

Supplementary Information

Open Access

Majda Pavlin, Arkadij Popović, Radojko Jaćimović, Milena Horvat*

Supplement 1 Mercury fractionation in gypsum using temperature desorption and mass spectrometric detection

Mass spectrometric approach to mercury fractionation in FGD gypsum

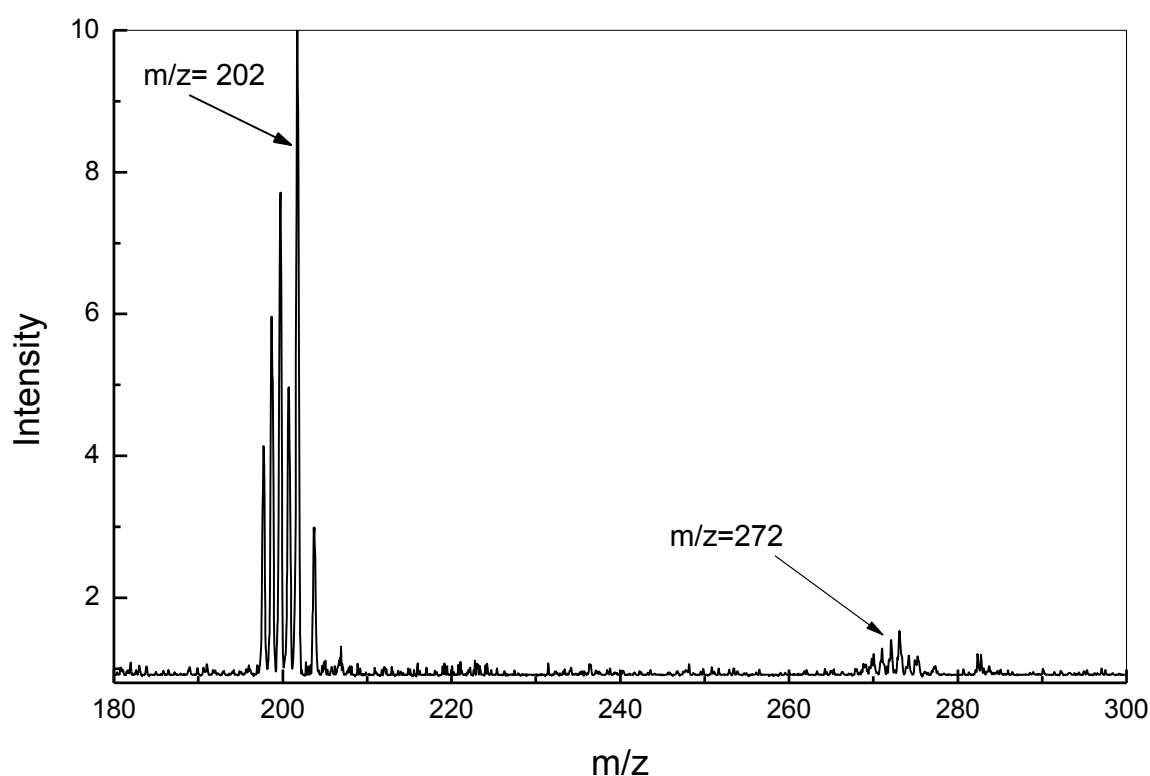


Figure S1: Mass spectrum of vapours obtained during TPD experiment of dry SiO_2 mixed with HgCl_2 (100 mg kg^{-1} mixture) at 70°C . Weak peaks at m/z 272 represent HgCl_2^+ ions.

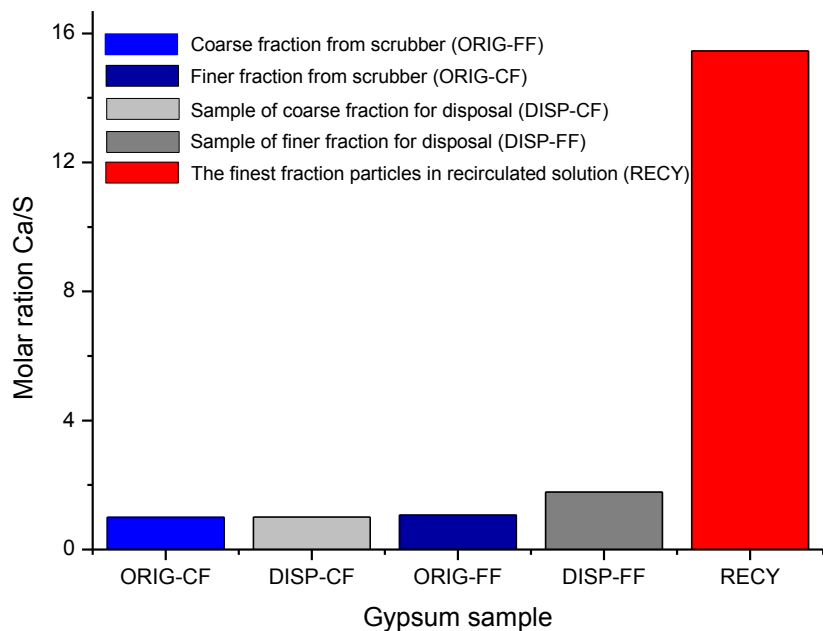


Figure S2: The molar ratio between Ca and S for various gypsum fractions.

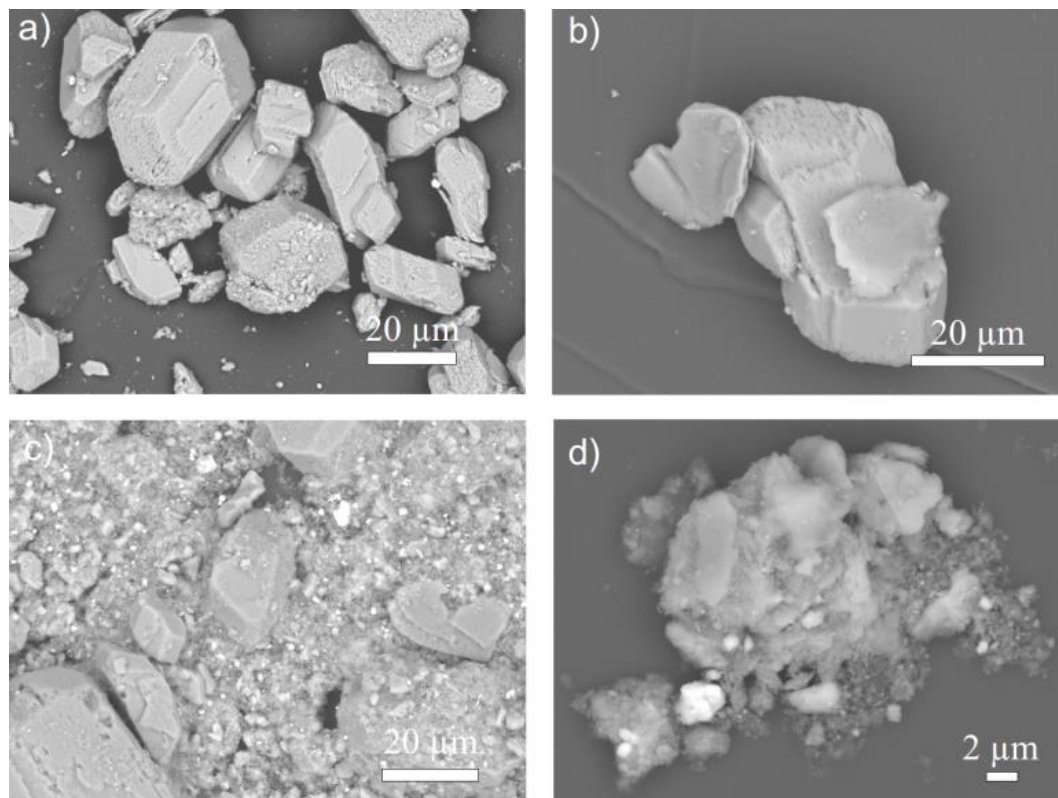


Figure S3: Scanning electron microscope (SEM) images of solid particles in gypsum: a) bulk fraction of ORIG gypsum sample, b) crystal of gypsum in a coarse fraction of DISP-CF, c) finer fraction of ORIG-FF gypsum and (d) an example of agglomerate present in the finest fraction of RECY gypsum.

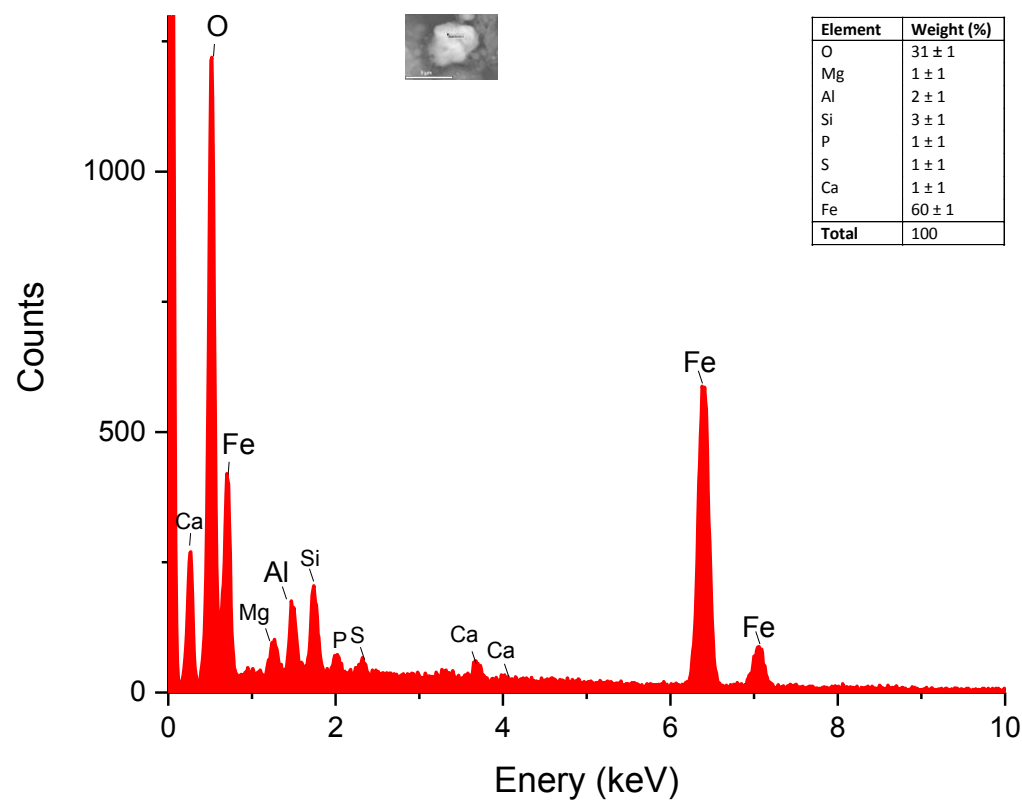


Figure S4: SEM-EDS spectrum and elemental quantitative data representative in the gypsum sample RECY.

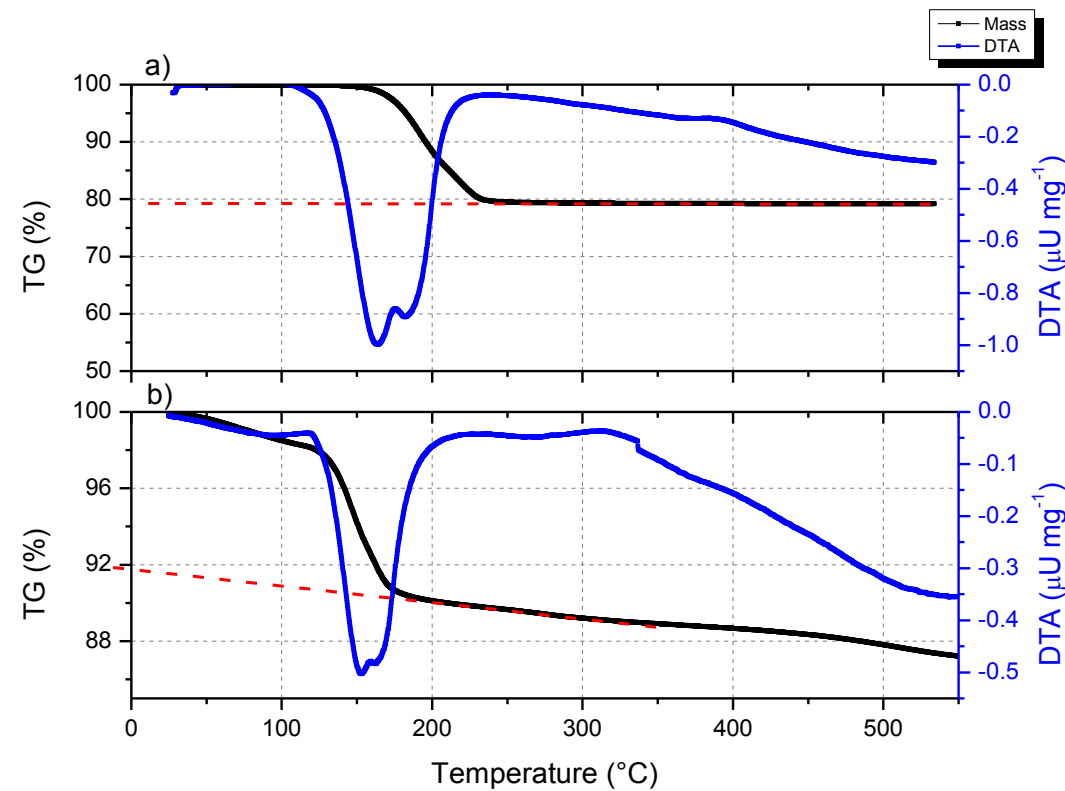


Figure S5: TG and DTA analysis of gypsum samples of a) coarse fraction (DISP-CF) and b) finer fraction (RECY) in the temperature intervals between 25 °C and 550 °C.

Table S1: Specification (chemical, supplier and declared purity) for eight different **mercury compounds** and three different substrates that were used for Hg standards (mixture) preparation, are provided.

Chemical	Supplier	Declared purity
HgCl ₂ – old chemical,	Kemika d.d., Zagreb	99 %
HgCl ₂ – new chemical	Sigma-Aldrich Co. LCC.	≥ 99.998 %
Hg ₂ Cl ₂	Sigma-Aldrich Co. LLC.	≥ 99.5 %
HgO – Red	Sigma-Aldrich Co. LLC.	≥ 99.5 %
HgO – Yellow	May & Baker Ltd.	≥ 99.5 %
HgS – Red	Mallinckrodt Chemical Works	99 %
HgSe	Sigma-Aldrich Co. LLC.	99.9 %
Hg ₂ SO ₄	Sigma-Aldrich Co. LLC.	98.0 %
HgSO ₄	Sigma-Aldrich Co. LLC.	≥ 99 %
Quartz, white powder, fine granulated, washed and calcined for analysis	Merck KGaA	99 – 100.5 % purity of substance is calculated on calcined substance
CaSO ₄ • 2H ₂ O, white powder	Sigma-Aldrich Co. LLC.	99 – 101 % purity of substance is based on anhydrous substance
FeO(OH)-, α-phase, Iron(III) hydroxide, brown powder	Alfa Aesar	99+ %

Table S2: Elemental concentration and uncertainty with a coverage factor k=1 (mg kg⁻¹) in gypsum samples (ORIG-FF, ORIG-CF, DISP-FF, DISP-CF and RECY) obtained by k₀-instrumental neutron activation analyses. The multielemental analysis was done for 43 elements.

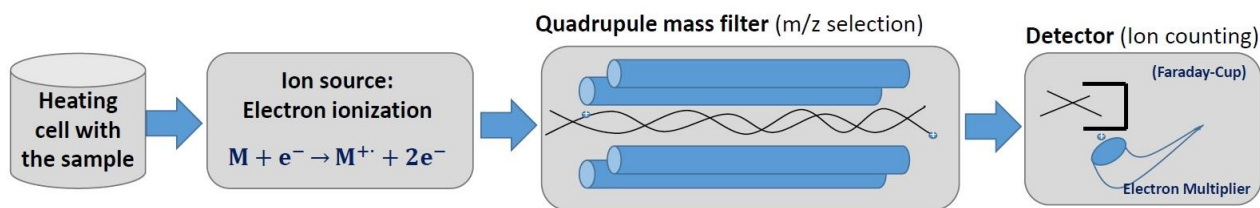
Sample	DISP-CF		DIPS-FF		RECY		ORIG-CF		ORIG-FF	
	Concentra- tion	Uncer- tainty	Concentra- tion	Uncer- tainty	Concentra- tion	Uncer- tainty	Concentra- tion	Uncer- tainty	Concentra- tion ±	Uncer- tainty
Element	mg/kg		mg/kg		mg/kg		mg/kg		mg/kg	
Al	522	19	36100	1300	52900	1900	622	22	21000	700
As	0.45	0.02	24.4	0.9	44.7	1.6	0.55	0.02	15.0	0.5
Ba	*	3.2	188	9	361	14	*	3.84	118	5
Br	0.87	0.03	21.5	0.8	2.98	0.11	16.6	0.6	14.7	0.5
Ca	232000	8000	144000	5000	98000	3500	228000	8000	176000	6000
Cd	*	0.12	5.89	0.25	3.52	0.24	*	0.24	2.17	0.16
Ce	0.95	0.04	24.2	0.9	43.6	1.6	0.93	0.04	15.6	0.6
Cl	38.2	1.8	202	12	41.7	4.5	247	10	214	8
Co	0.133	0.005	8.28	0.29	7.59	0.27	0.13	0.01	3.30	0.12
Cr	1.82	0.09	98.7	3.5	153	5	2.23	0.10	59.9	2.1
Cs	0.113	0.004	8.38	0.29	12.6	0.4	0.15	0.01	5.11	0.18
Dy	0.17	0.01	2.72	0.11	4.15	0.15	0.16	0.01	1.68	0.06
Eu	0.034	0.002	0.60	0.03	0.97	0.04	0.03	0.00	0.35	0.02
Fe	393	14	22200	800	35200	1200	474	17	13600	500
Ga	*	0.14	8.37	0.47	16.4	0.7	*	0.31	6.07	0.26
Hf	0.026	0.002	1.17	0.04	1.97	0.07	0.03	0.00	0.71	0.03
Hg	0.22	0.01	12.5	0.5	20.6	0.7	0.31	0.02	8.94	0.32

Table S2: Elemental concentration and uncertainty with a coverage factor $k=1$ (mg kg^{-1}) in gypsum samples (ORIG-FF, ORIG-CF, DISP-FF, DISP-CF and RECY) obtained by k_0 -instrumental neutron activation analyses. The multielemental analysis was done for 43 elements.

Sample	DISP-CF		DIPS-FF		RECY		ORIG-CF		ORIG-FF	
	Concentration	Uncertainty	Concentration	Uncertainty	Concentration	Uncertainty	Concentration	Uncertainty	Concentration $\pm$	Uncertainty
I	0.44	0.04	15.5	0.8	18.6	0.8	1.17	0.11	10.4	0.4
In	*	0.001	*	0.02	0.06	0.01	*	0.01	0.023	0.002
K	155	6	10100	400	15800	600	246	10	6200	200
La	0.65	0.02	15.0	0.7	25.1	1.1	0.69	0.03	9.33	0.38
Mg	1040	50	39400	1400	53300	1900	1520	60	23700	900
Mn	3.61	0.13	203	7	129	5	7.09	0.25	73.7	2.6
Mo	1.38	0.10	44.0	2.0	78.2	3.3	1.57	0.08	29.3	1.2
Na	24.6	0.9	978	34	1180	40	129	5	594	21
Nd	*	0.61	12.1	0.7	21.9	1.0	0.68	0.09	8.08	0.36
Rb	1.56	0.12	74.3	2.7	111	4	1.91	0.12	44.6	1.6
S	180000	11000	64700	10600	*	5077	183000	9000	131000	12000
Sb	0.091	0.004	4.71	0.17	8.28	0.29	0.14	0.01	2.84	0.10
Sc	0.16	0.01	8.20	0.29	12.5	0.4	0.19	0.01	5.01	0.18
Se	1.21	0.05	52.0	1.9	83.8	2.9	1.57	0.06	34.4	1.2
Sm	0.13	0.01	3.15	0.12	5.06	0.19	0.14	0.01	1.68	0.11
Sr	211	8	195	10	191	8	208	8	177	8
Ta	*	0.006	0.49	0.02	0.64	0.02	*	0.013	0.22	0.01
Tb	0.021	0.001	0.38	0.01	0.62	0.02	0.02	0.00	0.24	0.01
Th	0.10	0.01	4.86	0.17	8.04	0.28	0.11	0.00	2.96	0.10
Ti	*	92	1800	80	2700	100	*	78	1040	50
U	0.97	0.04	57.2	2.0	82.1	2.9	0.99	0.04	24.8	0.9
V	3.42	0.15	212	8	317	11	4.05	0.17	126	5
W	*	0.03	0.98	0.07	1.59	0.10	*	0.03	0.71	0.04
Yb	0.08	0.00	1.71	0.06	2.79	0.10	0.086	0.003	1.06	0.04
Zn	2.02	0.11	209	7	148	5	2.11	0.11	62.4	2.2
Zr	*	8.5	89.0	7.0	168	9	*	10.1	43.9	3.4

Table S3: Releasing temperatures of various mercury compounds mixed with dry $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, in a saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and a saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with added FeOOH .

Mercury compounds	Dry $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (°C)	Saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (°C)	Saturated solution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{FeOOH}$ (°C)
HgCl_2	154	236	228
Hg_2Cl_2	150	230	257
$\text{HgO}(\text{red, R})$	270-345; 580	-	-
$\text{HgO}(\text{yellow, Y})$	307; 485	240	242
HgSO_4	676	250	216
Hg_2SO_4	315; 564	256	258
HgS	368	-	-



Scheme S1: Schematic illustration of set-up (flow diagram) for measuring Hg and other gases with TPD method. For NT-MS and QMS, ionization process is performed by electron ionization.

Multi-elemental analysis using k0-INAA

Homogenized samples (160–200 mg) were sealed into pure polyethylene ampoules (SPRONK system, The Netherlands), stacked together in sandwich form with an Al–0.1% Au alloy (IRMM-530R) standard and irradiated in a 250 kW TRIGA Mark II reactor (Jožef Stefan Institute, Ljubljana, Slovenia). Two irradiations were performed at a thermal neutron flux of $1.1 \cdot 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$: a short irradiation (5 minutes) to determine elements via their corresponding short half-life radionuclides and a second irradiation (12 hours) to determine elements via their corresponding medium or long half-life radionuclides. For QA/QC purposes, the certified reference material BCR-320R channel sediment was used. After an appropriate cooling time, samples were measured on an calibrated HPGe detector (45% relative efficiency). HyperLab software was used to evaluate peak area and the Kayzero software package to determine the elemental content and calculate the effective solid angle [1–3]. The k0-INAA procedure is accredited according to ISO/IEC 17025:2005 by the Slovenian Accreditation Agency (Accreditation certificate LP-090).

References

- [1] Smodiš B, Jačimović R, Medin G, Jovanović S. Instrumental neutron activation analysis of sediment reference materials using the k0-standardization method. *J Radioanal Nucl Chem* 1993;169:177–85. doi:10.1007/BF02046792.
- [2] Jačimović R, Smodiš B, Bučar T, Stegnar P. k0-NAA quality assessment by analysis of different certified reference materials using the KAYZERO/SOLCOI software. *J Radioanal Nucl Chem* 2003;257:659–63. doi:10.1023/A:1026116916580.
- [3] Xilei L, Corte F, Moens L, Simonits A, Hoste J. Computer-assisted reactor NAA of geological and other reference materials, using the k0-standardization method: Evaluation of the accuracy. *J Radioanal Nucl Chem* 1984;81:333–43. doi:10.1007/BF02135386.