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Chemical, Physical and Thermodynamic Evaluation of Arsenic Species and Their Transformation during Cigarette Smoking

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Background & Objectives

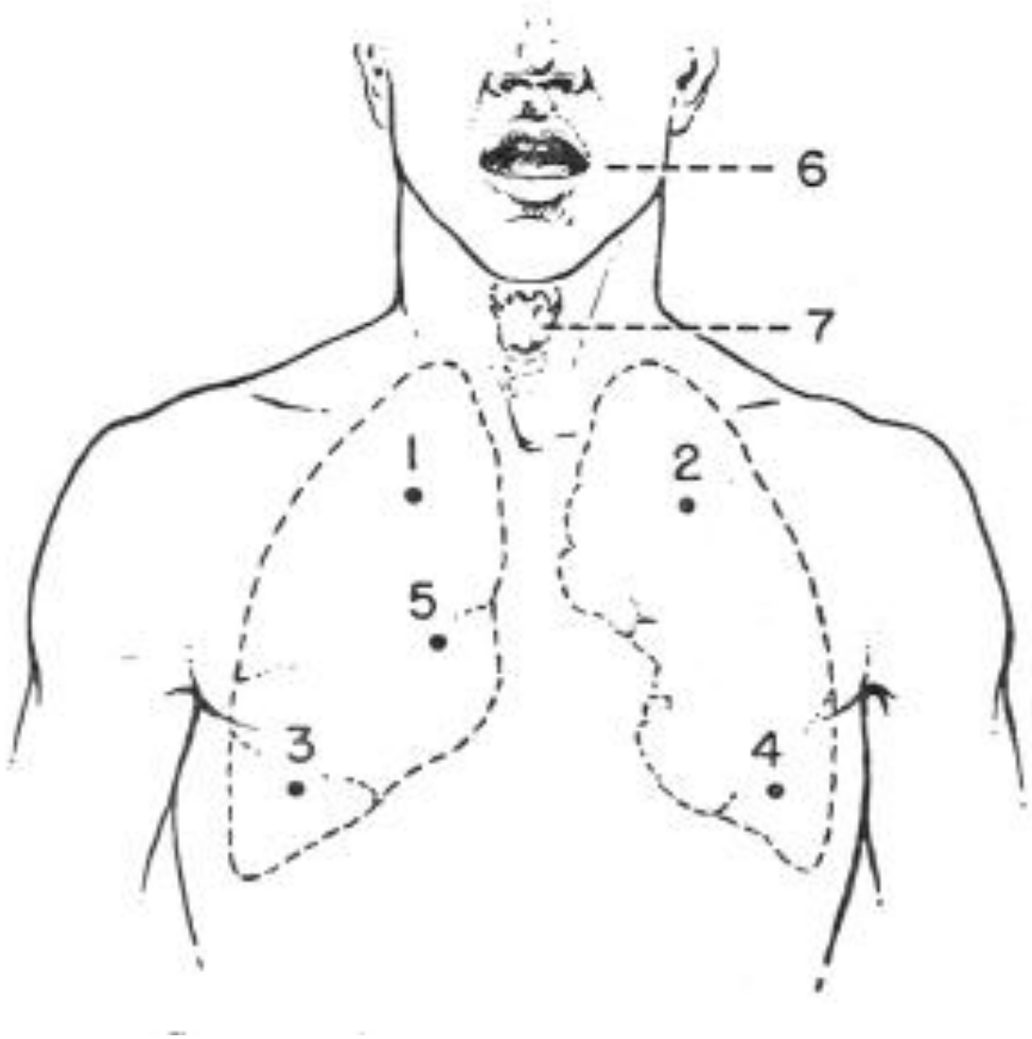
- Trace metals in smoke: important?
  - As, Cr, Cd, Ni, Pb, Se
  - Toxicity depending on: level and speciation
- Trace metals analysis: challenges
  - Matrix: over 5600 identified constituents in tobacco/smoke
  - Routine metal analysis in smoke: total level
  - Smoke collection: special care needed
- X-ray absorption spectroscopy: synchrotron radiation
- Objective: further understanding of As speciation via chemical analysis

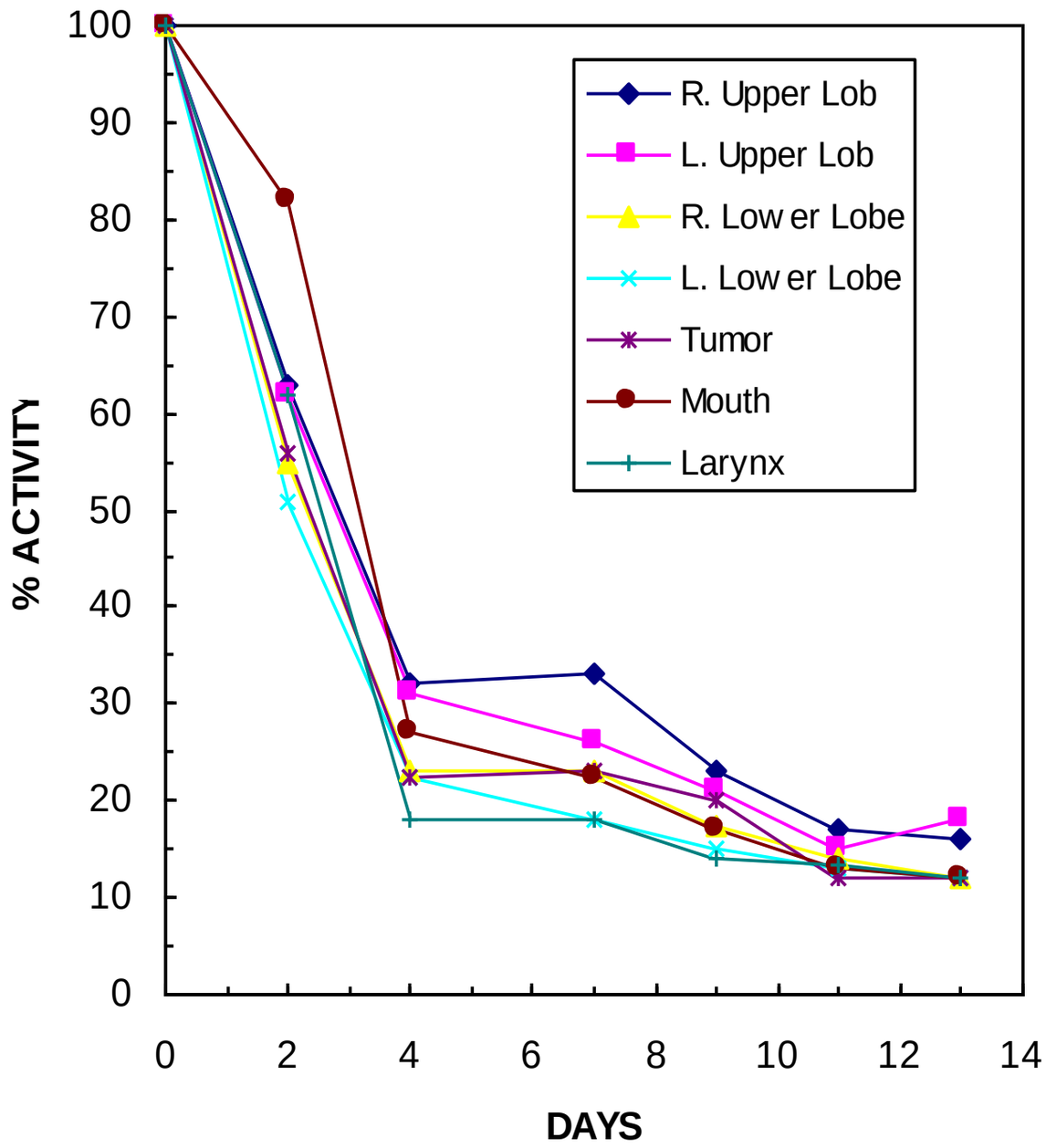
Arsenic Toxicity: Valence & Speciation

- Inorganic:
  - **Arsenite (+3)** — LD_{50} (mg/kg) = 15 to 42
  - **Arsenate (+5)** — LD_{50} (mg/kg) = 20 to 200
- Organic: less toxic
  - **Monomethyl arsenic acid (MMA): +3 & +5** — LD_{50} (mg/kg) = 700 to 1800
  - **Dimethylarsenic acid (DMA): +3 & +5** — LD_{50} (mg/kg) = 1,200 to 2,600
  - **Arsenocholine** — LD_{50} (mg/kg) = 6,500
  - **Arsenobetaine (AsB)** — LD_{50} (mg/kg) $\geq$ 10,000

(C.O. Abernathy, HECD/OST, US EPA)

Time Scale in Human Body: Arsenic





26.4 ppm in smoke (1933), 14.4 ppm in smoke (1959) (Wynder & Hoffmann: Tobacco & Tobacco Smoke), ~1.0 ppm (2008)

R.H. Holland, et al, Cancer Research, 19 (1959), pp. 1154 - 1157

SAMPLE PREPARATIONS

- Tobacco & ash preparation
  - Tobacco: cut rag from as-received 3R4F cigarette (x20)
  - Ash: ISO, machine-smoked 3R4F cigarette (x10)
- Smoke sample preparation
  - ISO, machine-smoking, metal-free substrate*
  - 'Fresh': solid-CO_2 cooled during smoking/storage/transfer
  - 'Aged': 1 day to 7 days, ambient temperature during storage/transfer
- Two dimensional HPLC with ICP-MS

*C. Liu, et al., *Spectrochim Acta B*, 2009, **64**, 1294

SYNCHROTRON-BASED XANES

CORESTA CONGRESS 2008, SSPT09
C. Liu *et al*., Shanghai, China
"X- Ray Absorption Spectroscopy for the Determination of Oxidation States of Trace Metals in Tobacco, Cigarette Smoke and Ash"

- XANES analysis of cut tobacco and ash samples suggest that As(V) was the dominant species.
- In MS smoke TPM, both As(III) and As(V) were detected. Ageing of the TPM samples promotes As(III) → As(V) transformation.

However

No species identification was possible

WATER-SOLUBLE ARSENIC IN CUT 3R4F TOBACCO: EXTRACTION

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> Total As (dry weight) in homogenate of 3R4F tobacco: **318 ± 9 ng g^{-1}**

Extraction	As (ng g^{-1})	Efficiency (%)
Water	135 ± 5	42
Driselase	40 ± 1	13
SDS	25 ± 2	8
Total	**200 ± 10**	**63**

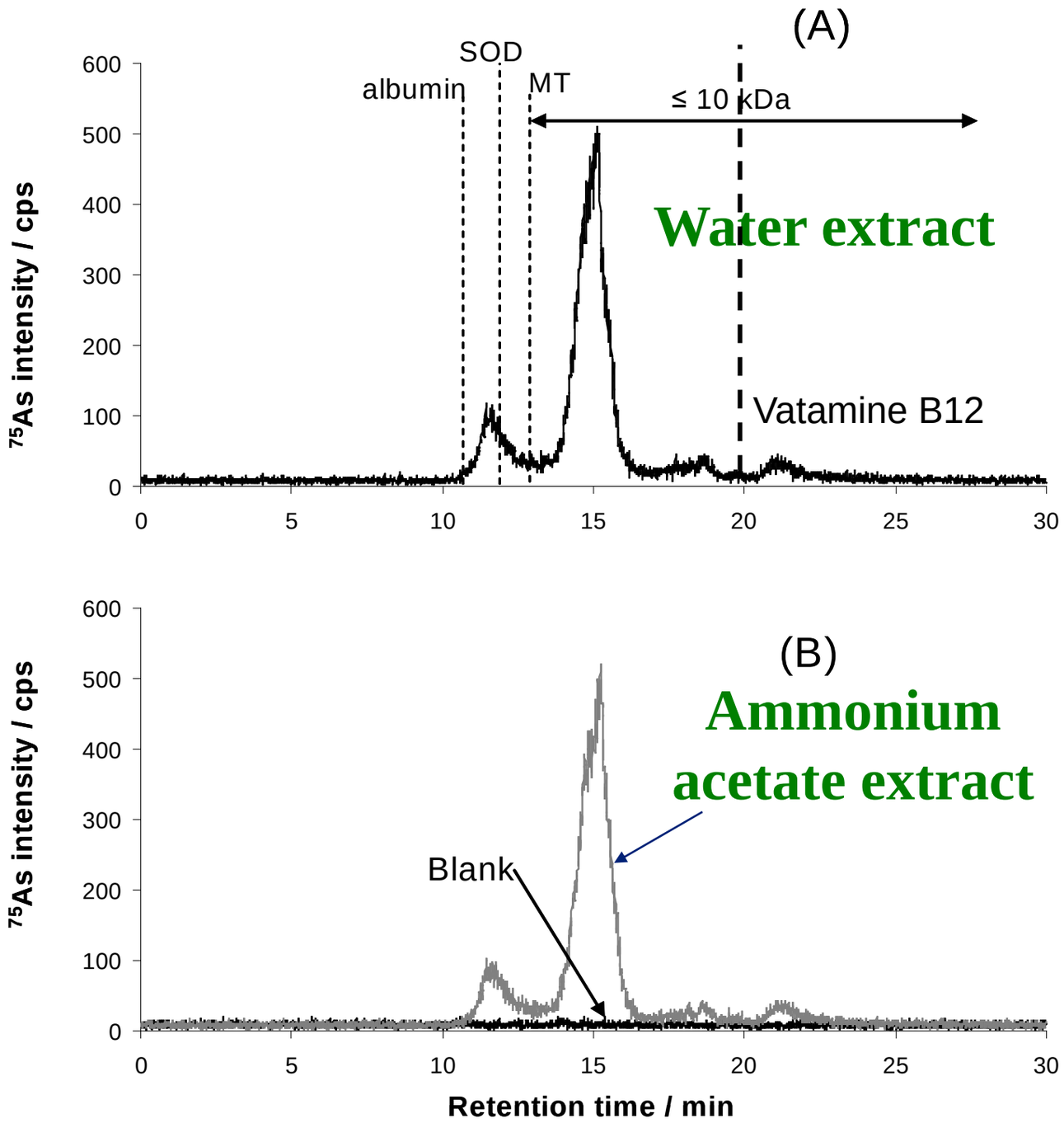
Optimisation of Extraction

- Compromise between total As in the extract and species preservation

- Comparison of 1% formic acid, water, ammonium acetate buffer, water-methanol (**optimal: water**)

- To enhance As ICP-MS transient signal intensity, optimisation of sample size to extractant ratio (**optimal: 0.2 g solid in 2 g water**)

- Optimisation of the extraction time (**optimal: 10 min by MAE**)

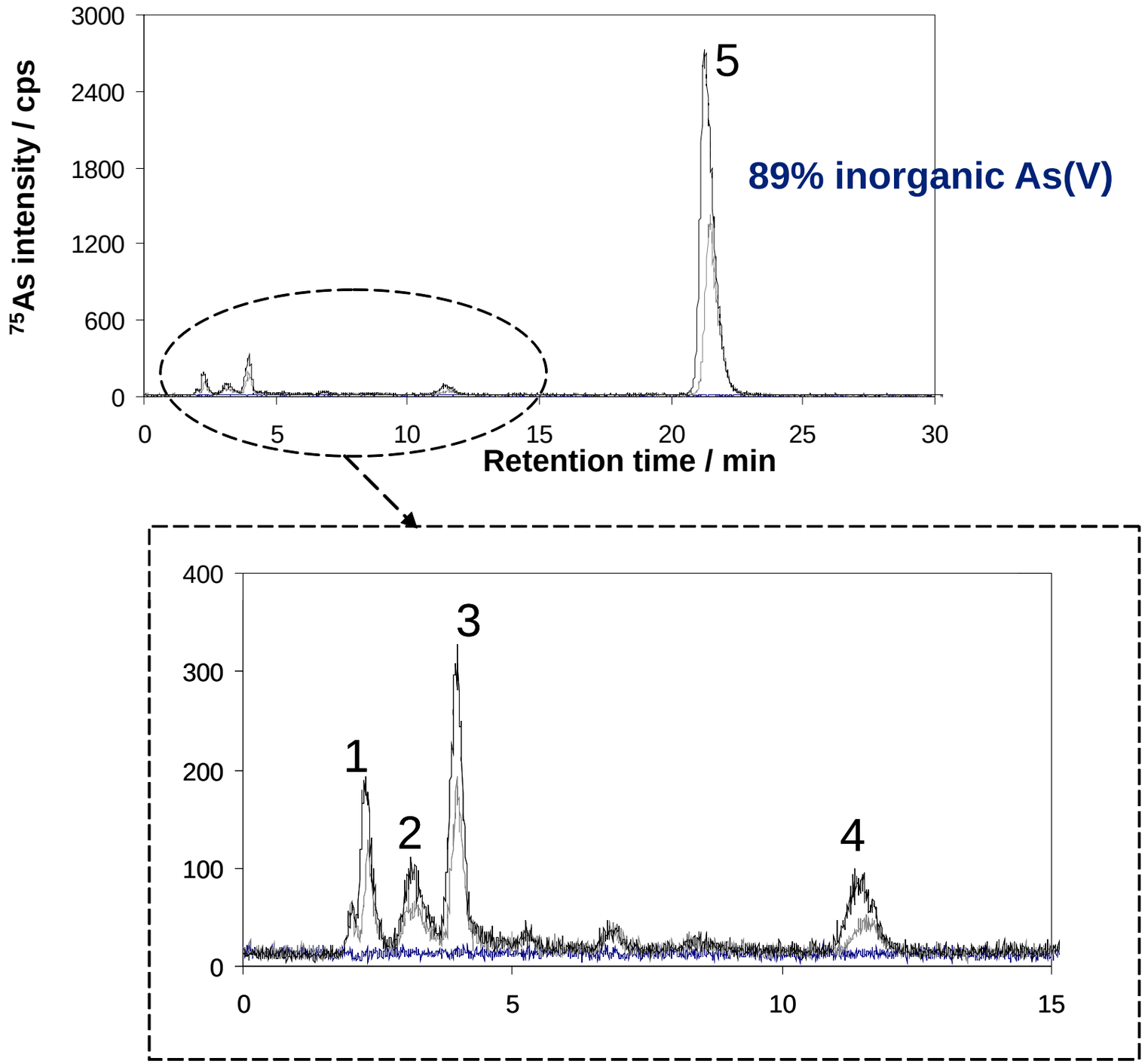


SEPARATION OF WATER-SOLUBLE ARSENIC SPECIES IN CUT 3R4F TOBACCO

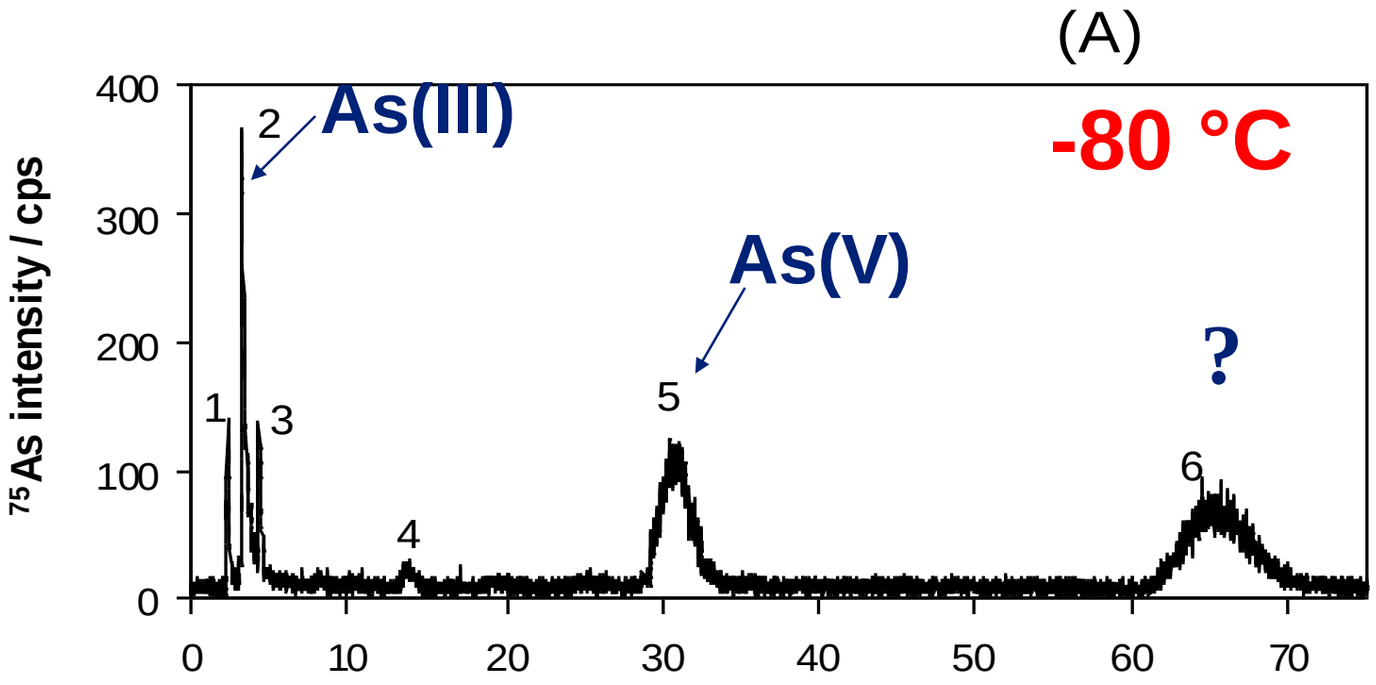
Peak ID:

1: Arsenobetaine (AsB)
2: Arsenite
3: Dimethylarsenic Acid (DMA)
4: Monomethylarsenic acid (MMA)
5: Arsenate

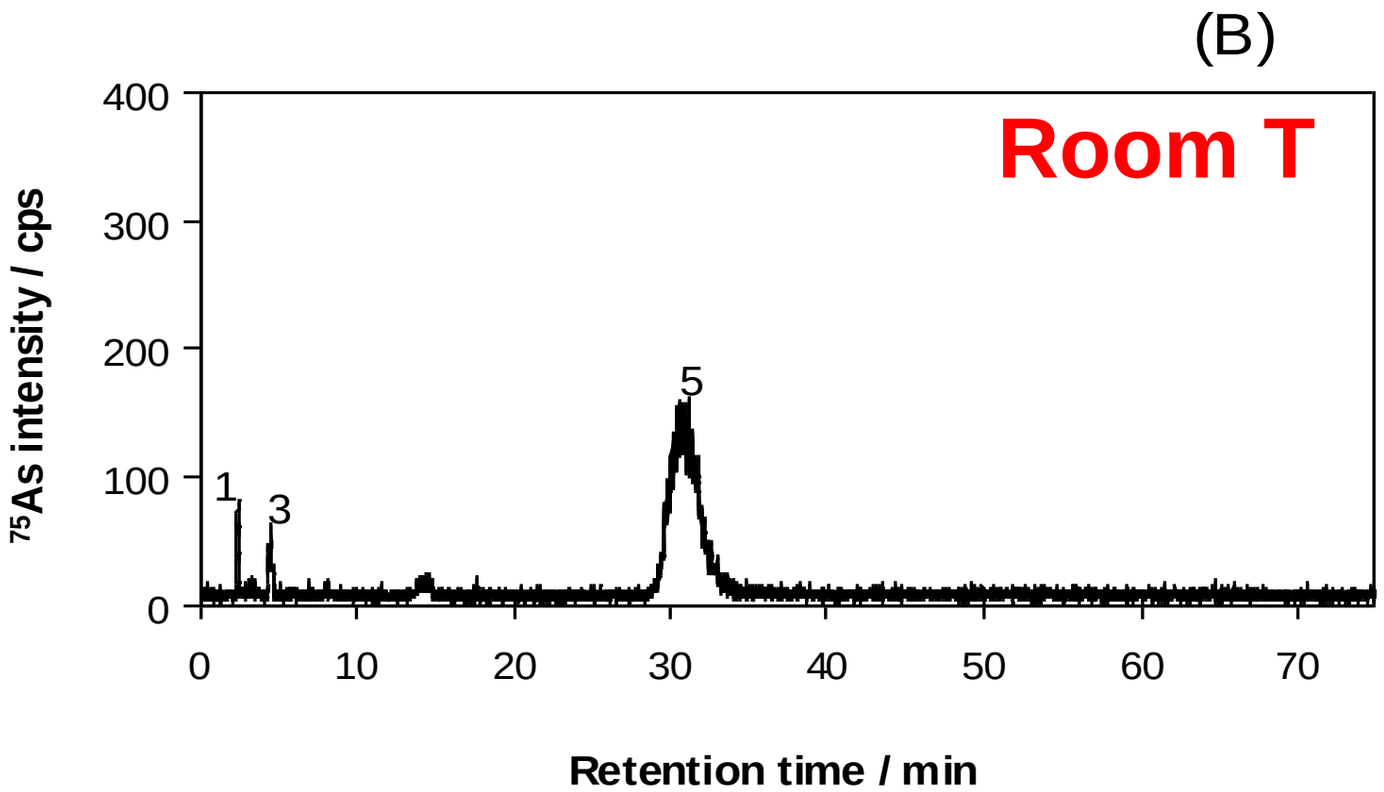
Agreement with XANES



SMOKE CONDENSATES WATER EXTRACT



Total As, water extract: 0.11-0.17 mg/kg



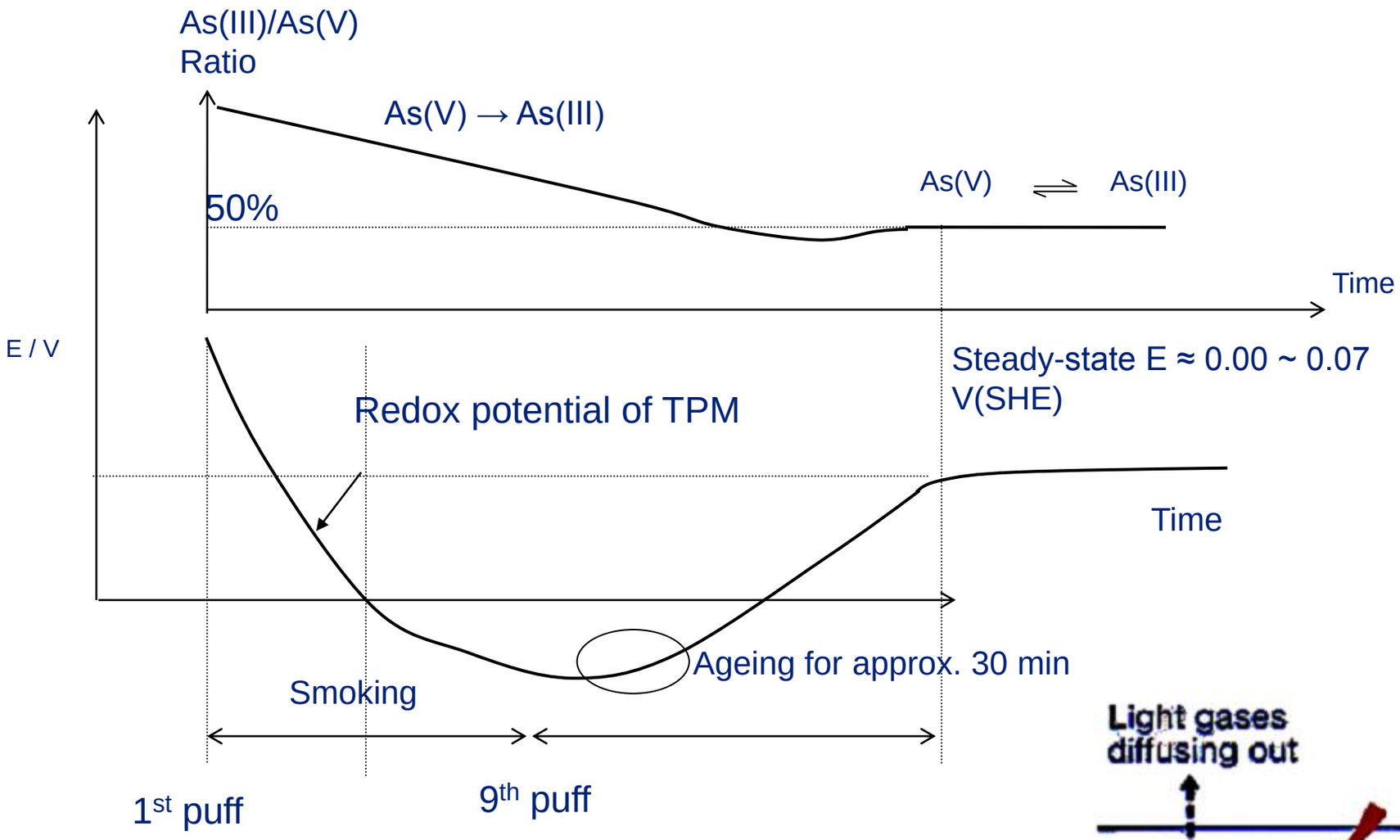
⇦ **As(III) + As(V): 51%**
U: 41%

1: AsB
2: Arsenite: As(III)
3: DMA
4: MMA
5: Arsenate: As(V)
6: Unknown

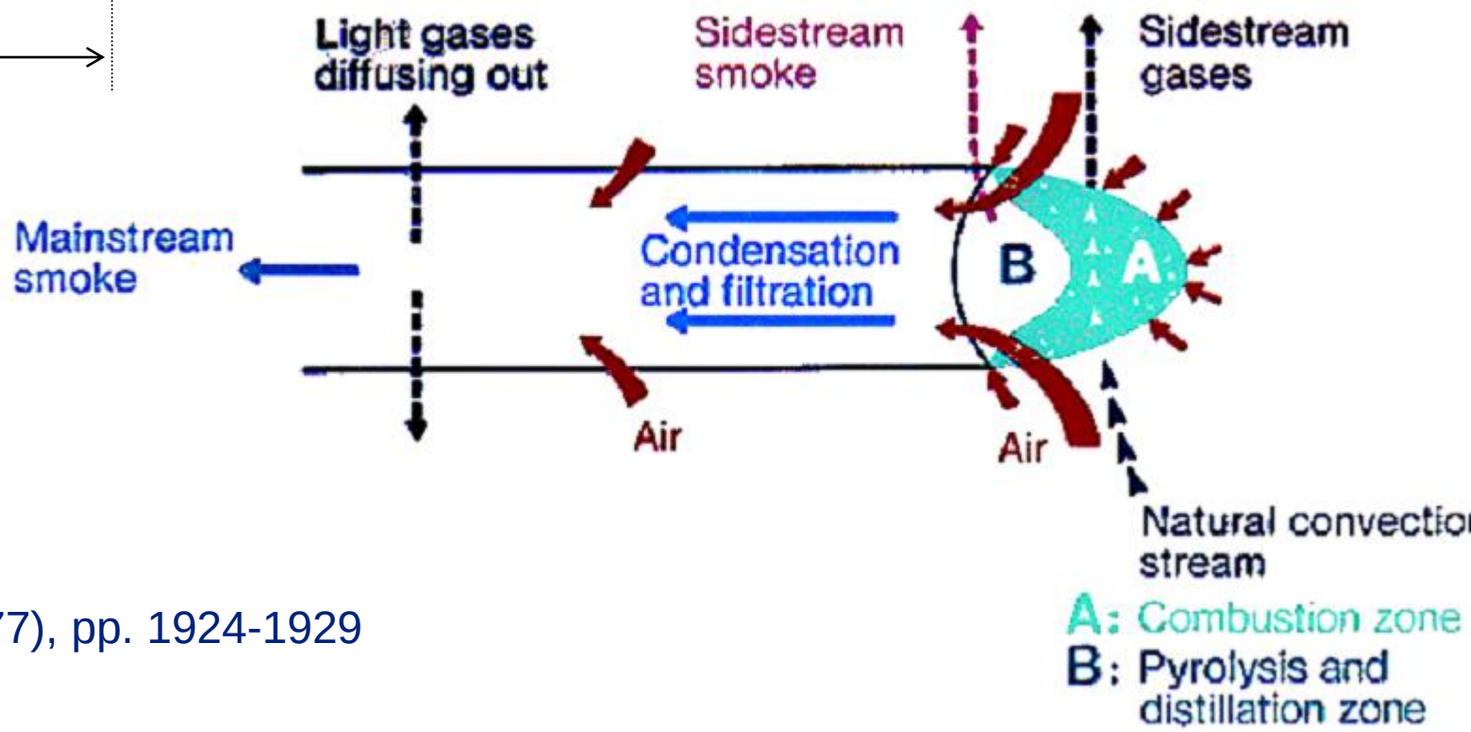
⇦ **As(V)**

Both Peak 2 As(III) and Peak 6 are temperature sensitive.

Arsenic Redox Reactions During Cigarette Smoke Formation & Ageing



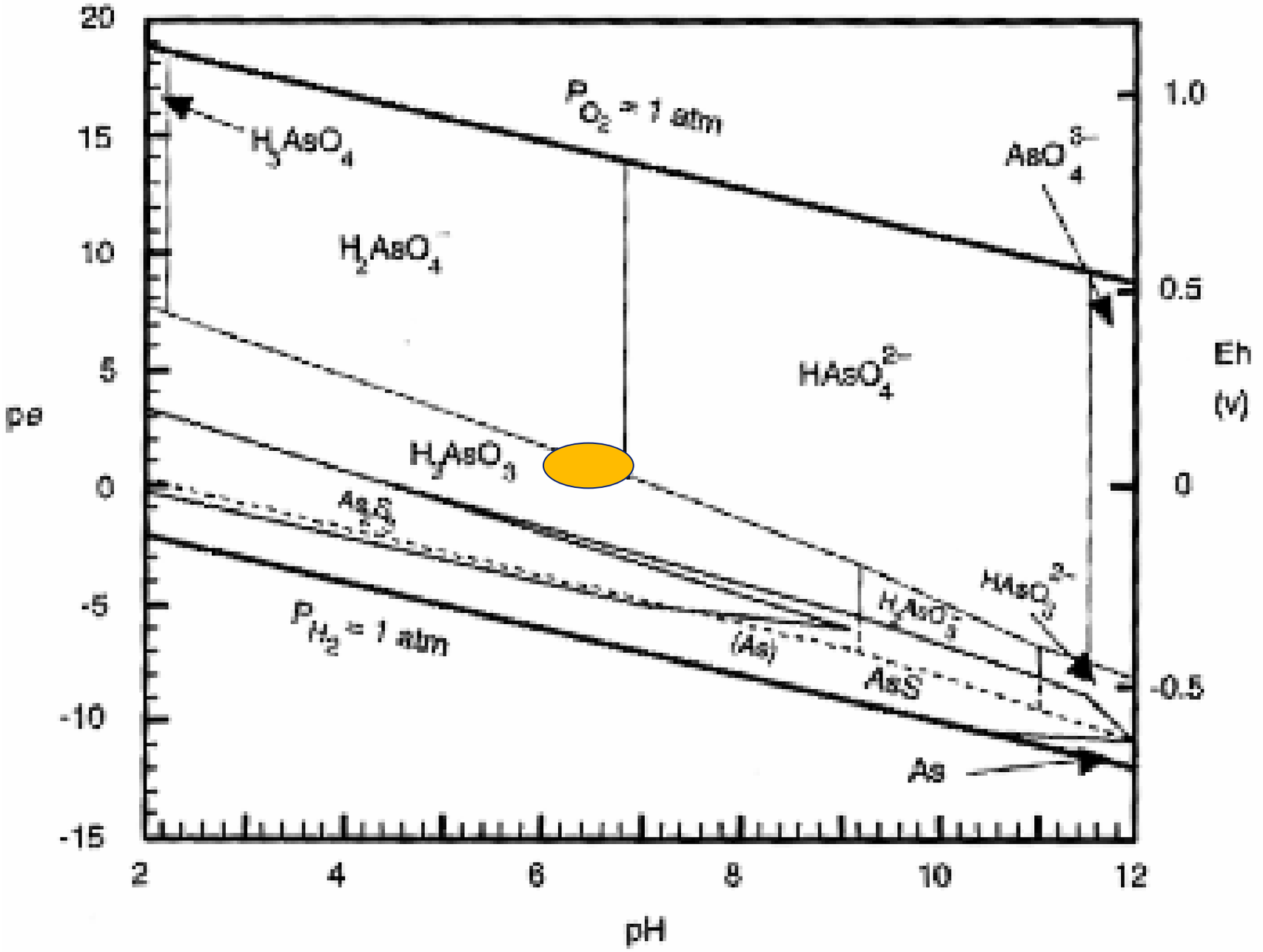
"Smoke pH" and redox potential: important parameters which decide the direction of arsenic species transformation



Schmeltz, I. *et al*. Analytical Chemistry, 49 (1977), pp. 1924-1929

Thermodynamically: Pourbaix Diagram of Arsenic

Smoke tar: E = +0.17 to +0.24V (S.C.E) = - 0.07 to 0.00 V(S.H.E)



SUMMARY

♦ Sequential extraction of As from 3R4F cut tobacco achieved overall efficiency of 63%.

♦ Microwave assisted extraction enhanced As available from cut tobacco in water, reducing extraction time significantly (2 h to 10 min).

♦ Physical (XANES) and chemical (HPLC-ICP-MS) methods agree that most As in cut tobacco is As(V). **However**, the latter provides additional information on As species & distribution.

♦ Complementary results were also achieved on mainstream smoke condensate, pointing to a As(III) → As(V) upon ageing and temperature increase.

♦ Further work is ongoing to identify the remaining unknown As species in smoke (most likely, thioarsenite).

This presentation is available on bat-science.com

Thank You & Any Question

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