values by three single distributions

Almost 80% of all results stay below 700 mg/kg. The values affect primarily organics and not halogenated polymers. Results between 700 and 7,000 mg/kg are found for halogenated polymers and less for organics and non-halogenated polymers. Values exceeding 7,000 mg/kg were contributed from halogenated polymers and some other polymers.

Seven out of one hundred articles provide a significant zinc load. This leads to comparably small sample sizes.

Zinc is widely used in chemical additives. White pigments and fillers may contain zinc as well as the standard additives for PVC.

4 Load portions and recommended sample sizes

A comparison of the load contributed by the different levels of concentrations shows that more than 50% of the total element load comes from very less particles with very high element concentrations.

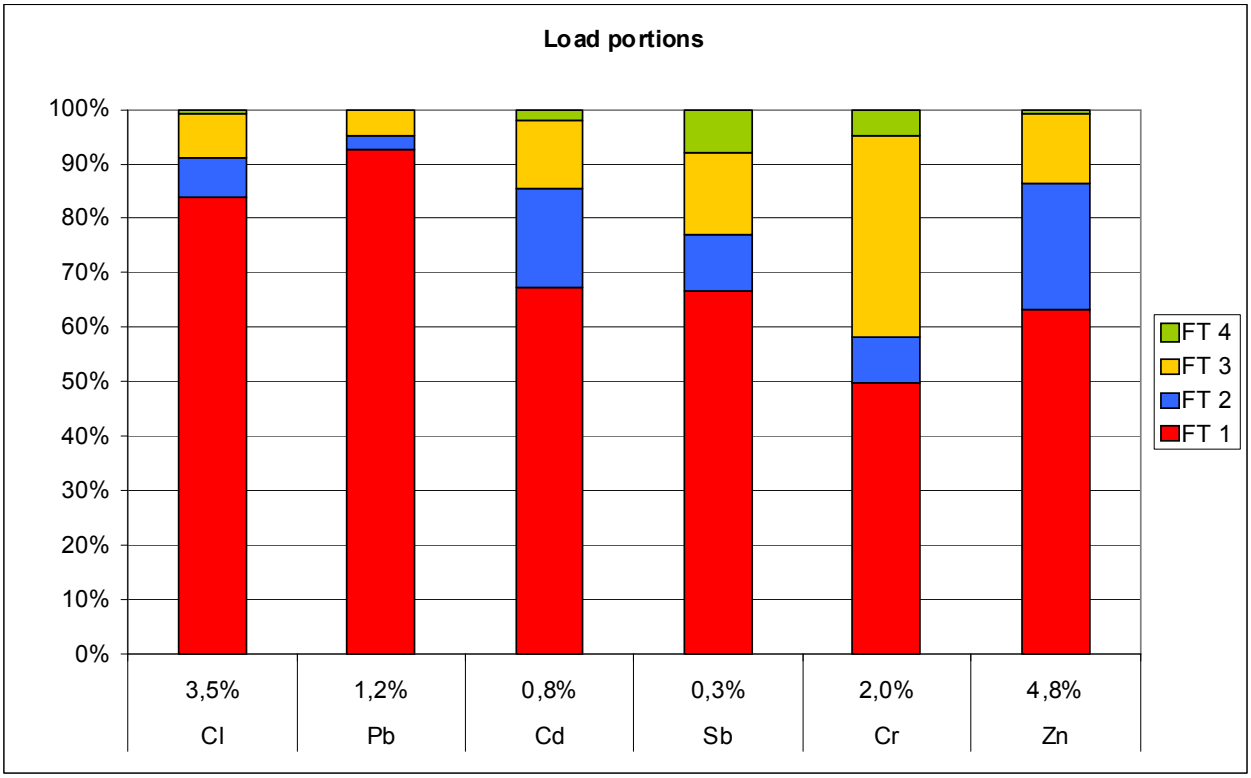

Figure 11: load contributions from different levels of concentration

While the load contribution from the highest concentration levels is around 50% for chromium it reaches values between 60 and 70% for the elements zinc, antimony and cadmium.

Regarding chlorine more than 80% of the total load is contributed by PVC. Concerning lead the portion may even reach 90%.

This makes clear that the concentrations measured in a single analysis for different elements have different reliabilities or to say it the other way round: for reaching a certain level of liability a specific sample size is needed for every single element.

The following figure compares the recommended sample sizes for this RDF based on the requirement to ensure the presence of 100 load contributors for the specific element.

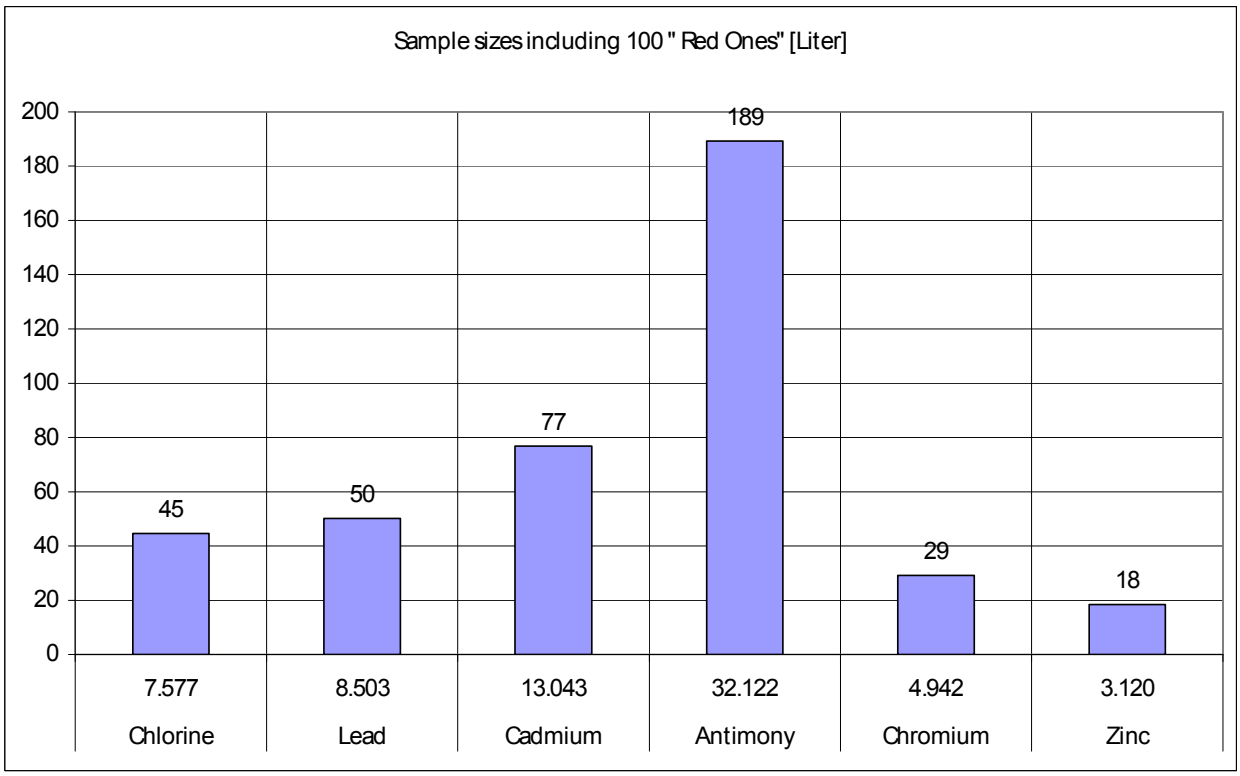

Figure 12: recommended sample sizes for different elements

The comparison shows that for an RDF with a d_{95} < 50 mm sample sizes below 20 Liters should not be used at all. Sampling 50 Liters will lead to acceptable results for zinc, chromium, lead and chlorine, while the generated values for cadmium and especially antimony will not be on the same level of liability. These values can easily under- or even overestimate the true element content.

In this case to produce a reliable analytical result for antimony 190 Liter of material is necessary. This 190 Liter must not be reduced without previous grinding to a smaller particle size.

Combining RF-Analysis and sorting analysis leads to very interesting findings concerning different sources for elemental loads. The attempt to achieve a fast and reliable on-site-analysis did not reach the target. For the particle sizes we have found here, RF-analysis can only deliver a screening. Producing reliable results either need an extremely high number of single “shots” or very small particle sizes.

The mobile RFA may ideally be used in cases where huge load contributors have to be identified in order to get separated.

5 Literature

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