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Supplementary material

Measurement of labile arsenic speciation in water and soil using diffusive gradients in thin films (DGT) and X-ray absorption near edge spectroscopy (XANES)

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HPLC–HG–AFS instrument and setting details

HPLC separation (Isocratic LC-20AT, Shimadzu equipped with manual injector) of inorganic As forms was carried out in the anion-exchange column at room temperature and a precolumn-guard of same material PRP-X100. Separation of As forms was carried out in 15 min with 5 min for the wash, using 10 mM phosphate buffer (pH 6.25) as mobile phase, with a flow rate set at 0.8 mL min^{-1}. Post-column hydride generation (HG) of volatile arsines were originated prior to detection, which was performed adding on-line solutions of 50% v/v HCL (flow rate of 9 mL min^{-1}) and then 0.7% m/v $NaBH_4$ (flow rate of 4.5 mL min^{-1}) in 0.1 mol L^{-1} NaOH as hydride stabiliser. Argon at a flow of 250 mL min^{-1} was used to transport the sample to the detector. To remove moister from the argon-transported sample nitrogen was used with a set flow of 2500 mL min^{-1} in a Perma-Dryer system. Determination of As forms was achieved by atomic fluorescent spectroscopy (AFS) using an Excalibur 10.055 detector (PS Analytical, UK) with a specific boosted discharge hollow cathode lamp (BDHCL) for the fluorescent of As (primary current of 27.5 mA, boost current of 35 mA).

Table S1. Physico-chemical properties and major cations of the water sample

	Creek water
pH	6.8
DOC (mg L^{-1})	4.1
Sulfate (mg L^{-1})	5.8
Nitrate (mg L^{-1})	11
Chloride (mg L^{-1})	34
Calcium (mg L^{-1})	5.8
Potassium (mg L^{-1})	2.3
Magnesium (mg L^{-1})	3.5
Sodium (mg L^{-1})	28
Total Alkalinity (mg L^{-1} $CaCO_3$)	32
Water hardness (mg L^{-1} $CaCO_3$)	29

Table S2. Comparison of relative proportion (%) of arsenic species in samples resulting from XANES fitting using FB-gels exposed to arsenic compound solutions and arsenic compound solutions (number in parentheses)

Fitting residuals from the arsenic compound in solution only are presented in the parentheses

Test	Type sample and method	Relative proportion (%)				Fitting residual
		iAs^V	iAs^{III}	$DMAs^V$	$MMAs^V$	
Kinetic binding gel disc (KB)	Intact FB gel – XANES (2 weeks)	52(55)	27(29)	21(17)	–	3.2 (7.7)
	Intact FB gel – XANES (fresh)	44(47)	31(34)	24(20)	–	2.7 (6)
Standard solution (SS)	Intact FB gel – XANES (2 weeks)	50(50)	22(25)	28(26)	–	2.8 (6.2)
	Intact FB gel – XANES (fresh)	50(66)	25(10)	26(25)	–	1.5 (9.5)
Water (CW)	Intact FB gel – XANES (2 weeks)	53(57)	29(31)	18(14)	–	1.3 (7.8)
	Intact FB gel – XANES (fresh)	64(66)	21(23)	15(12)	–	2.7(7.3)
Tailings (TD)	Intact FB gel – XANES (2 weeks)	–	4(15)	81(72)	–	92(63)
	Intact FB gel – XANES (fresh)	8(0)	6(16)	70(70)	–	112(79)
Soil (MR)	Intact FB gel – XANES (2 weeks)	19(30)	75(72)	7(0)	–	1.3(12)
	Intact FB gel – XANES (fresh)	16(31)	70(69)	13(0)	–	6(5.7)

Table S3. Total mass of arsenic in FB-gels and DGT concentrations (C_{DGT})

n/a is not applicable: the DGT concentration (Fick's law) is not applicable to these tests because only the FB gel disc was exposed to arsenic solution not DGT device

Test	As concentration in gel ($\mu g\ mL^{-1}$ gel)	Total mass As per gel (μg/DGT unit)	DGT concentration (C_{DGT}, $\mu g\ L^{-1}$)
Table 3			
KB	159	40.6	n/a
SS	331	84.4	625
CW	140	35.7	260
TD	3.8	1.0	7
MR	165	42.1	285
Table 4			
As^{V}	92	23.5	n/a
As^{III}	52	13.3	n/a
DMA^{V}	35	8.9	n/a
MMA^{V}	32	8.2	n/a
iAs^{V}, iAs^{III}, $DMAs^{V}$, $MMAs^{V}$	159	40.6	n/a
iAs^{V}, iAs^{III},$DMAs^{V}$	280	71.4	n/a
iAs^{V}, $DMAs^{V}$, $MMAs^{V}$	281	71.7	n/a

Table S4. Chemical properties of soil and tailings

Samples	pH (1:5)	EC (1:5) ($\mu S\ cm^{-1}$)	Water extraction (1:5) ($mg\ kg^{-1}$)									
			As	Al	Cr	Cu	Cd	Mn	Mg	Fe	Ni	Zn
MR	6.02	119	127	99	46	0.09	n/a	0.6	18	27	0.03	3
TD	5.64	2167	46	0.03	4.2	0.08	0.02	0.03	476	0.24	0.013	1.8

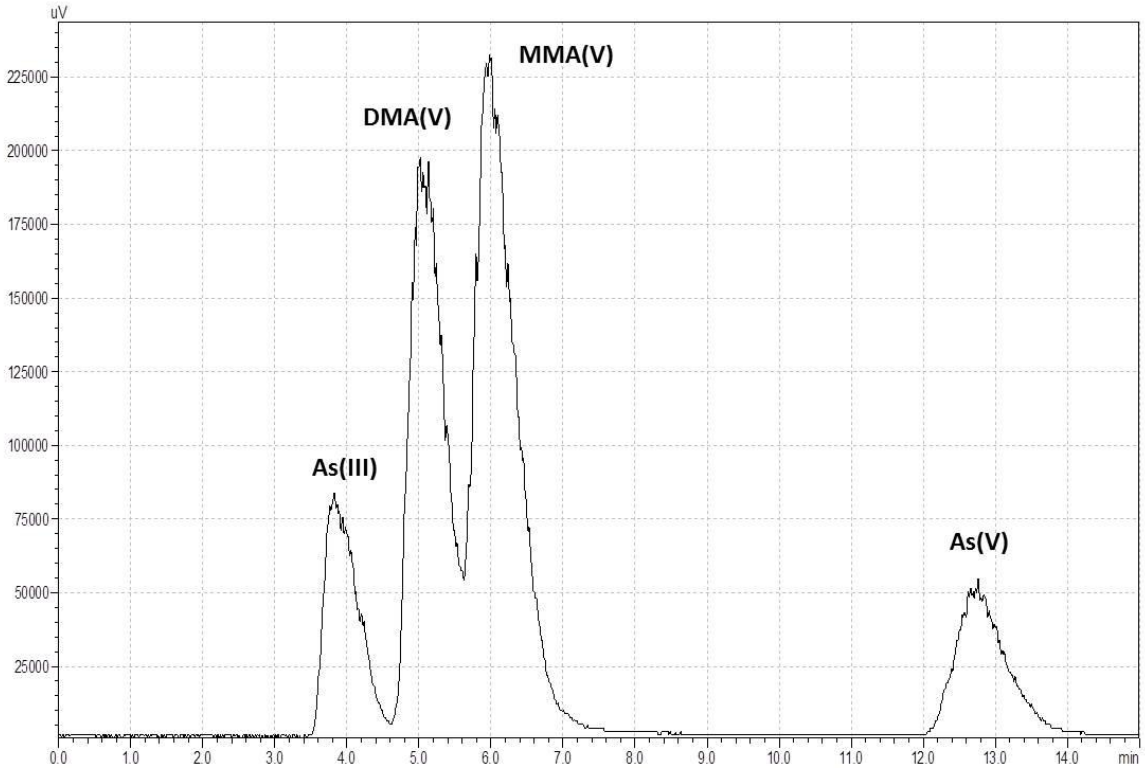


Fig. S1. Chromatogram of 0.5 mg L^{-1} standard solution of arsenic species As^{III}, DMA^{V}, MMA^{V} and As^{V}.

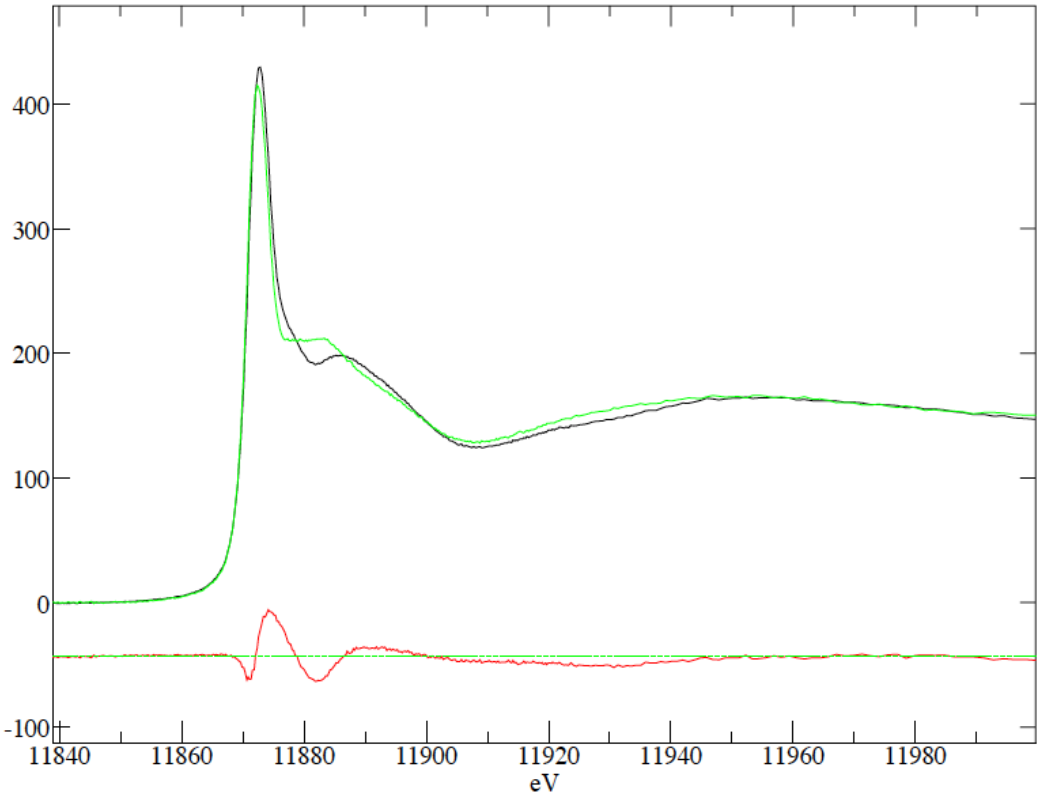
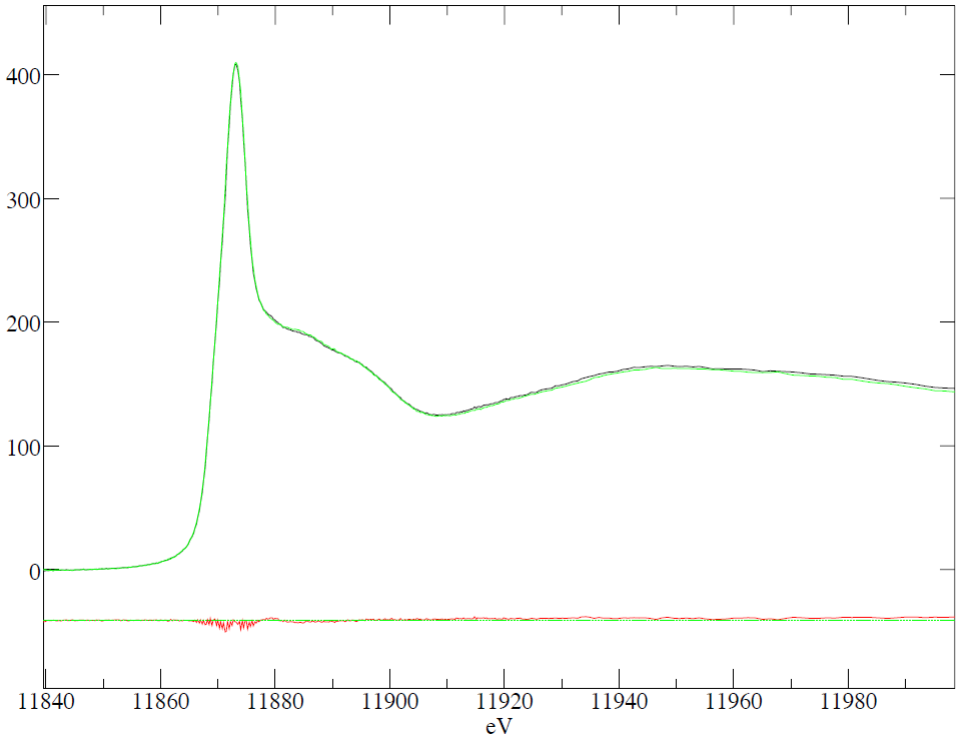
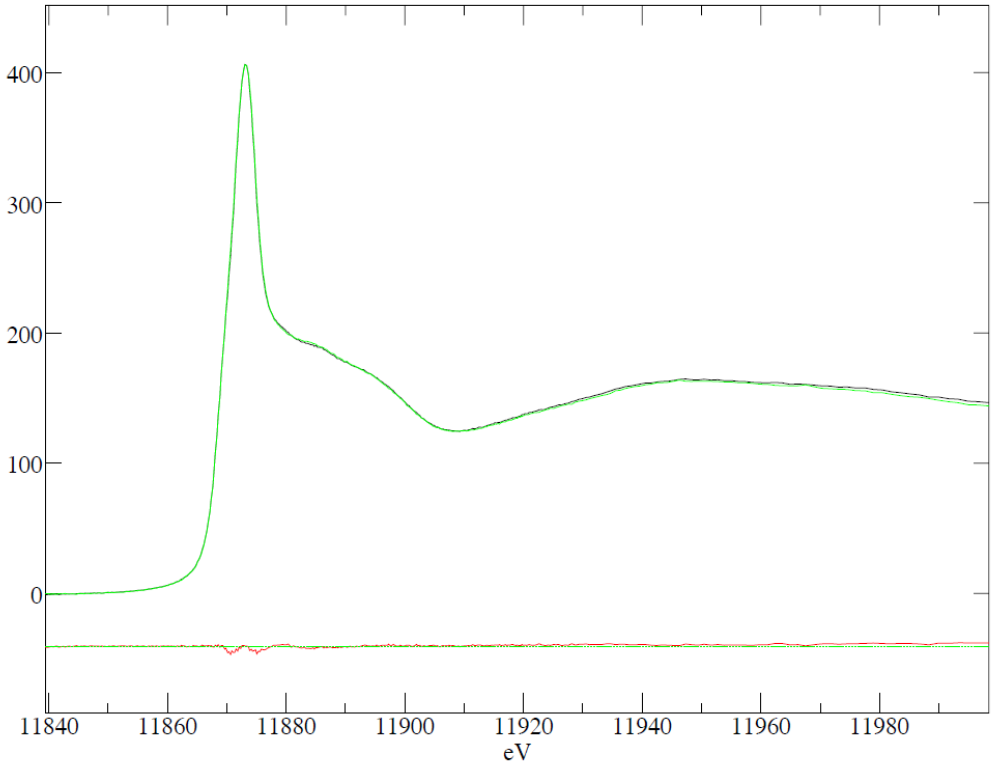


Fig. S2. The difference plot of the two spectra from the XANES scan for $MMAs^{V}$ (black spectrum) and $DMAs^{V}$ (green spectrum).

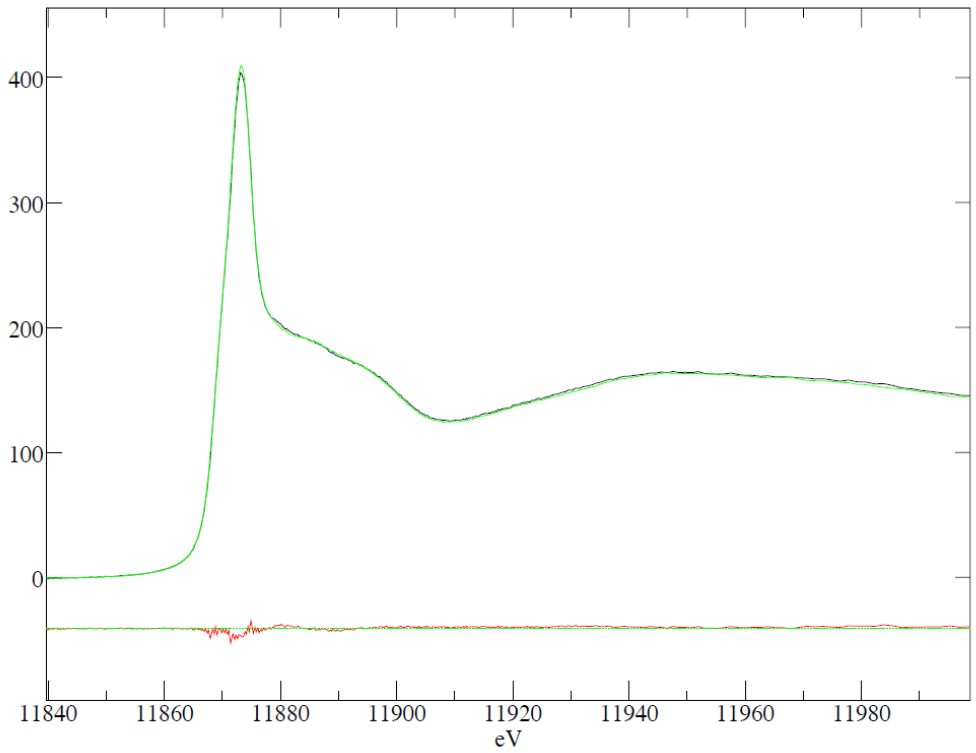
SS (2 weeks)



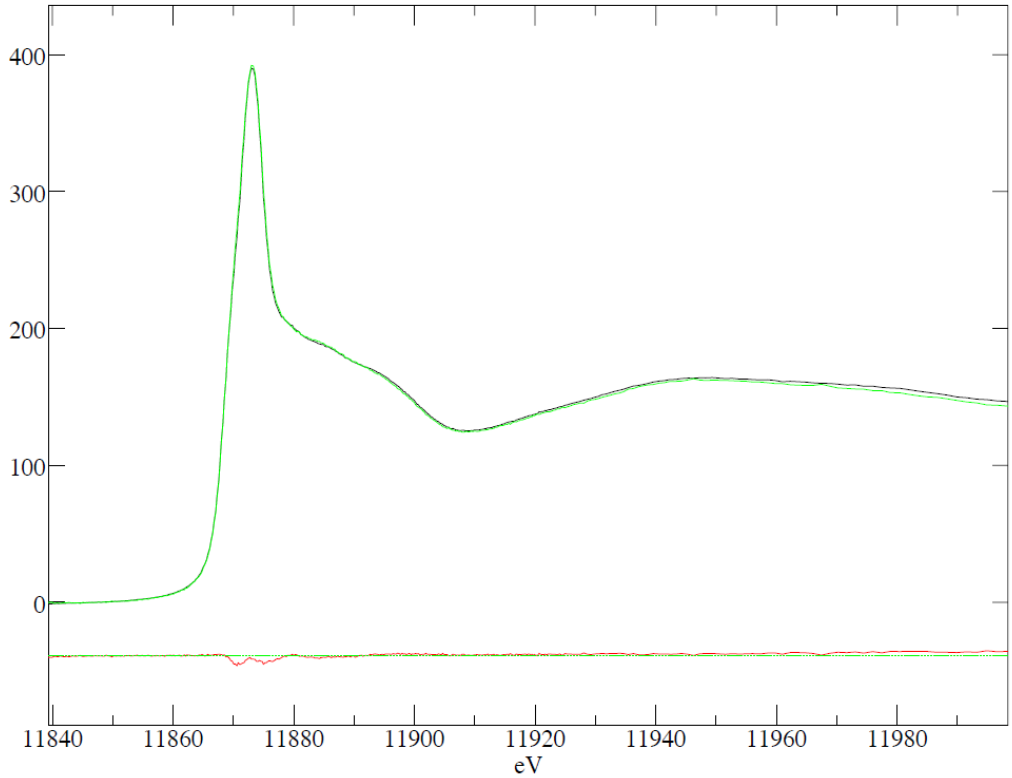
SS (fresh)



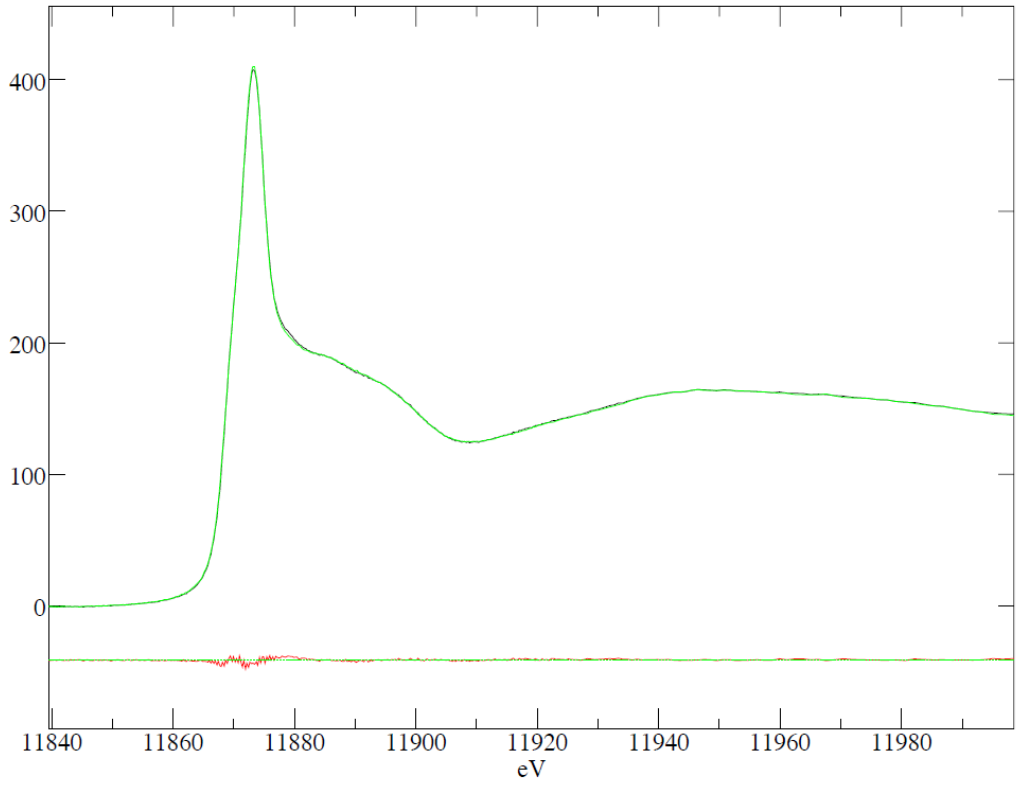
KB (2 weeks)



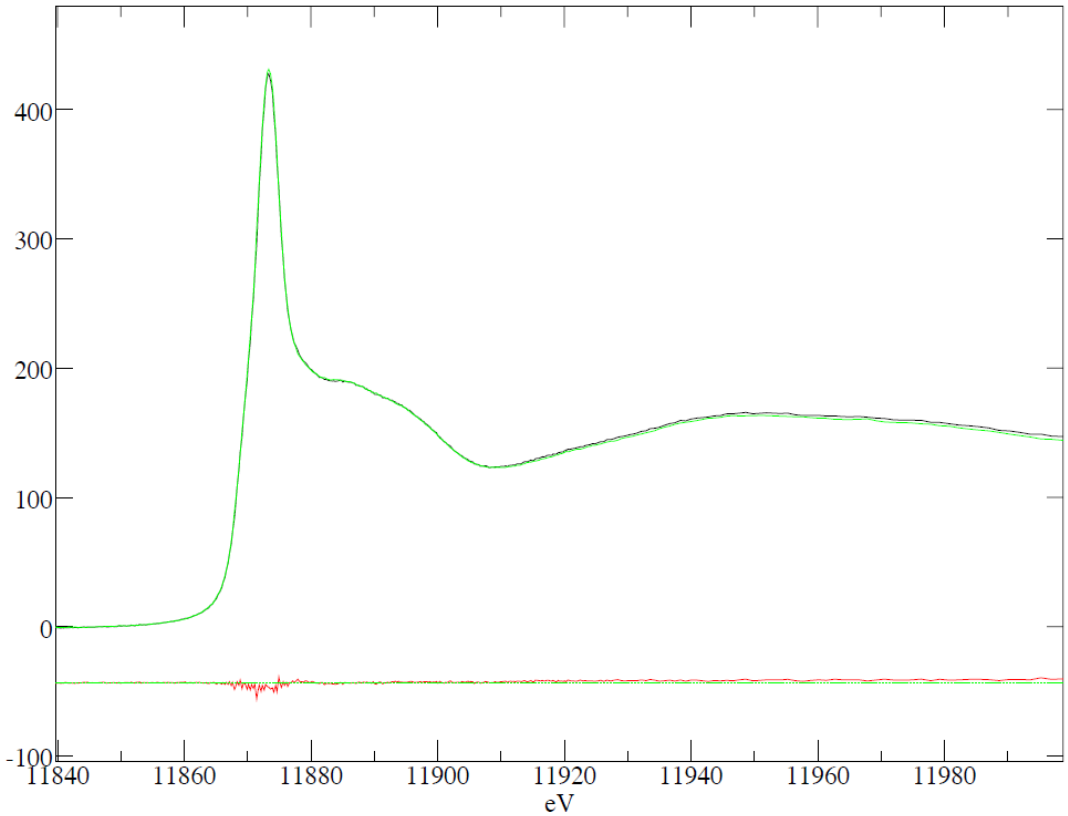
KB (fresh)



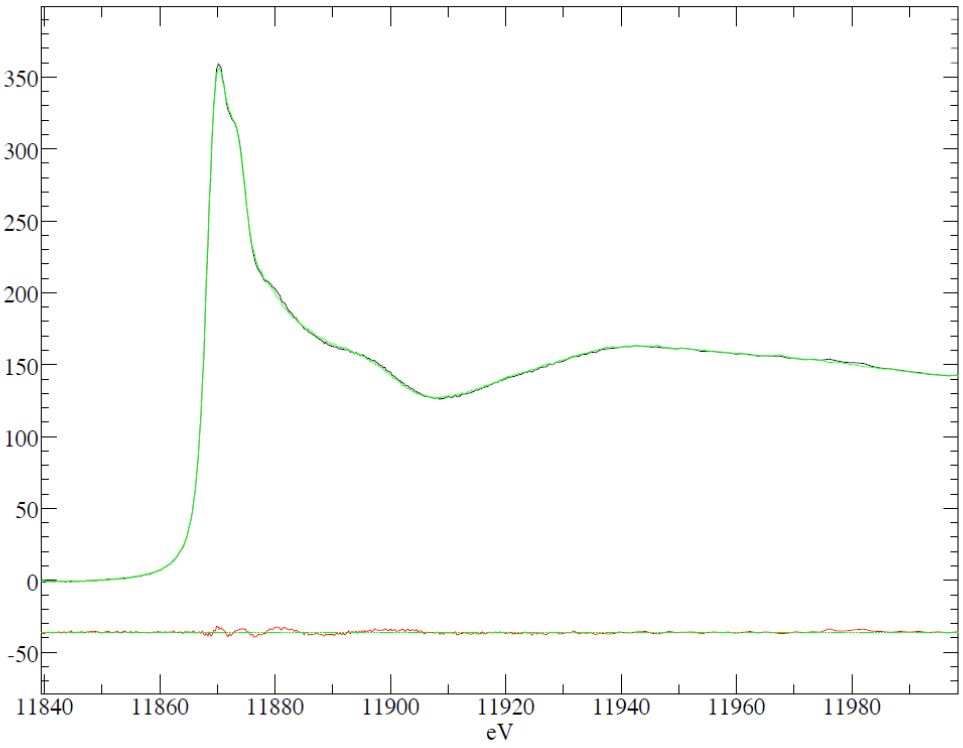
CW (2 weeks)



CW (fresh)



MR (2 weeks)



MR (fresh)

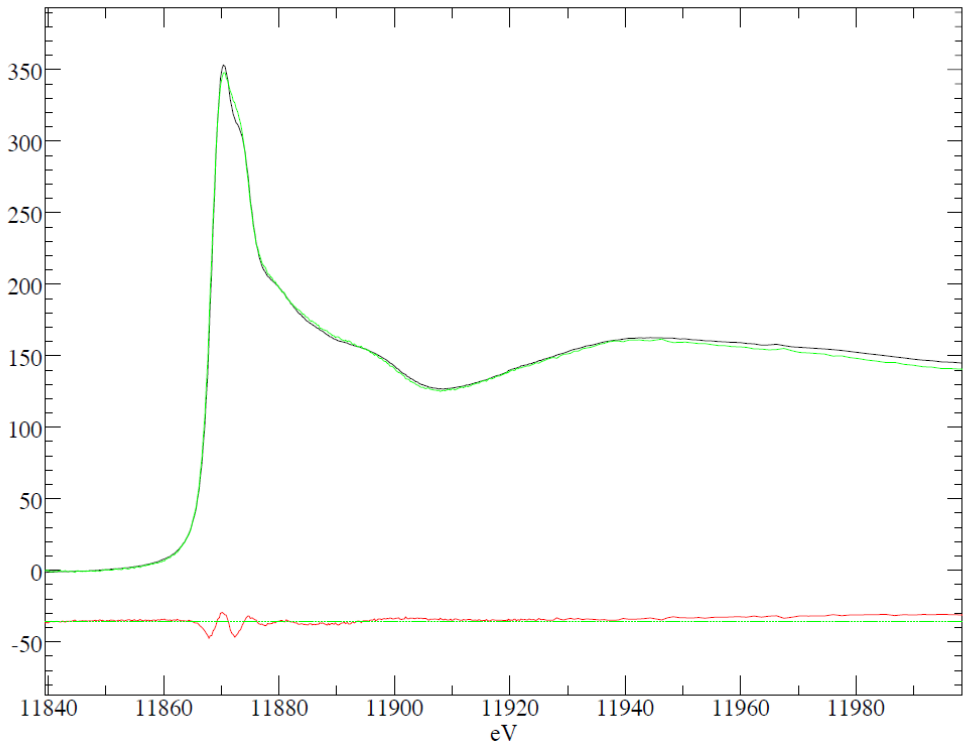


Fig. S3. Fitting plots of XANES spectra of the samples resulted using 4 FB-DGT gels exposed in arsenic solution as fitting models.