Step 1: get an overview of elements and their distribution in the whole head.
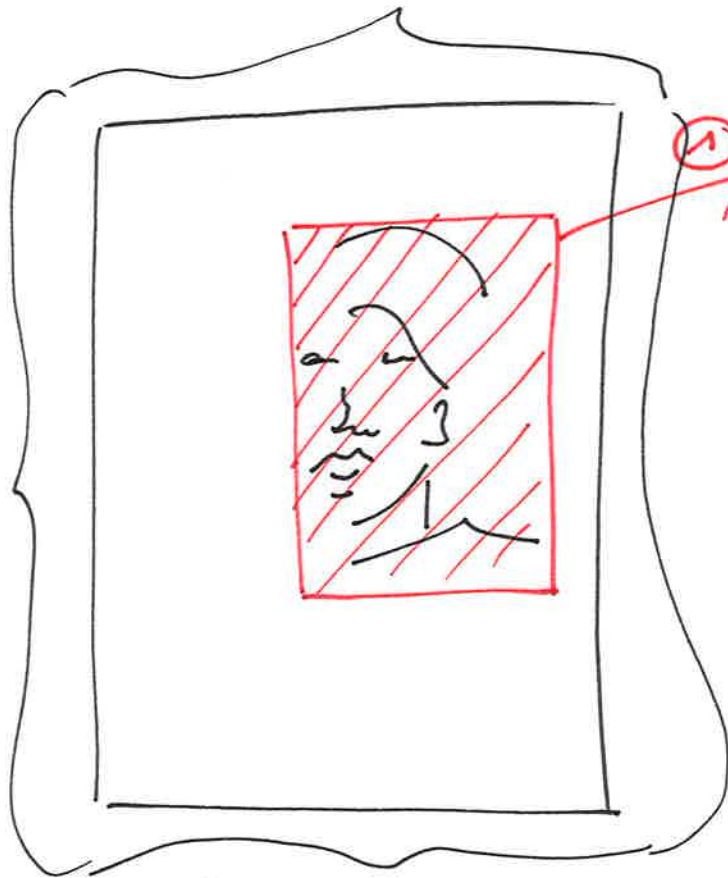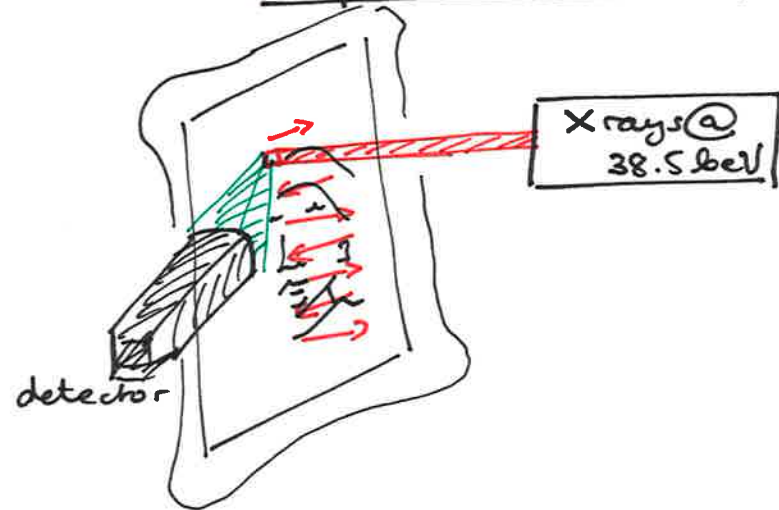

(1) μXRF imaging

raster-scanning with pencil-beam 0.5×0.5 mm²
FOV (field of view): 17.5 × 17.5 cm²
E Xrays in: 38.5 keV
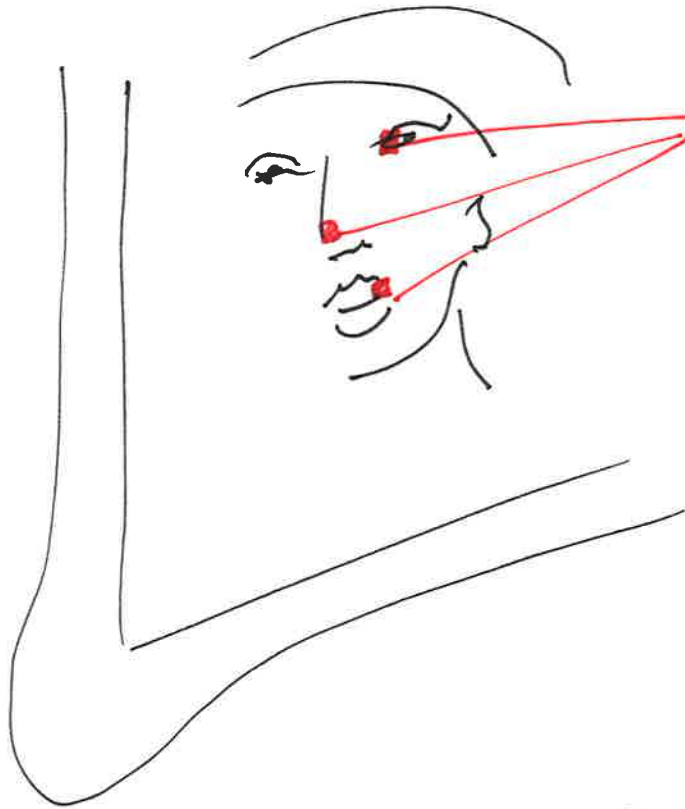
1. Experimental Set-up:

X rays @ 38.5 keV

detector

2. Why? to get overview of elements in the whole head and possible correlation between elements (hint for pigments)

3. How: 38.5 keV? Sufficient to get main elements possibly found, include Sb (Kα 26 keV) and Ba (Kα 32 keV)

3. How: 0.5×0.5 mm²? Compromise to get enough signal (S/N ratio) in a feasible time: 2s/pixel → 2 days

→ larger: faster but less resolution
→ smaller pixel: need more acq. time to longer

② µXANES at Sb K-edge
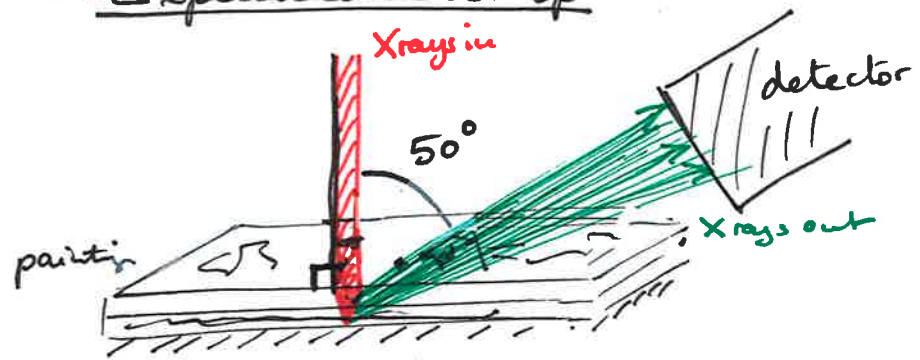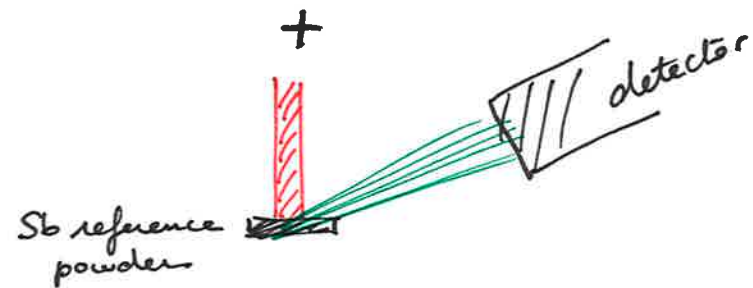
punctual, incremental scan of Xrays
around (30 491 eV edge)
spectra recorded in fluorescence mode
non-invasive

1. Experimental set-up

Xrays in

50°

detector

painting

Xrays out

+

Sb reference
powder

detector

2. Why? to get information about
Sb structural environment
and give some links on
potential pigments containing Sb
(Reference Sb pigments used for
finger print)

3. How? non-invasive to explore many
spots in the painting,
Xray beam // to painting to increase depth penetration and reach layer of the head
fluorescence mode also for reference to avoid pbs with self-absorpt ≠.

Step 3 : Confirm identification of the pigments, get their distribution and check they belong to the head and not the upper painting
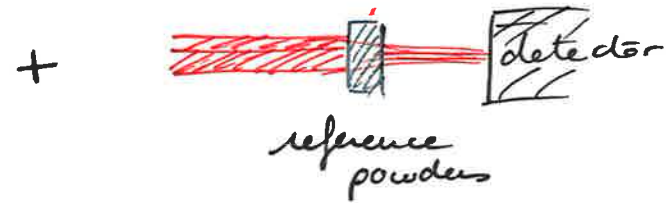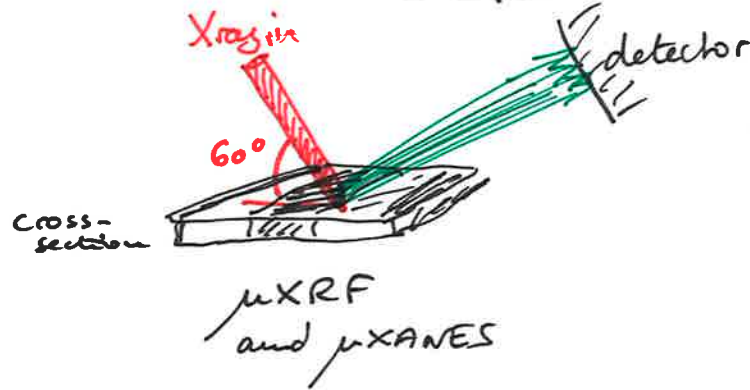

sample extraction

cross-section

+ + ③ **SEM + low-energy μXRF + μXANES**
mapping   punctual
raster scanning, vacuum, beam size : $1.1 \times 0.3 \, \mu m^2$
low energy ($2.1 - 7.2 \, keV$) and $\sim 4.8 \, keV$ (L edge Sb)

1. Experimental set-ups

X ray in

detector

60°

cross-section

+   detector

reference powders

μXRF and μXANES
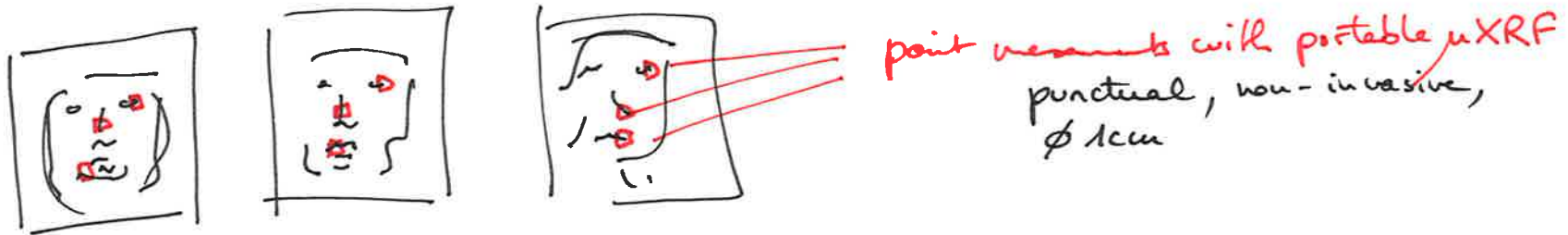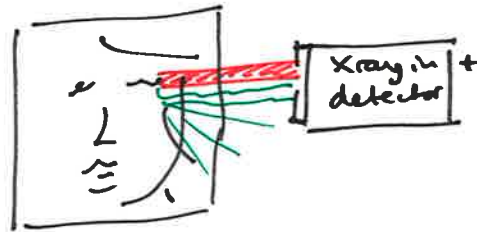
2. Why? Confirm pigment and their location within the head and not in upper painting

3. How? - small beam size to target single grains
- low energy to better identify pigments (L-edge more distinct than K-edge)
- X ray in beam bent to increase surface analysis

Step 4: Confirm representativity of the pigments found and stylistic aspects by analysis of other heads paintings by Van Gogh (same period)

point measurements with portable µXRF
punctual, non-invasive, ϕ 1cm

1. experimental set-up

Xray in + detector
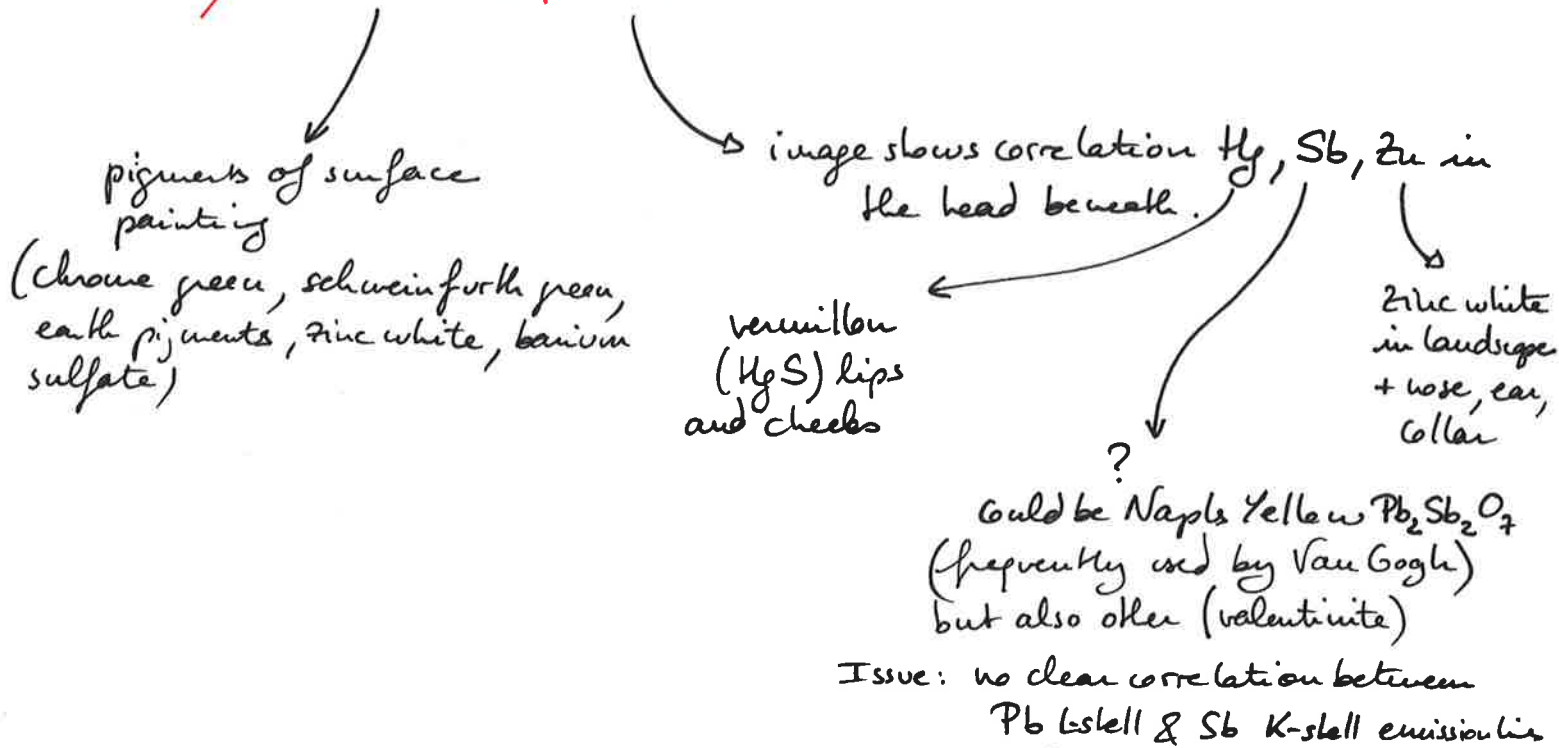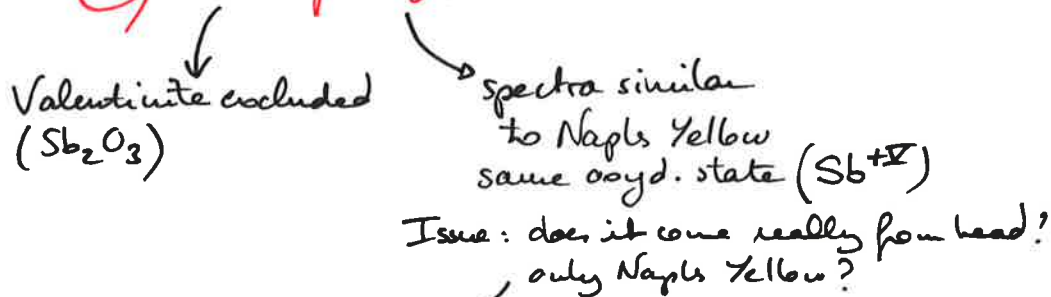
2. Why? to confirm that the pigments detected were also found in other paintings of the same period (representativity)

3. How? Several punctual spots, large enough to get good average overview non-invasive required as it is just "a check".
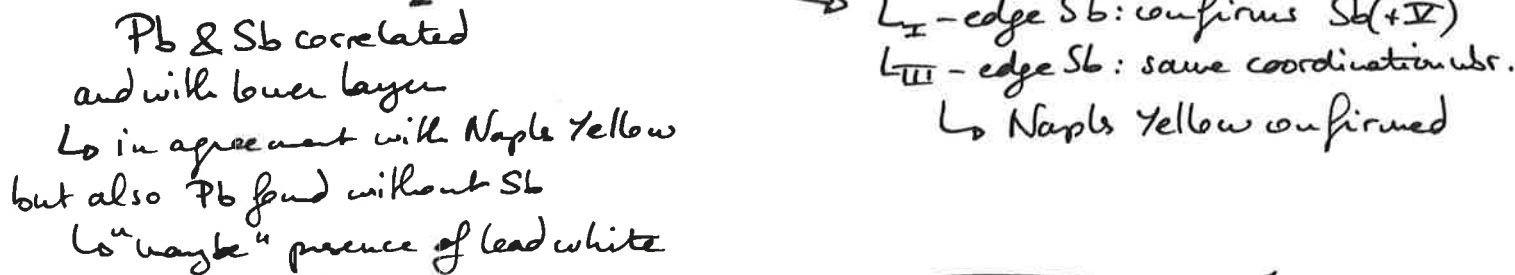
Results – Analytical pathway

① μXRF mapping painting

→ pigments of surface painting
(chrome green, schweinfurth green, earth pigments, zinc white, barium sulfate)

→ image shows correlation Hg, Sb, Zn in the head beneath.

← vermillon (HgS) lips and cheeks

→ Zinc white in landscape + nose, ear, collar

?
Could be Naples Yellow $Pb_2Sb_2O_7$ (frequently used by Van Gogh) but also other (valentinite)

Issue: no clear correlation between Pb L-shell & Sb K-shell emission lin.

② μXANES painting

↓ Valentinite excluded (Sb_2O_3)

→ spectra similar to Naples Yellow same oxyd. state (Sb^{+V})

Issue: does it come really from head? only Naples Yellow?

③ microsample μXRF + μXANES

↓ Pb & Sb correlated and with lower layer
└→ in agreement with Naple Yellow
but also Pb found without Sb
└→ "maybe" presence of lead white

→ L_I – edge Sb: confirms $Sb(+V)$
L_{III} – edge Sb: same coordination nbr.
└→ Naples Yellow confirmed

Reconstruction of head color possible – certainty?

④ XRF other Van Gogh paintings

↓ Same elemental co-position + other elements ⟶ Reconstruction good but only partial.