Ink as Testimony: Examination of Inks in Written Materials from the United States Holocaust Memorial Museum

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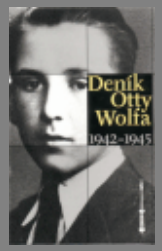
Ink as Testimony: Examination of Inks in Written Materials from the United States Holocaust Memorial Museum

- 20th century ink overview
- setup of the Bruker XRF for analysis of historic documents
- the Otto Wolf Diary
  - written in hiding in Czechoslovakia
  - XRF data



- the Mandel postcard
  - sent from Radomsko Ghetto (Poland), censored by Gestapo
  - XRF, ESEM, and HSI data

20th Century Inks

Printing inks generally oil-based; colorants may include oil-soluble dyes and/or pigments; carbon black traditional and still used

Writing inks generally aqueous; need to flow and not clog (e.g., fountain pens); colorants often sulfonated and/or made into salts to solubilize; can also include pigments in suspension.

Iron gall inks -- commonly ferrous sulfate + gall extract mixture -- still used, but mostly in official and legal documents, due to permanence; coal-tar dyes known to be subject to fading.

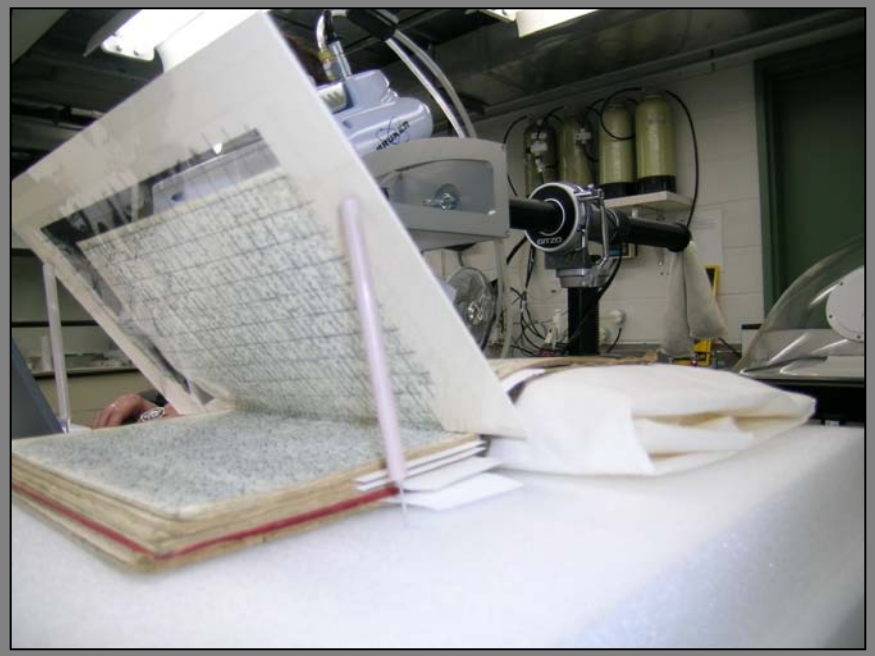
Inks often complex mixtures of:

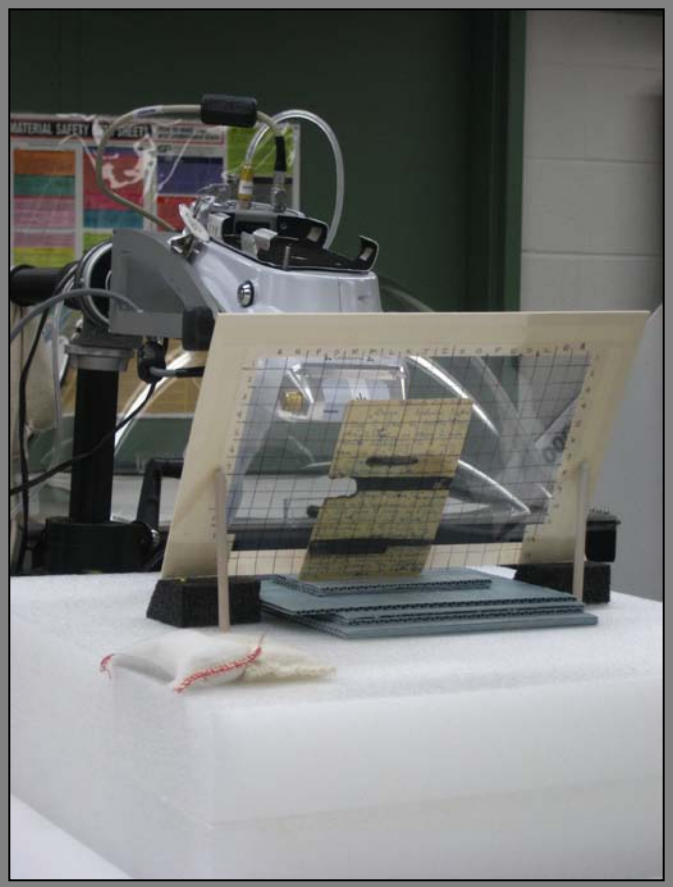
multiple colorants;

organic additives/media, e.g., oils, gums, resins, solvents;

inorganic additives/residues, e.g., pigments, drying agents.

In-situ qualitative XRF analysis of inks at USHMM

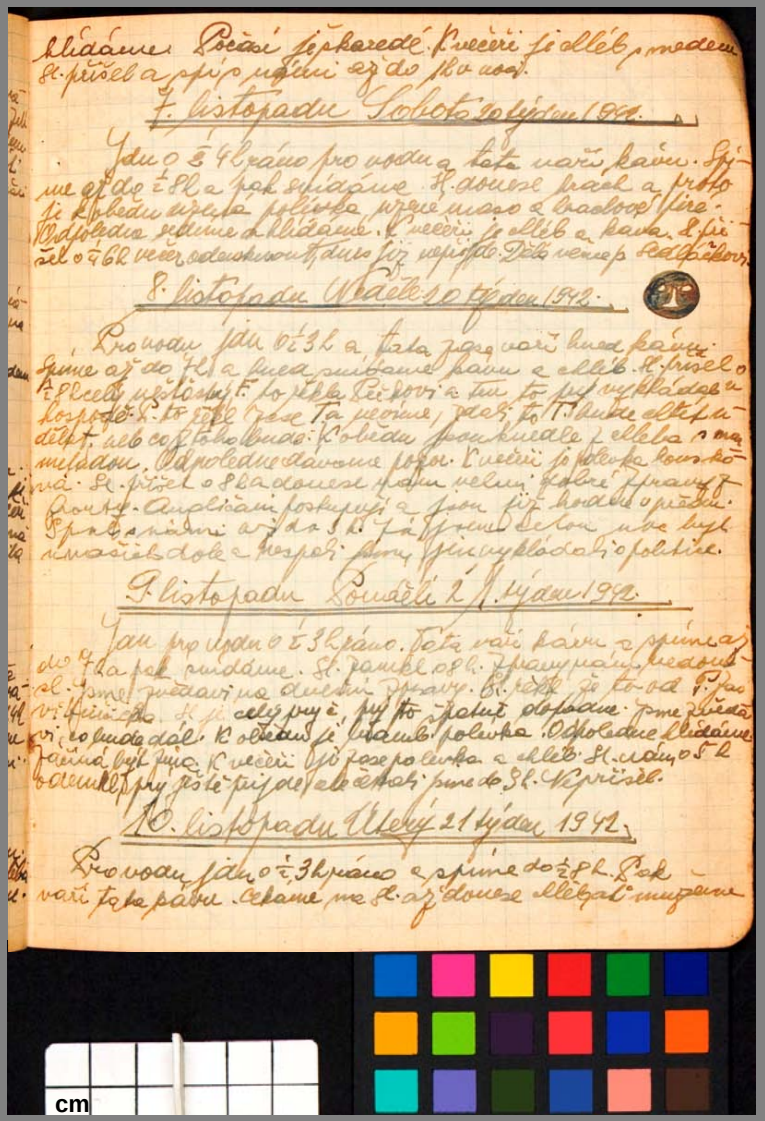




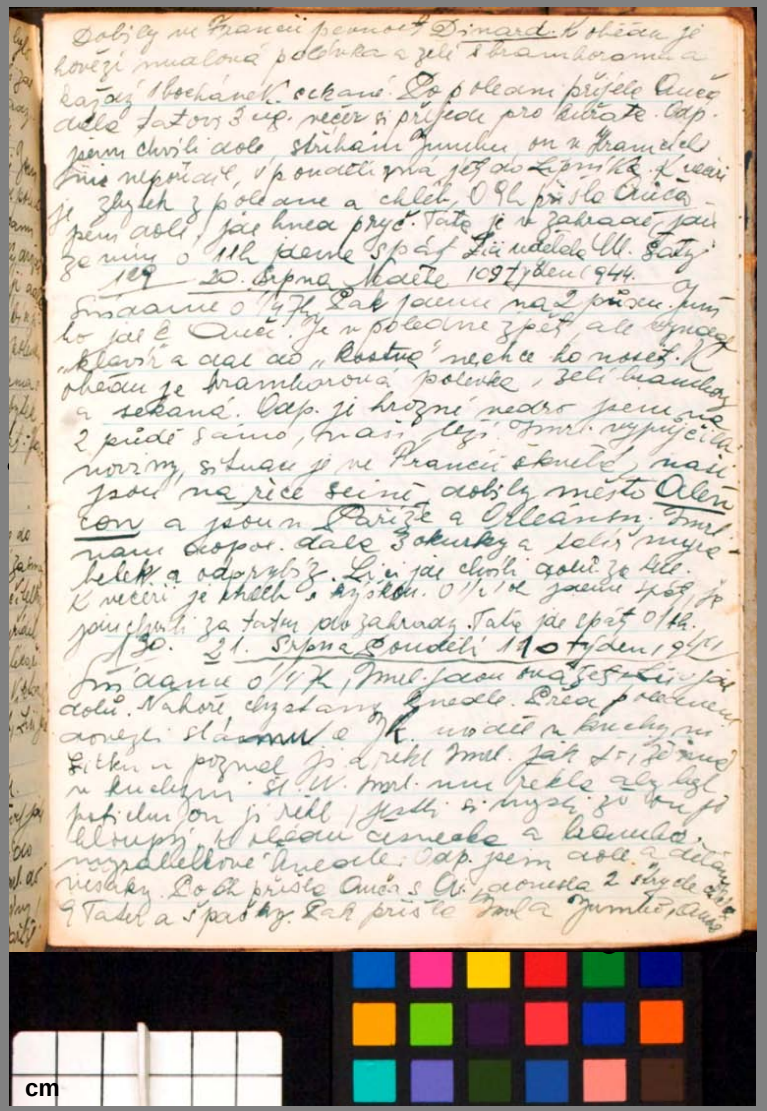
Bruker Tracer Handheld XRF
Rh tube, 300 sec. exposures
1) 15 kV, 14.6 - 25 μA, Ti filter, vacuum, for Al – Fe
2) 40 kV, 7 μA, Cu-Ti-Al filter, vacuum, for heavier elements

Qualitative XRF analysis of the Wolf Diary

Book I, section 1, 7 Nov. 1942

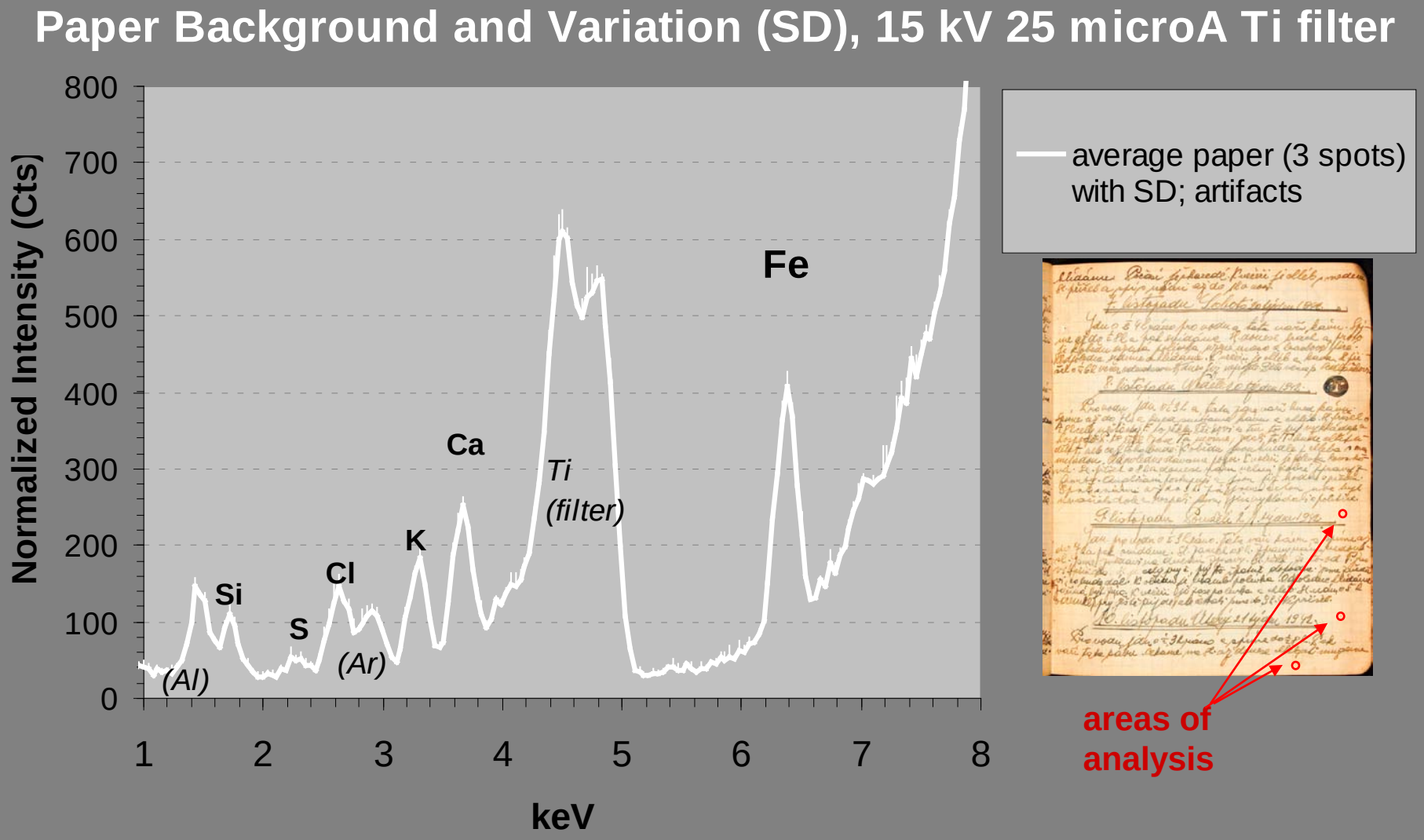


Book I, section 8, 20 August 1944



~ 20 x 17 cm (page)

XRF spectra of Wolf Diary 1, Sec. 1, Nov. 7, 1942



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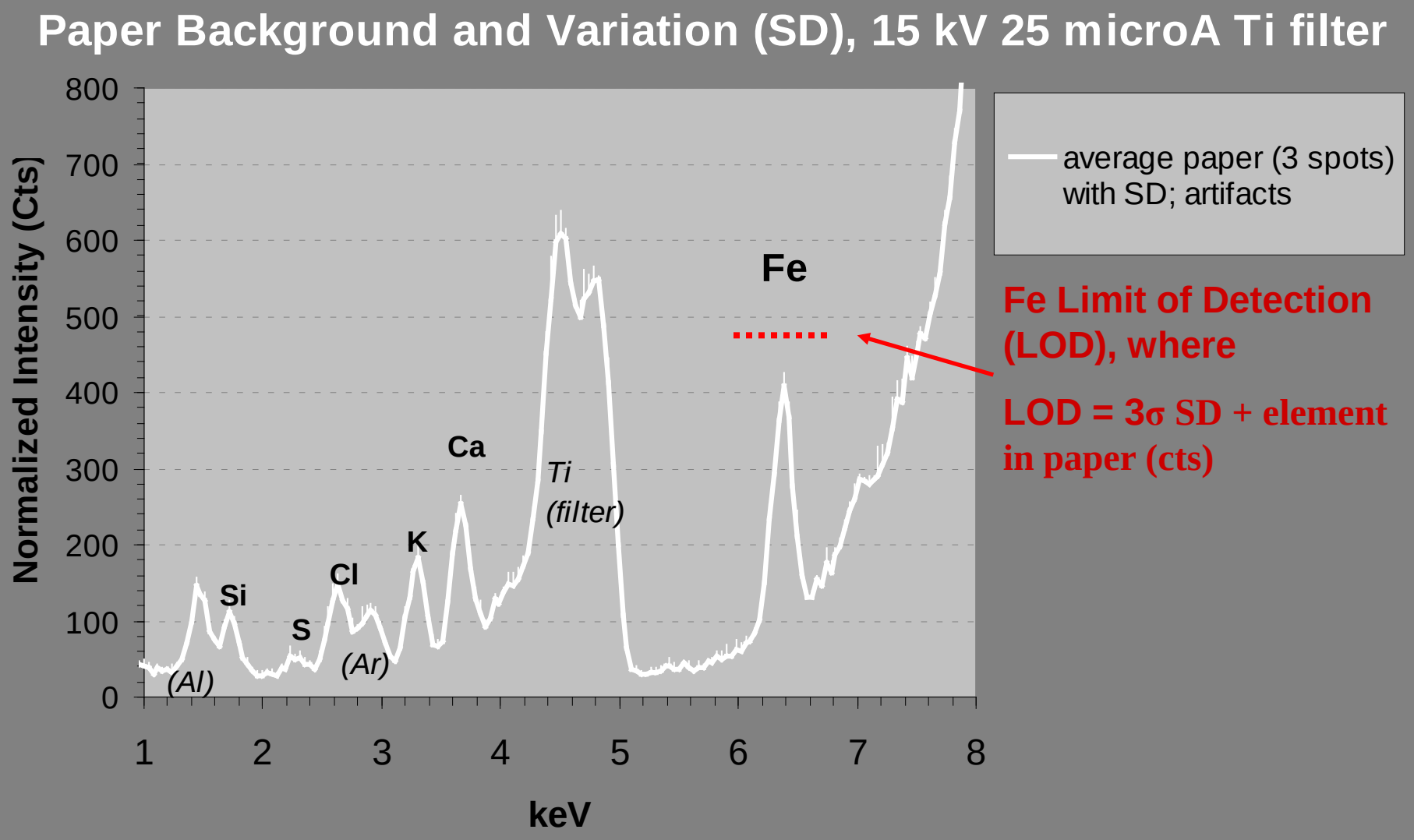

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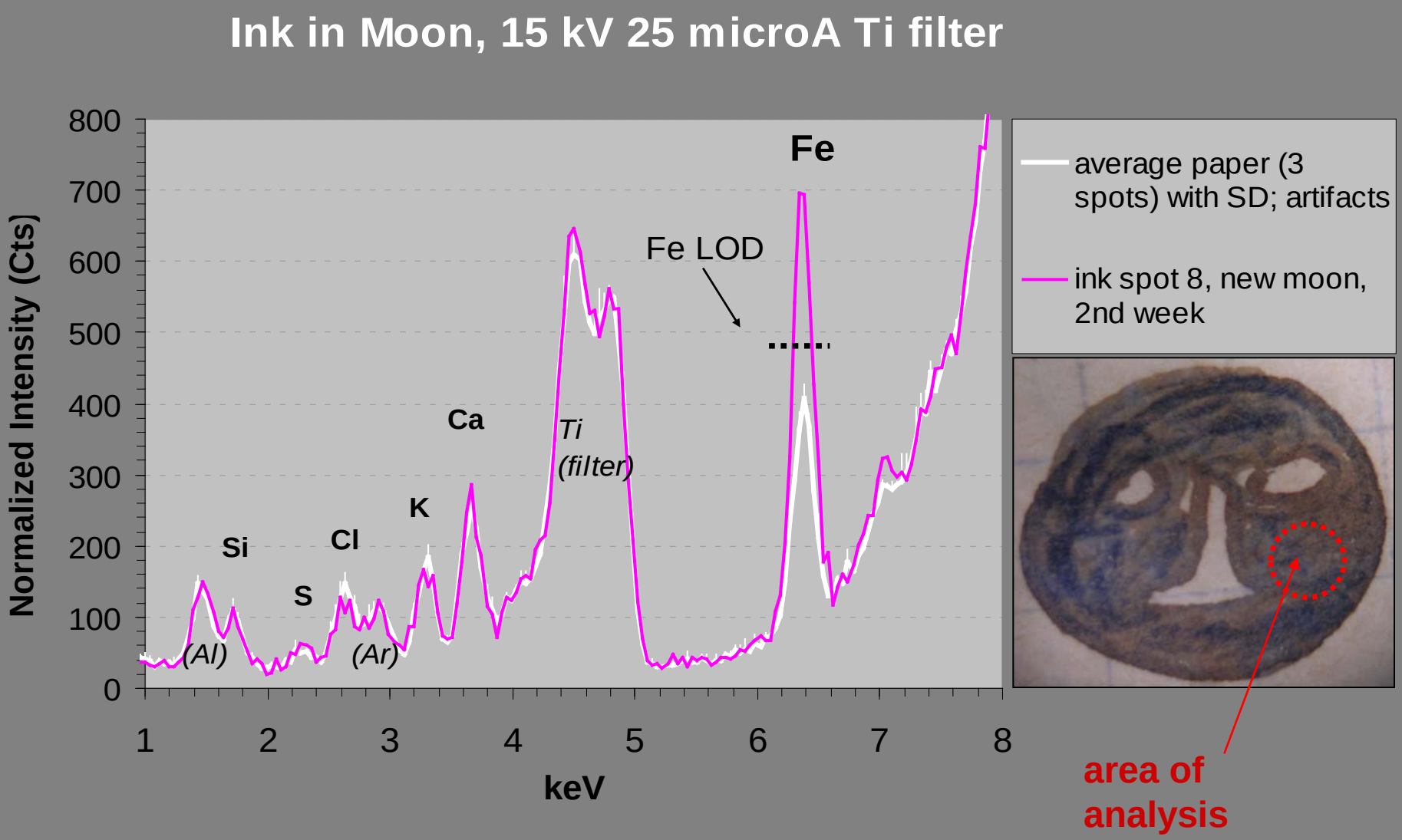
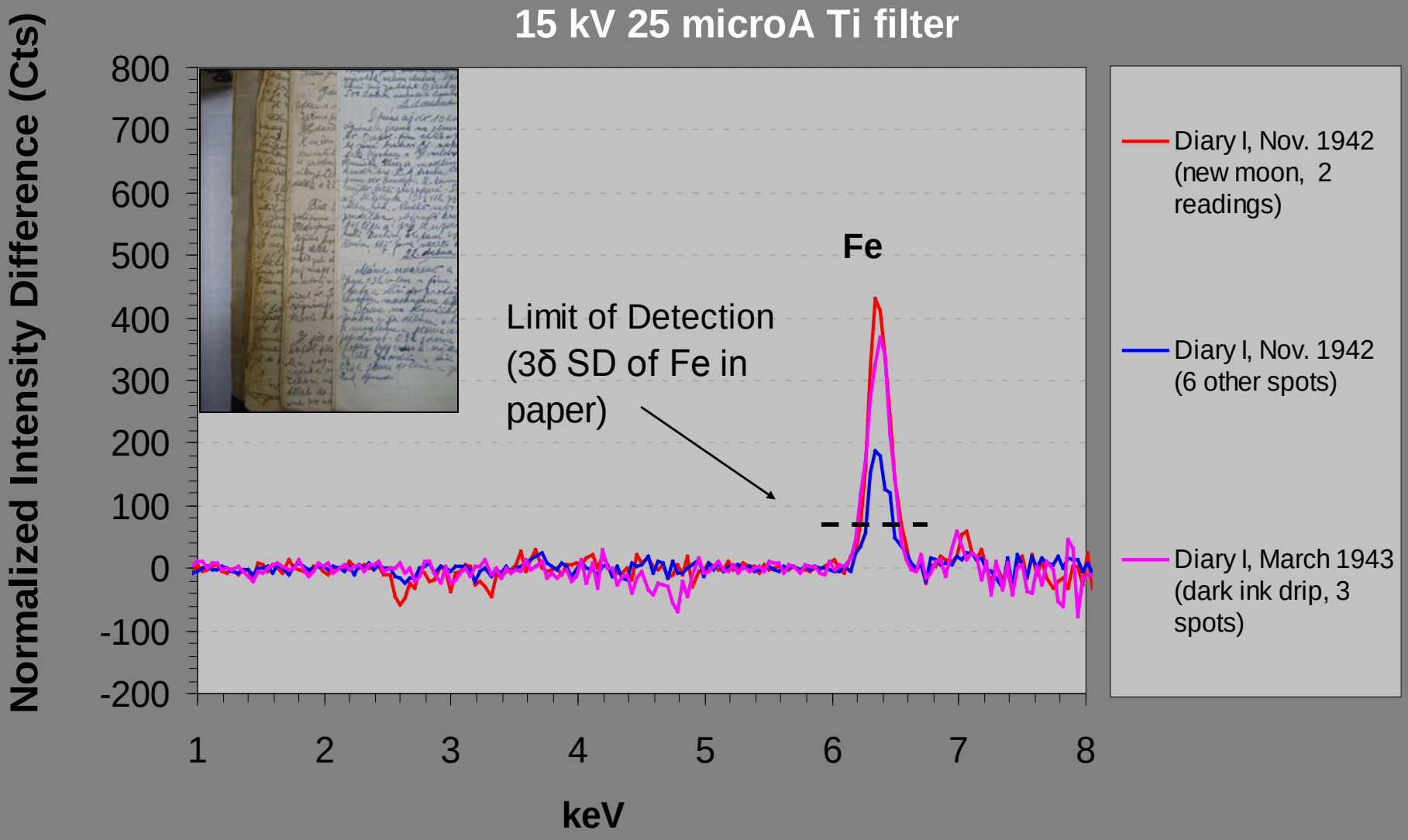


Wolf Diaries: XRF subtraction spectra of average ink readings from various pages (ave. paper subtracted)



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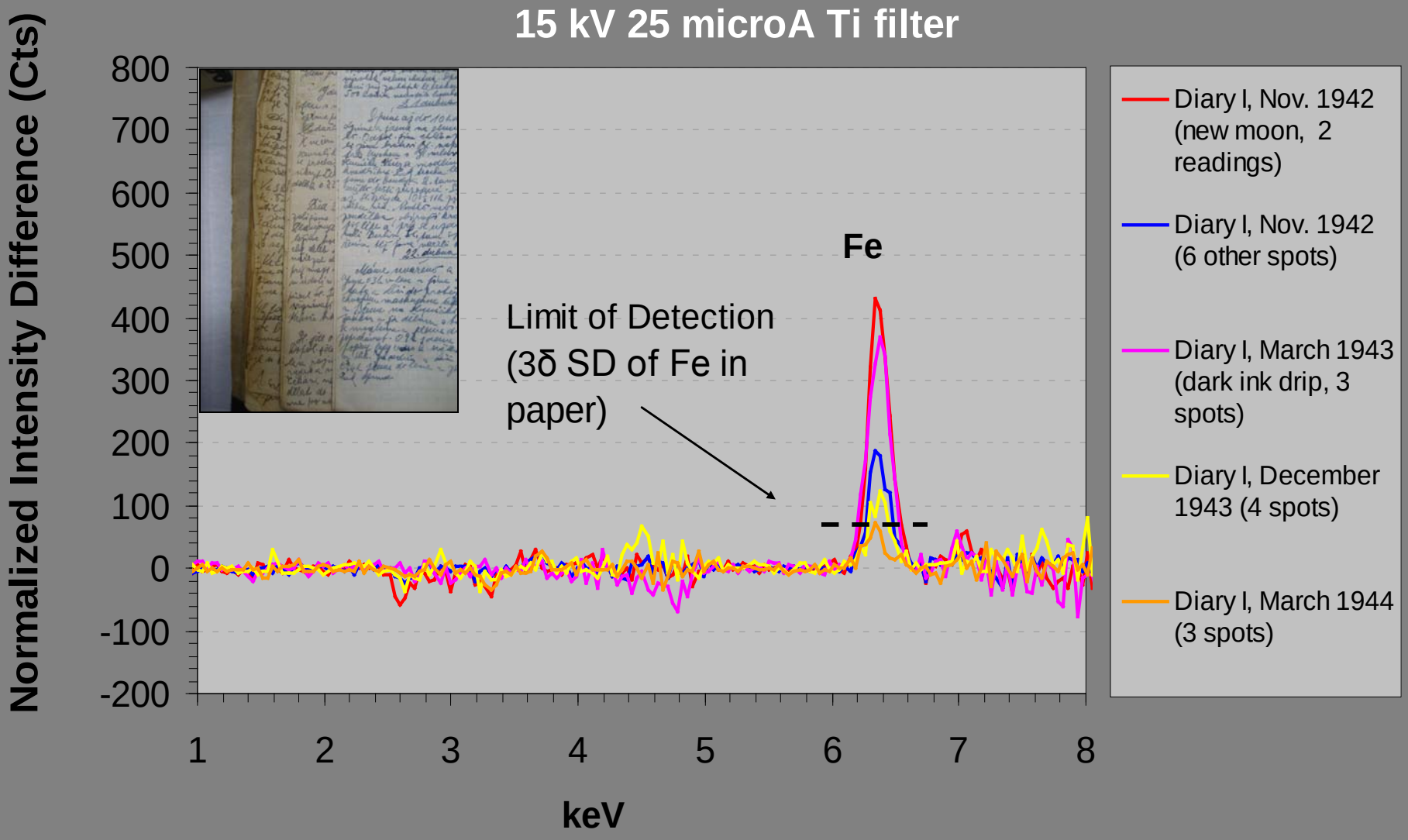

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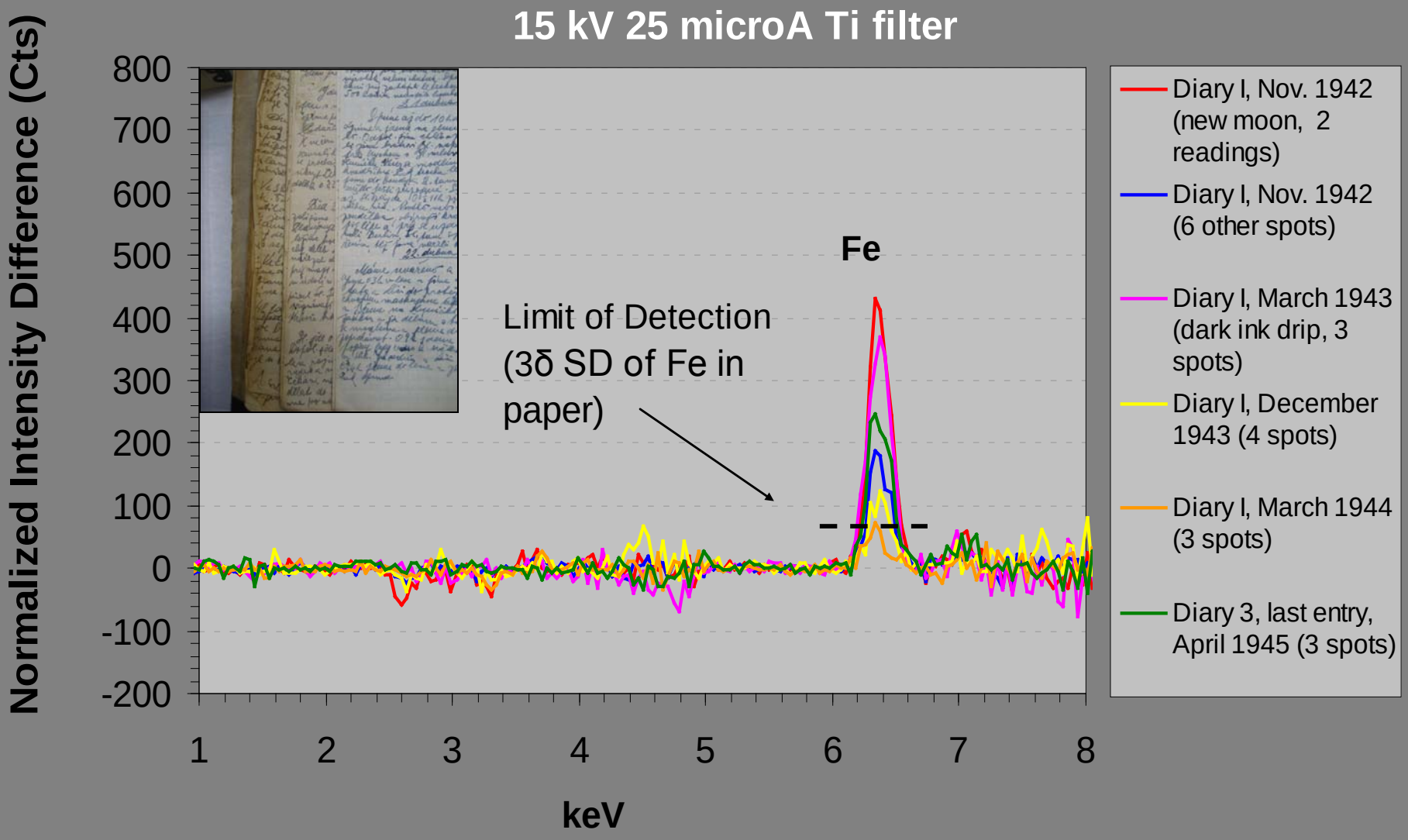
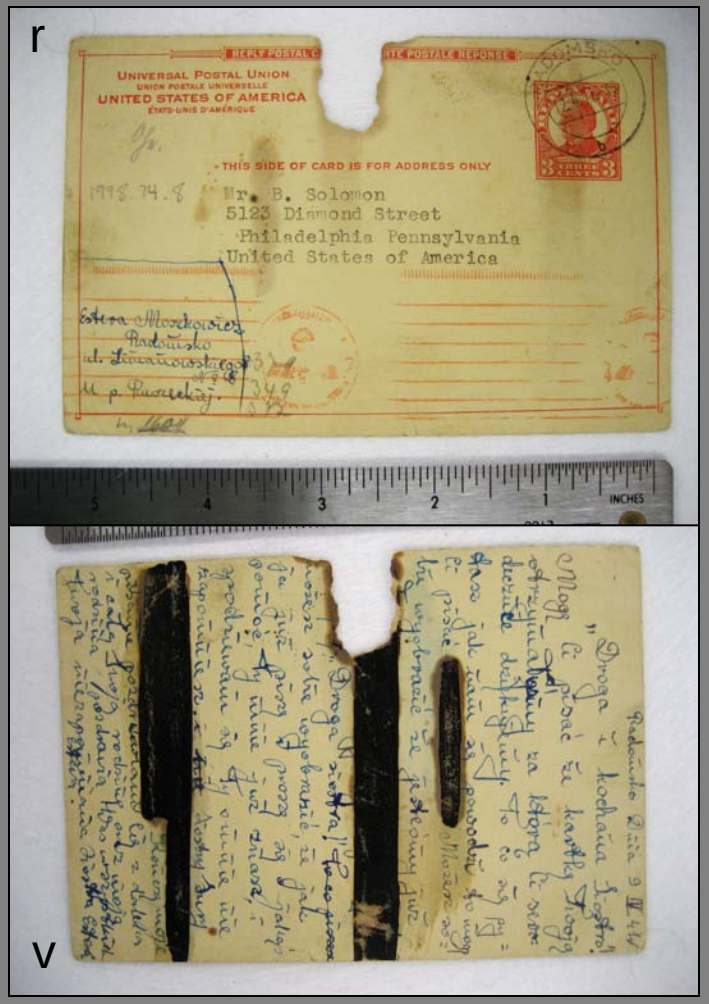


Qualitative XRF analysis of the Mandel postcard



13.9 cm x 9.2 cm

Blue ink of text (recto and verso)

Brown-black redaction ink (verso)

Red Gestapo stamp ink (recto)

Red printing ink of postcard (recto)

Black postal cancellation stamp ink (recto)

Grey-black typewriter ink (recto)

Grey pencil marks (recto)

Subtraction spectra of three inks (paper-subtracted) from Mandel postcard

XRF-derived, elemental intensity ratios in paper and inks

	paper 1	paper 2	paper 3	blue ink 1	blue ink 2	blue ink 3	blue ink 4	censor ink 1	censor ink 2
Ca/Cl	**4.9**	**4.8**	**5.4**	**6.0**	**6.7**	**6.0**	**6.0**	*-4.7*	*-11*
Ca/S	**8.4**	**8.0**	**8.6**	*21*	*18*	*31*	*20*	*0.19*	*0.13*
Fe/S	**7.8**	**7.3**	**7.6**	*-2.8*	*0.27*	*1.3*	*1.3*	**3.5**	**4.1**
Fe/K	**6.3**	**5.3**	**6.5**	*98*	*-0.79*	*-6.4*	*3.4*	**6.5**	**7.0**
Fe/Ca	**0.93**	**0.91**	**0.89**	*-0.14*	*0.015*	*0.042*	*0.066*	*18*	*31*
Fe/Mn	*4.2*	*4.0*	*3.4*	*3.2*	*-1.2*	*8.9*	*11*	**0.70**	**0.75**
Fe/Si	**6.7**	**6.9**	**7.0**	*-110*	*-0.93*	*4.4*	*6.8*	*220*	*120*

- Relative intensity ratios give method of describing and comparing detected elements in one material
- Ratios are NOT CALIBRATED; represent relative intensities *detected with this instrument at this particular set of parameters,* not amounts
- Ratios in *paper* : from sum of 3-channel, normalized intensity of elements
- Ratios in *inks:* from sum of 3-channel, normalized intensity of elements after subtraction of average paper counts

XRF-derived, elemental intensity ratios in paper and inks

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- Six of these ratios appear characteristic for the paper
- Ca/Cl ratios characterize the blue ink

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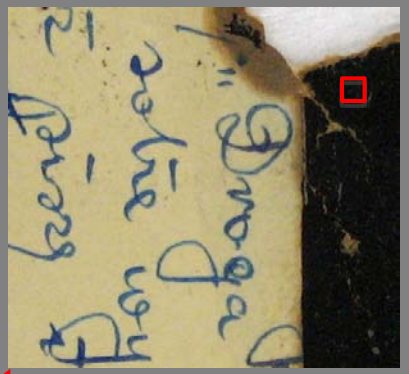
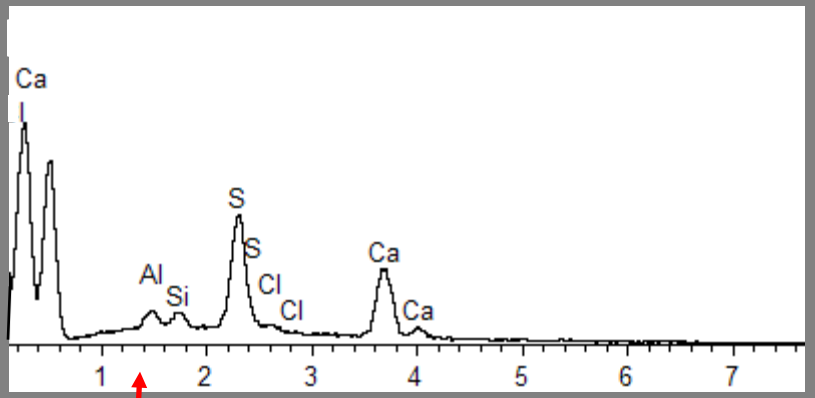
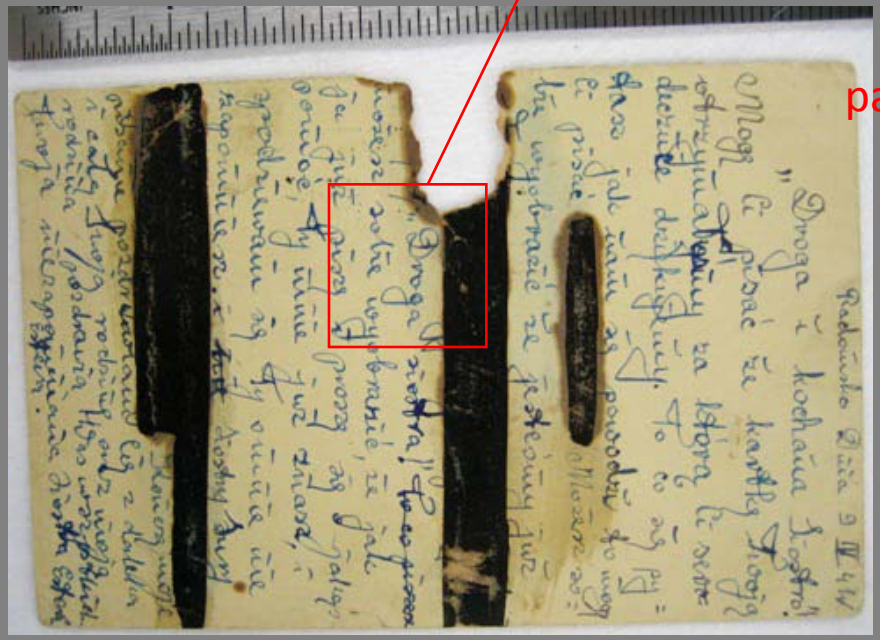
- Several intensity ratios characterize the censor's redaction ink
- Fe, S, K and Mn ratios represent ink chemistry and recipe, regardless of thickness
- Ratios containing Ca suggest interference from underlying blue ink
- Ratios of Fe/Si reflect difference in thickness of redaction in areas of analysis

Preliminary results of ESEM/EDS of the postcard

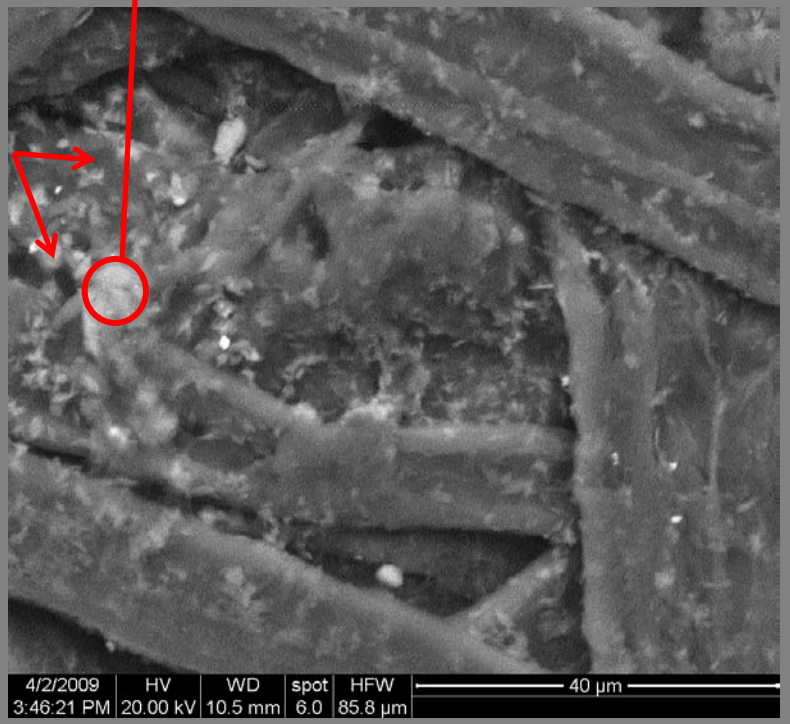
Blue ink: almost invisible to SEM: likely organic-based
- similar elements to XRF
- Ca- and S-rich particles in areas where blue ink suspected (gypsum as additive or product?)







particles



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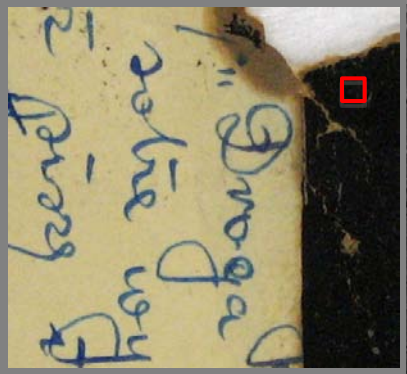
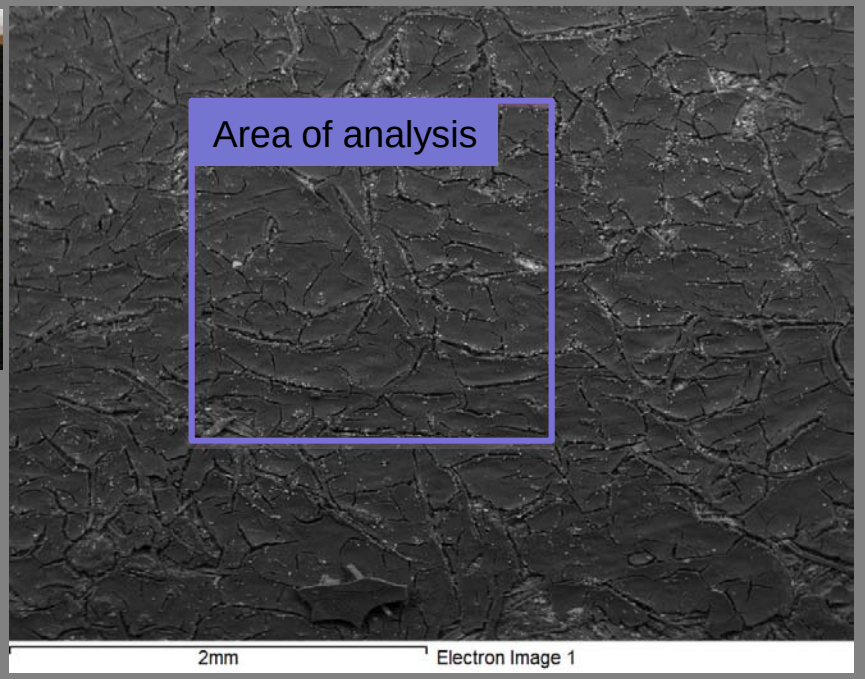
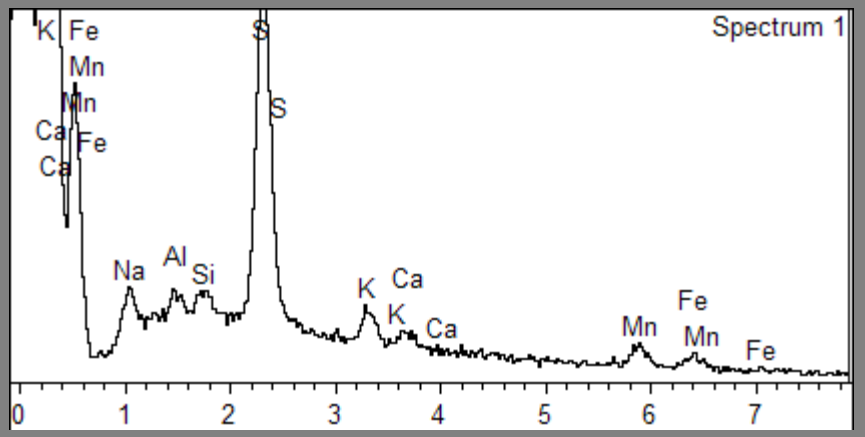
- elements detected by EDS generally agree with XRF







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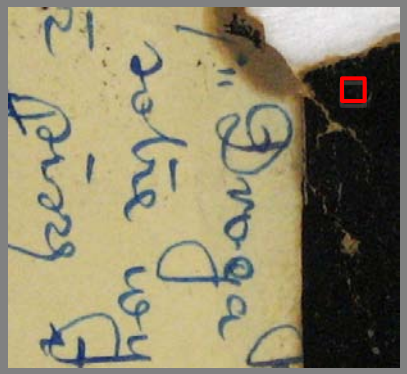

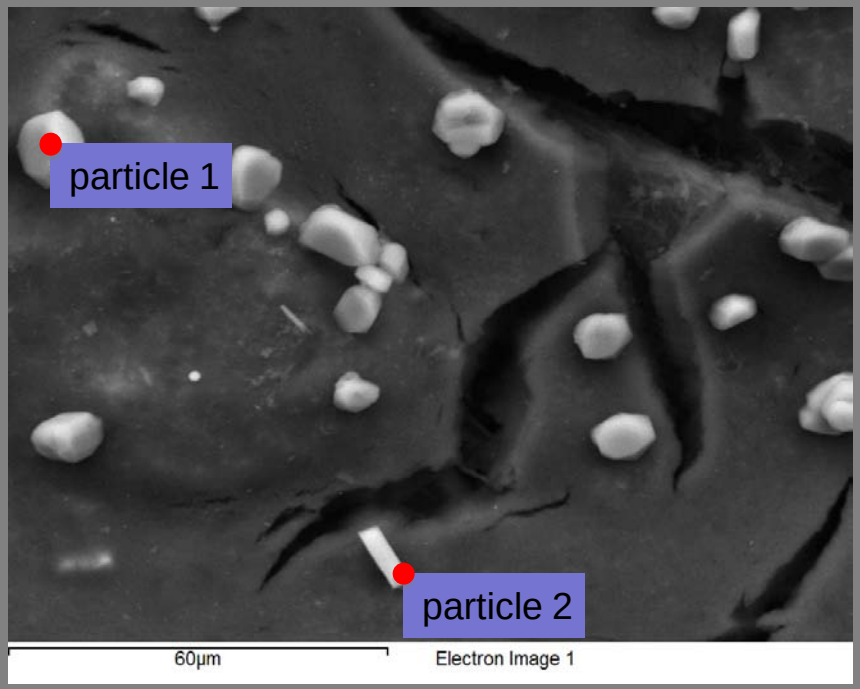

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- surface cracked; particles around cracks
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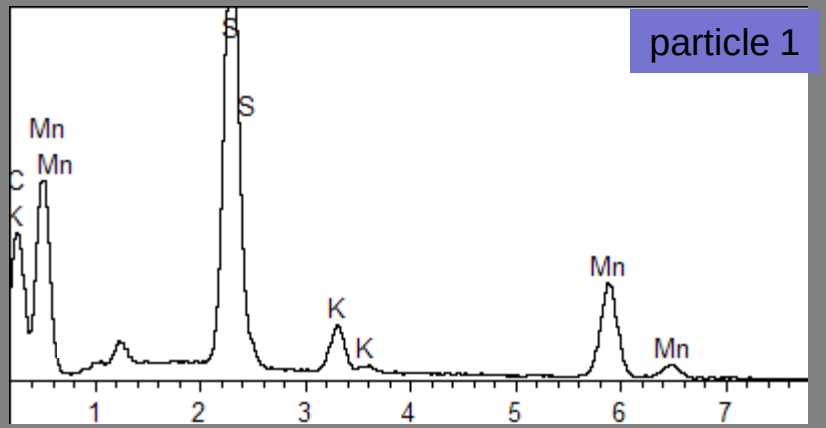
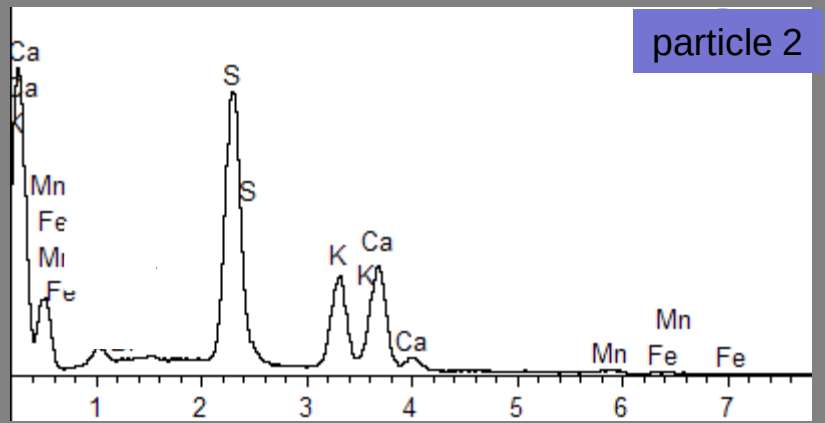
- hexagonal Mn-rich particles
- rod-shaped S-, K-, Ca- rich crystals near cracks





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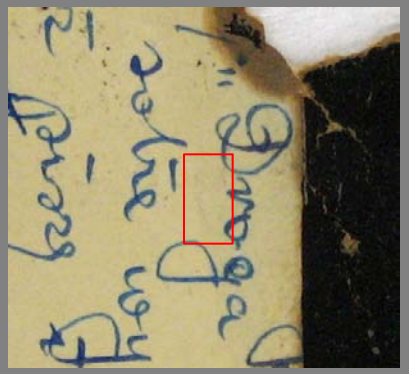

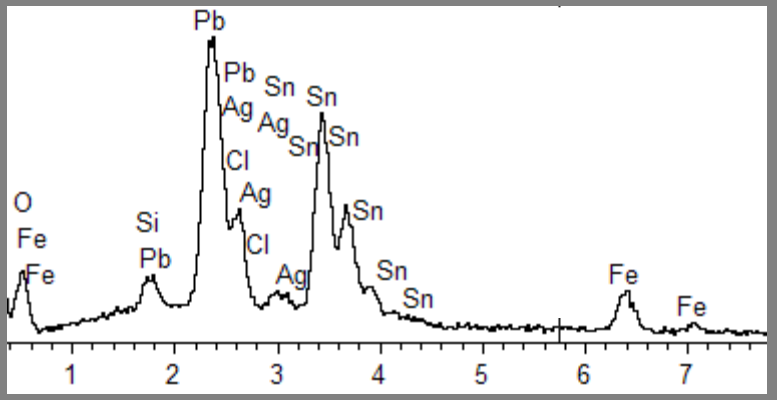

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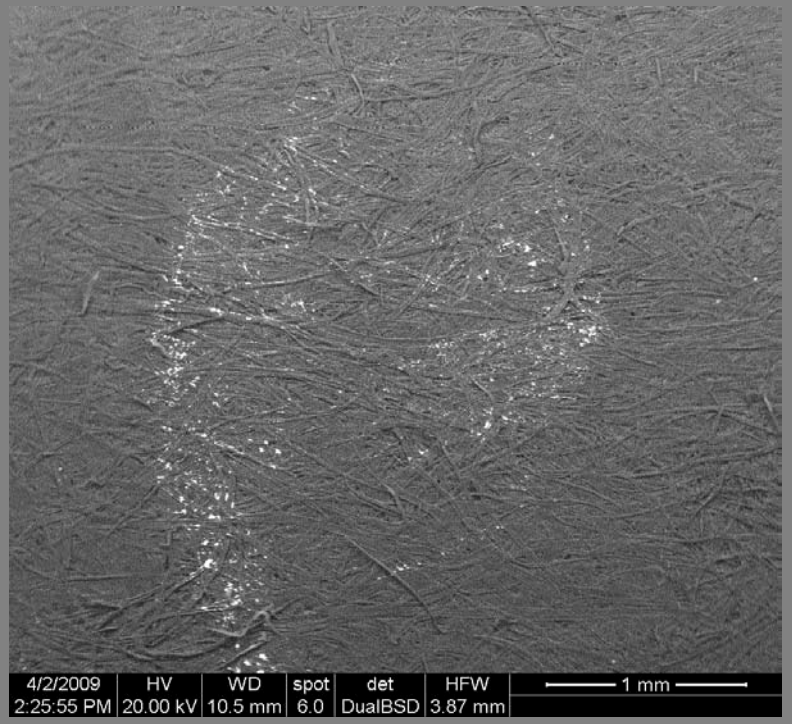
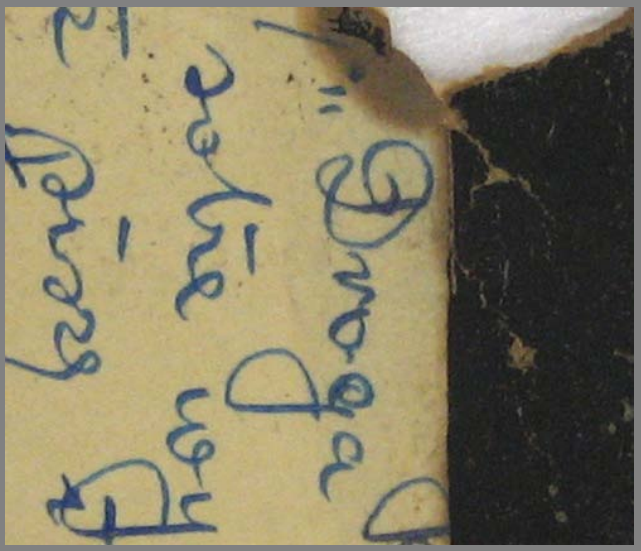


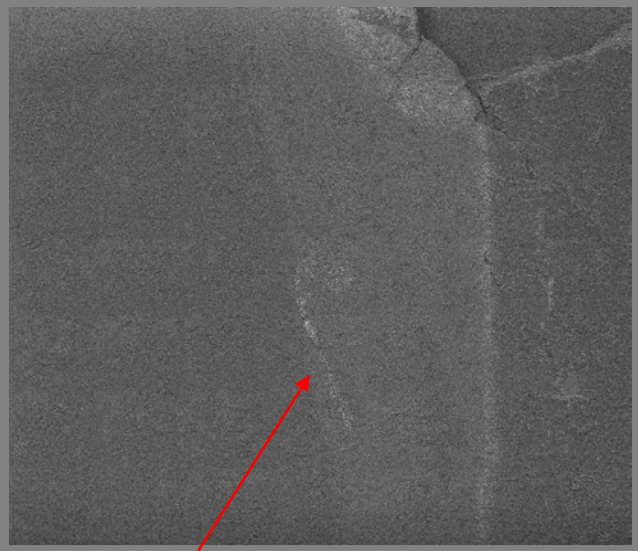
Miscellaneous feature:
- Pb-Sn particles, possibly metal particles deposited from printing process

Follow-up analyses of Mandel postcard at LC: Hyperspectral Imaging (HSI)

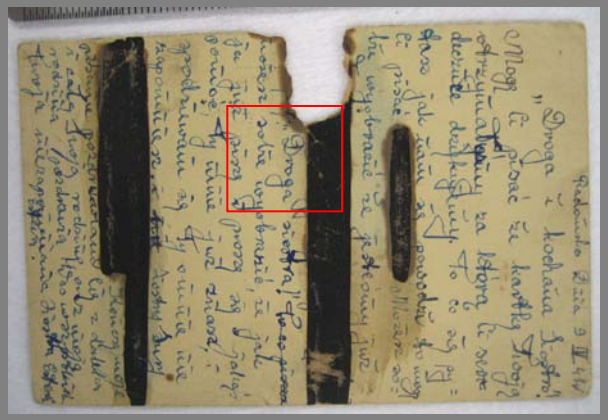
daylight-balanced fluorescent light, rgb image



backscattered electron image, ESEM



feature not seen upon visual inspection



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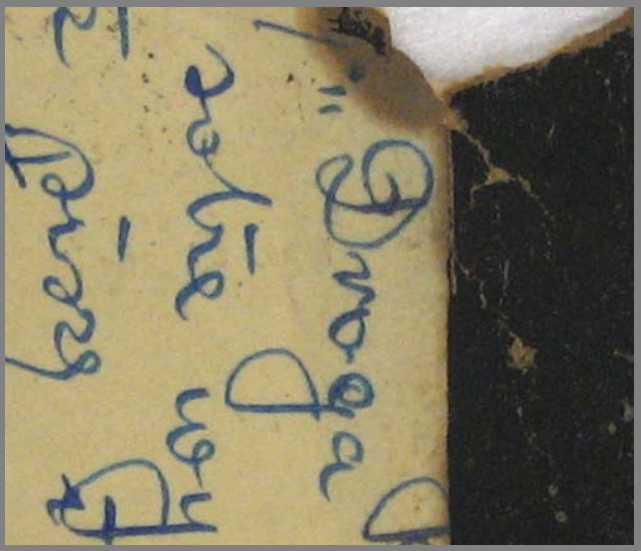

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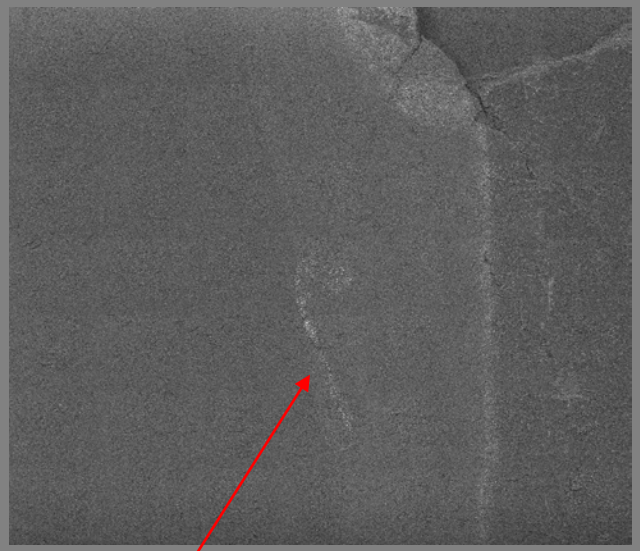
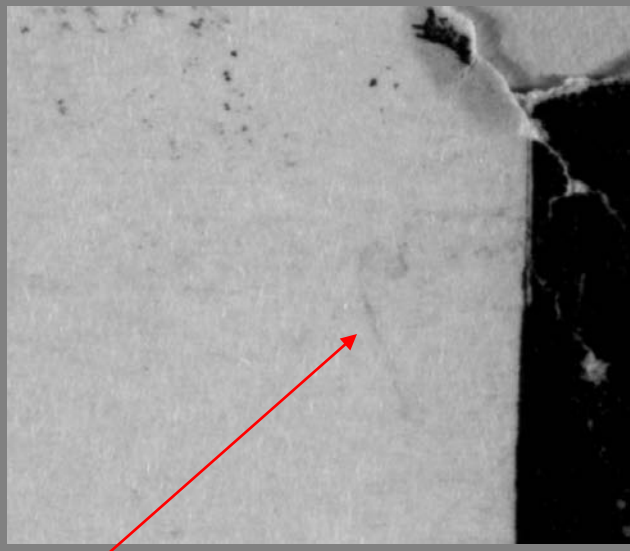
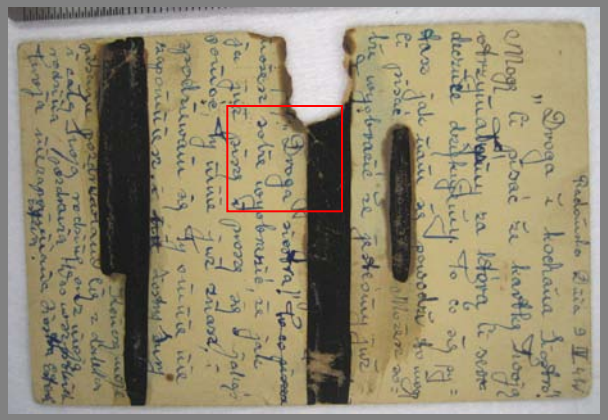


monochrome camera, infrared (850nm) image



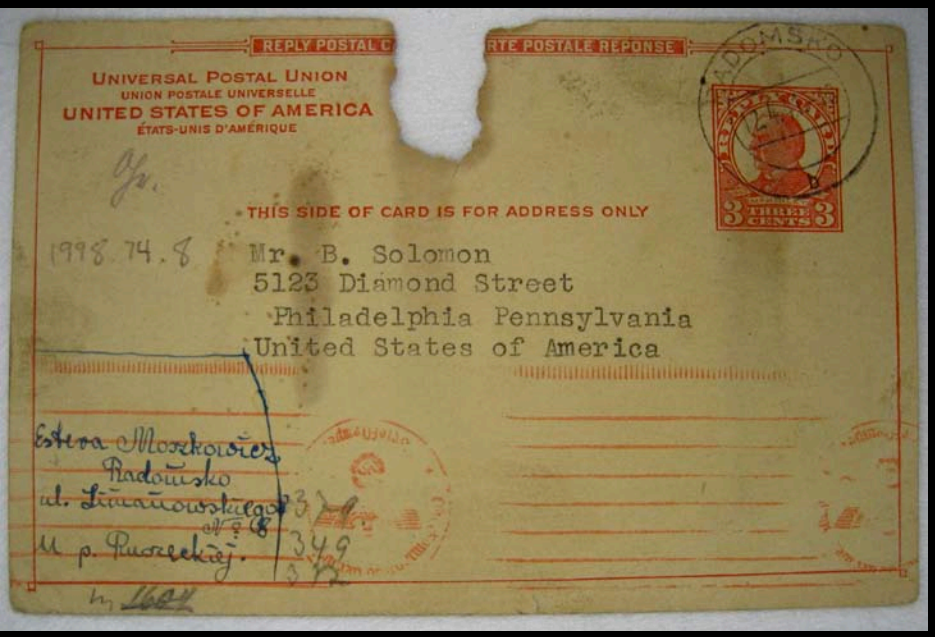


feature not seen upon visual inspection, but confirmed during hyperspectral imaging

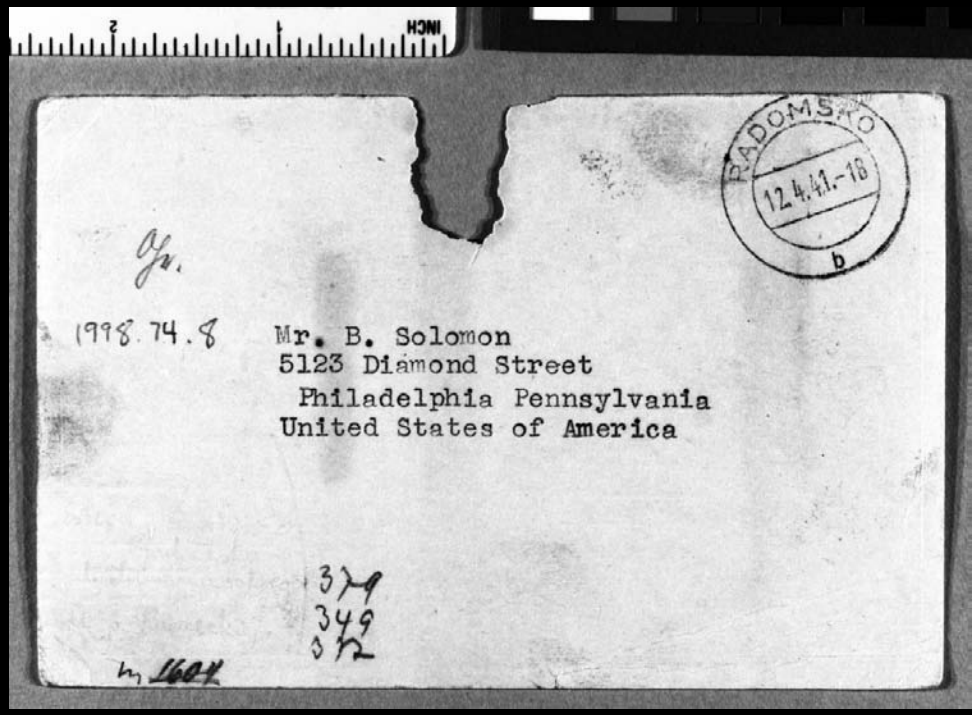
Conclusions

- XRF successful at categorizing inks in Wolf Diary as Fe-containing or not, mostly suggesting changes in dilution in parts of diary or delivery of new ink supplies
- Fe-containing ink does not necessarily mean Fe gall ink, e.g., may contain Prussian blue (with or without indigo and aniline dyes)
- XRF successful at categorizing, characterizing and differentiating several of inks on the Mandel postcard
- For non-invasive analysis of inks, XRF especially useful when supplemented by other techniques, such as HSI, ESEM/EDS, FT-IR-ATR, Raman

Conclusions and On-going Work



visible light



780 nm

Complementary, non-invasive techniques can provide important clues in the analysis of complex ink mixtures, can guide further steps in their analysis, and can inform conservation treatment decisions without sampling.

Acknowledgments

Eric Hansen, Chief of the Preservation Research & Testing Division
Dianne van der Reyden, Director of the Preservation Directorate
Fenella France, Research Chemist (HSI)

Aleksandra Borecka, Archivist
Anne Marigza,
Paper and Book Conservator

Bruce Kaiser

Radomsko 9 April 41

Dear and lovely Sister,

I can write that I received your postcard and we warmly thank you. You are ask how we are doing. I can write …….. you can imagine we are already

……

……

?? Dear sister! You understand that I am writing because I am asking for some help. You know me, and I expect you to not forget about me, your sister.

……

…….. I am ending this by sending greetings from far away for your and my entire family. Greetings for everybody. Your unforgettable sister Estera.

Estera