Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

SI

LA-ICP-MS analysis for XRF validation

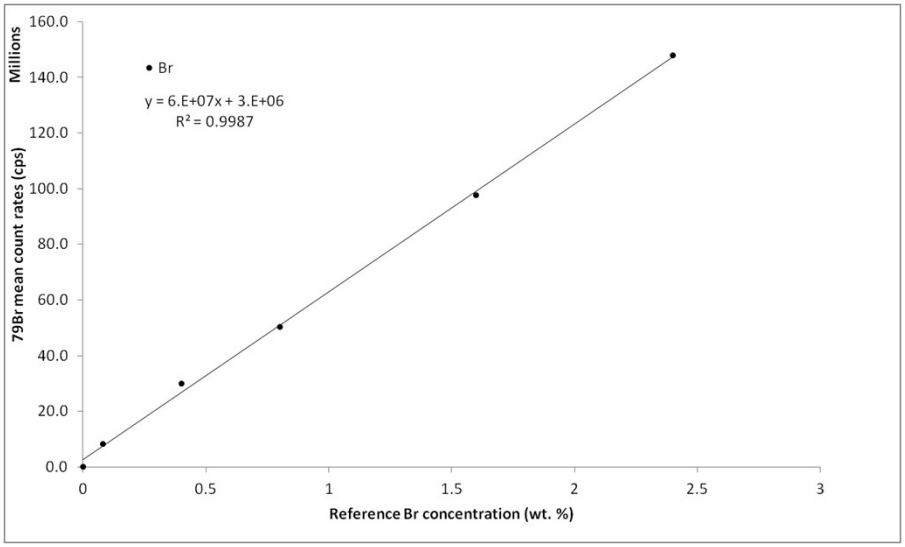

Figure 1 Calibration curve for ^{79}Br in solid reference material done with LA-ICP-MS. The reference concentration was provided with the reference material's certificate and measured with neutron activation analysis.

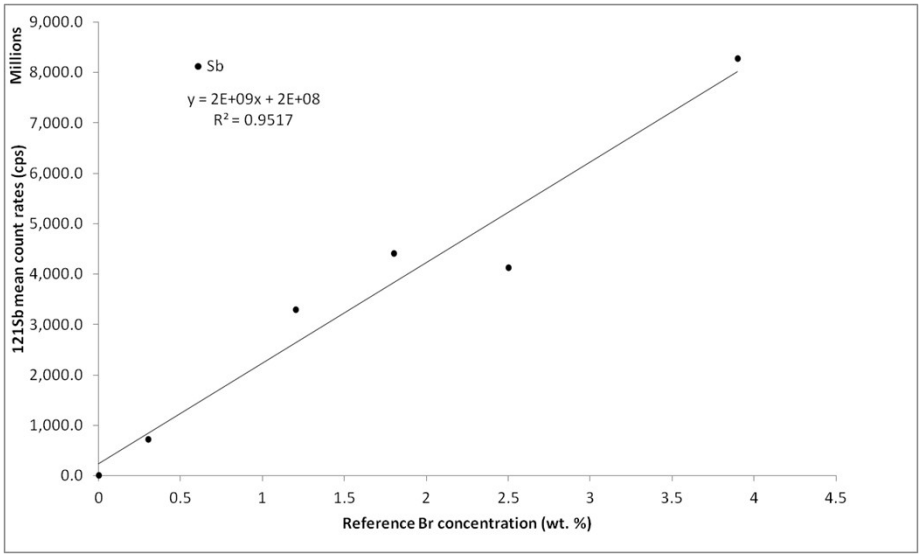

Figure 2 Calibration curve for ^{121}Sb in solid reference material done with LA-ICP-MS. The reference concentration was provided with the reference material's certificate and measured with neutron activation analysis.

For LA-ICP-MS the LOD was 0.0001% of Br and 0.001% of Sb. The average accuracy was 93.3%, with the lowest value of 79%.

For XRF the LOD was 0.001% of Br and 0.0005% of Sb. The average accuracy, calculated comparing the XRF equivalent concentration values and the reference values was 93.9%.

For Br measurements of the calibration standards, the R^2 observed is 0.9985, for the measurements of the real samples instead, when compared to the XRF data, the average relative residual was 11.1%. For Sb the calibration curve shows a slightly worse correlation (R^2=0.9517) with the XRF results: this is likely due to the difference in micro-homogeneity (due to different polarities) between Sb_2O_3 and BDE209, which affects the LA-ICP-MS (having a micrometric sampling area) but not XRF (0.8 cm sampling area)[1].

The optimal thermal desorption settings, having the lowest debromination yield for decaBDE209, were: initial temperature 150°C, ramp rate 80°C min–1 to 350°C and held for 2 min. Due to the risk of thermal debromination of PBDEs, an optimal GC interface temperature has been found at 300°C with a high and safe yield for decaBDE-209 and the lowest formation of thermal debromination products (heptaBDEs, octaBDEs and nonaBDEs). At higher temperatures than 310°C, thermal degradation of decaBDE-209 occurs with loss of sensitivity as a consequence.

Pyrolysis and thermal desorption GC-MS methods use the same hardware. After analysis, the sample cup is removed from the furnace by a pressurized shot system and caught in a sample cup-recovery container. The thermal desorption sequence is programmed so that firstly a blank sample cup without any sample or toluene extract is injected and measured in order to evaluate the background of the whole sample path and to screen potential carryover effects from a previous measured sample (sample path and carryover check). As a next step, a sample cup spiked with toluene and quartz wool plugs (without sample) is measured in order to see if there is any contamination from the toluene/quartz wool plug (reference blank measurement) and is then compared with two following measurements of a sample extract/or solid sample (generally performed in duplicate). This 4-position cycle including four measurements is repeated as many times as there are samples. The decision of repeating the measurements twice (instead of 3 times) is due to the fact that these analysis are merely done to confirm the presence of Br in the samples is due to BFRs and subsequently to use their relative content to obtain a semi-quantitative result when combined with total elemental Br quantification. The demonstrated hardware configuration and application has proven its effectiveness and stability in the past and is described elsewhere in more detail [2-6].

Table 1 Composition report of the Inter laboratory TV casing sample used for TD-GC-MS calibration.

Results of TV casing composites (InterLab Sample Waste TV backplate)			
Compounds	*n*	Mean Conc.	%RSD
PBDEs		(μg/g)	
2,4,4'-TrBDE (#28)	*4*	0.024	10
2,2',4,4'-TeBDE (#47)	*4*	1.3	15
2,2',4,4',5-PeBDE (#99)	*4*	3.2	27
2,2',4,4',6-PeBDE (#100)	*4*	1.1	39
2,2',4,4',5,5'-HxBDE (#153)	*4*	520	26
2,2',4,4',5,6'-HxBDE (#154)	*4*	59	22
2,2',3,4,4',5',6-HpBDE (#183)	*4*	3700	21
2,2',3,3',4,4',5,6'-OBDE(#196)	*2*	930	--
2,2',3,3',4,4',6,6'-OBDE(#197)	*2*	2100	--
2,2',3,3',4,4',5,5',6-NoBDE(#206)	*2*	3000	--
2,2',3,3',4,4',5,6,6'-NoBDE(#207)	*2*	1950	--
DeBDE (#209)	*4*	90000	19
TrBDEs	*4*	0.059	7
TeBDEs	*4*	1.4	14
PeBDEs	*4*	5.8	26
HxBDEs	*4*	620	24
HpBDEs	*4*	3700	21
OBDEs	*4*	3000	25
NoBDEs	*4*	4800	19
Other BFRs		(μg/g)	
TBBPA	*3*	6800	11
2,4,6-Tribromophenol (TBP)	*3*	5	44
HBCD	*2*	13	--
n: number of analysis			
--: not calculated			

The Inter laboratory TV casing sample was a composite of 50 cathode ray tube (CRT) back casings (high impact polystyrene) that had been melted and remoulded to form a material for interlaboratory tests. The data in this table was part of a recent study [7] and obtained analyzing four replicates of the TV casing using methods reported previously [8]

Table 2 TD-GC-MS method operating ranges

Compound	**Method operating range (mg/Kg^{-1})**
PBDEs (tri- to decaBDE)	1-10000
TBBPA	70-7000
DBDPE	20-10000
BTDPE	90-10000

Table 3 Br and Sb concentrations obtained with XRF. The analytical error is calculated as a function of SD between triplicate measurements

	Manufactured	Purchased	Br%	+/- Br%	Sb %	+/- Sb %
Shield toy	China	Czech Republic	0.01346358	0.002168	0.011346	0.004734
sword toy	China	Czech Republic	0.010814214	0.007282	0.012588	0.007516
Olympics medal toy	China	Czech Republic	0.009899217	0.004288	0.008359	0.005798
Rubik's cube - Czech Republic	China	Czech Republic	0.018397253	0.006736	0.014477	0.004642
Rubik's cube - German	China	Germany	0.071483044	0.001688	0.029365	0.006126
Black Gun toy	China	Germany	0.501407974	0.02219	0.257966	0.015084
Star Wars cereal bowl	China	Germany	<LOD	0.002602	<LOD	0.004134
thermal cup	China	Germany	<LOD	0.008238	<LOD	0.004462
small gun toy	China	Italy	<LOD	0.000392	<LOD	0.004522
binocular toy	China	Italy	<LOD	0.001238	<LOD	0.004694
target man toy	China	Italy	0.002427124	0.000768	<LOD	0.004814
spring gun toy	China	Italy	0.072438773	0.000834	0.037547	0.004422
spring gun red toy	China	Italy	<LOD	0.001326	<LOD	0.006126
black spring car	China	Germany	0.207827177	0.000482	0.089293	0.010273
black spring car	China	Germany	0.124255989	0.000512	0.054242	0.008074
blue car louncher	China	Germany	0.053600627	0.000634	<LOD	0.008182
grey car louncher	China	Germany	1.697292321	0.002308	0.843595	0.005174
grey miniature car	China	Germany	0.121146101	0.000454	0.091256	0.006018
black miniature car	China	Germany	0.150725521	0.000422	0.069648	0.003352
thermal cup	China	Czech Republic	0.002147532	0.000404	0.003619	0.007189
thermal cup	China	Czech Republic	<LOD	0.002672	<LOD	0.004286

thermal cup	China	Czech Republic	0.122153203	0.00035 2	0.07190 7	0.00593
thermal cup	China	Czech Republic	<LOD	0.00272 4	<LOD	0.0043
thermal cup	Turkey	Czech Republic	0.124649681	0.00878 6	0.07365 2	0.00787 4
thermal cup	Turkey	Czech Republic	<LOD	0.00034 8	<LOD	0.00463 6
thermal cup	Turkey	Czech Republic	<LOD	0.0003	<LOD	0.00432 4
Radio back panel	China	Czech Republic	0.511882529	0.00037	0.34397 4	0.00499 8

Table 4 Overview of ATR-FTIR and pyrolysis GC-MS data on polymer composition

Sample	Main polymer[a]	Impurities/majors[b]				
		PS/HIPS/ABS/SAN	PC	PMMA	PA6	PET/PBT
Rubik's cube	HIPS	+	+	+	+	+
Toy gun	HIPS	+	+	+	+	+
Spring car	HIPS	+	+	+	n.d.	+
Spring car	HIPS	+	+	+	n.d.	+
Car launcher	HIPS	+	+	n.d.	n.d.	+
Miniature car	PS	+	+	+	n.d.	+
Miniature car	PS	+	+	+	n.d.	+
Spring gun	HIPS	+	+	+	n.d.	+
Thermal Cup	ABS	+	+	+	n.d.	+
Thermal Cup	ABS	+	+	+	n.d.	+
Radio cover	ABS	+	+	+	n.d.	+

[a]Data obtained by FTIR

[b] Data obtained by pyrolysis GC-MS; the symbol ``+`` means that polymer's specific precursors were detected in the pyrogram while ``n.d``. means not detected. The polymer precursors in the pyrogram are styrene (PS/HIPS/ABS/SAN); bisphenol A (PC); methylmethacrylate (PMMA); caprolactam (PA6) and benzoic acid (PET/PBT).

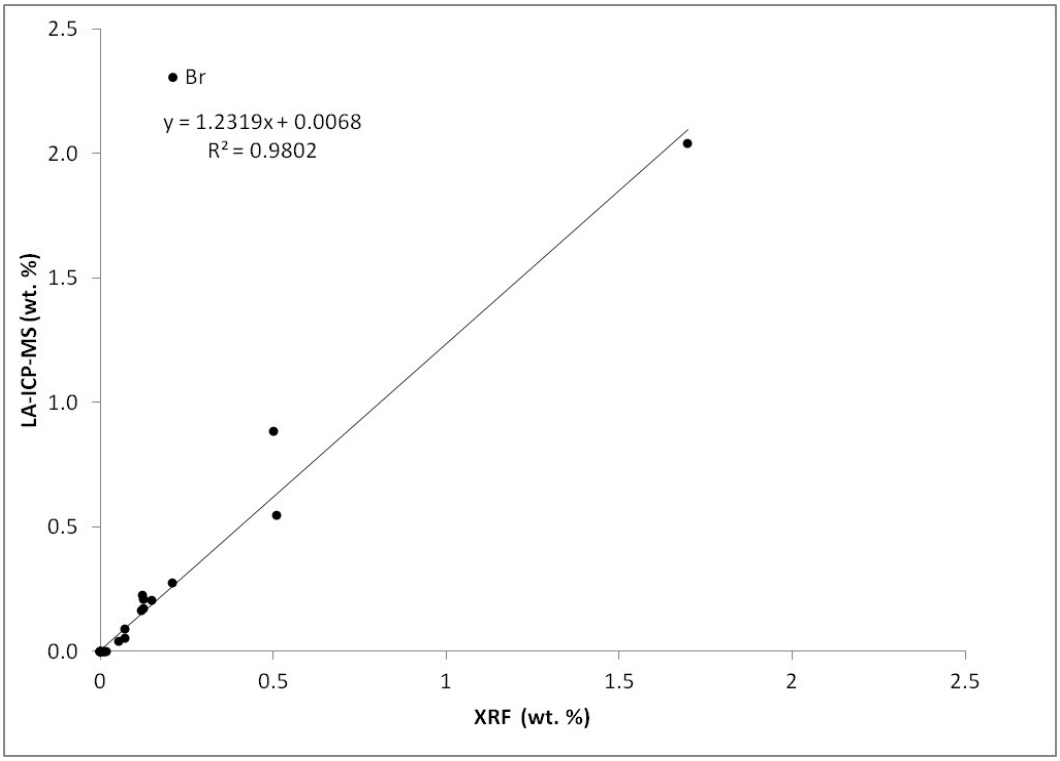

Figure 3 Comparison of Br concentration values obtained with XRF and with LA-ICP-MS (^{79}Br).

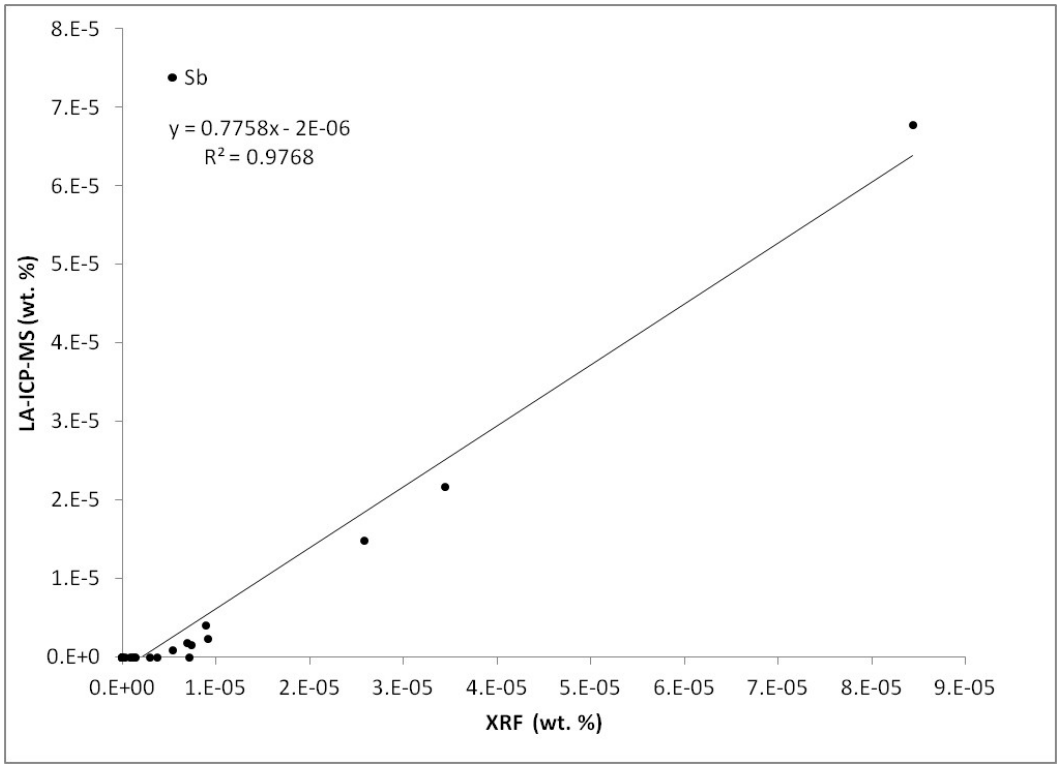

Figure 4 Comparison of Sb concentration values obtained with XRF and with LA-ICP-MS (^{121}Sb).

References

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