

# Characterisation of chemical waste from illegal amphetamine synthesis to support forensic assessment of clandestine drug laboratories

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## Introduction

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1.3 million (1%) young adults (15 - 34) have used amphetamine-type-stimulants in Europe during 2015.<sup>[1]</sup> Clandestine production of amphetamine takes place mainly in Belgium, the Netherlands, Poland and the Baltic States but also in Germany.<sup>[1]</sup>

6.7 tonnes of amphetamine were seized in the EU (2013) and more than half of it was accounted by Germany, the United Kingdom and the Netherlands.<sup>[1]</sup> One of the most common synthesis approaches for amphetamine is the Leuckart method. Large quantities of potentially hazardous chemicals like solvents, acids and bases are used for this synthesis. Aqueous synthesis waste is often disposed into the environment or the sewage system. This disposal can have serious environmental impacts<sup>[2]</sup> but can also aid forensic investigations. In order to use waste discharges for scale and frequency estimation of a production during a forensic investigation, it is important to characterise it first.

- European Monitoring Centre for Drugs and Drug Addiction. European drug report 2015. Luxembourg: Publications Office of the European Union; 2015.
- Pal R, Megharaj M, Kirkbride KP, Naidu R. Illicit drugs and the environment - a review. *The Science of the total environment*. 2013; 463-464: 1079-92

## Aims

- Controlled amphetamine synthesis and characterisation of aqueous waste
- Measurement of pH and conductivity
- Determination of key compounds in synthesis waste using SPE and GC/MS
- Determination of solubility of key compounds in pure water using HPLC/DAD
- Quantification of ions in aqueous synthesis waste using CE/C4D

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## Conclusion

- Controlled amphetamine synthesis following the Leuckart route was conducted
- pH and conductivity measurements were performed showing highly conductive and strongly alkaline or acidic behaviour
- Aqueous waste samples were prepared by SPE and methanolic extracts were measured directly by GC/MS
- Key compounds were: benzyl methyl ketone,  $\alpha$ -phenylacetoacetonitrile, N-formylamphetamine, amphetamine and 4-methyl-5-phenylpyrimidine
- Solubilities of key compounds using a HPLC/DAD method were found to be between <1 and 18 g/L
- Ions found were ammonium, sulphate, chloride, sodium and formate with concentrations from 0.03 - 6.2 mol/L
- Results could be used to support forensic investigations in case aqueous synthesis waste is available as evidence

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## Methods

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### SPE

conditioning MeOH/H<sub>2</sub>O    3 mL sample 1:2 diluted    washing H<sub>2</sub>O    drying vacuum    elution 2 mL MeOH

### GC/MS

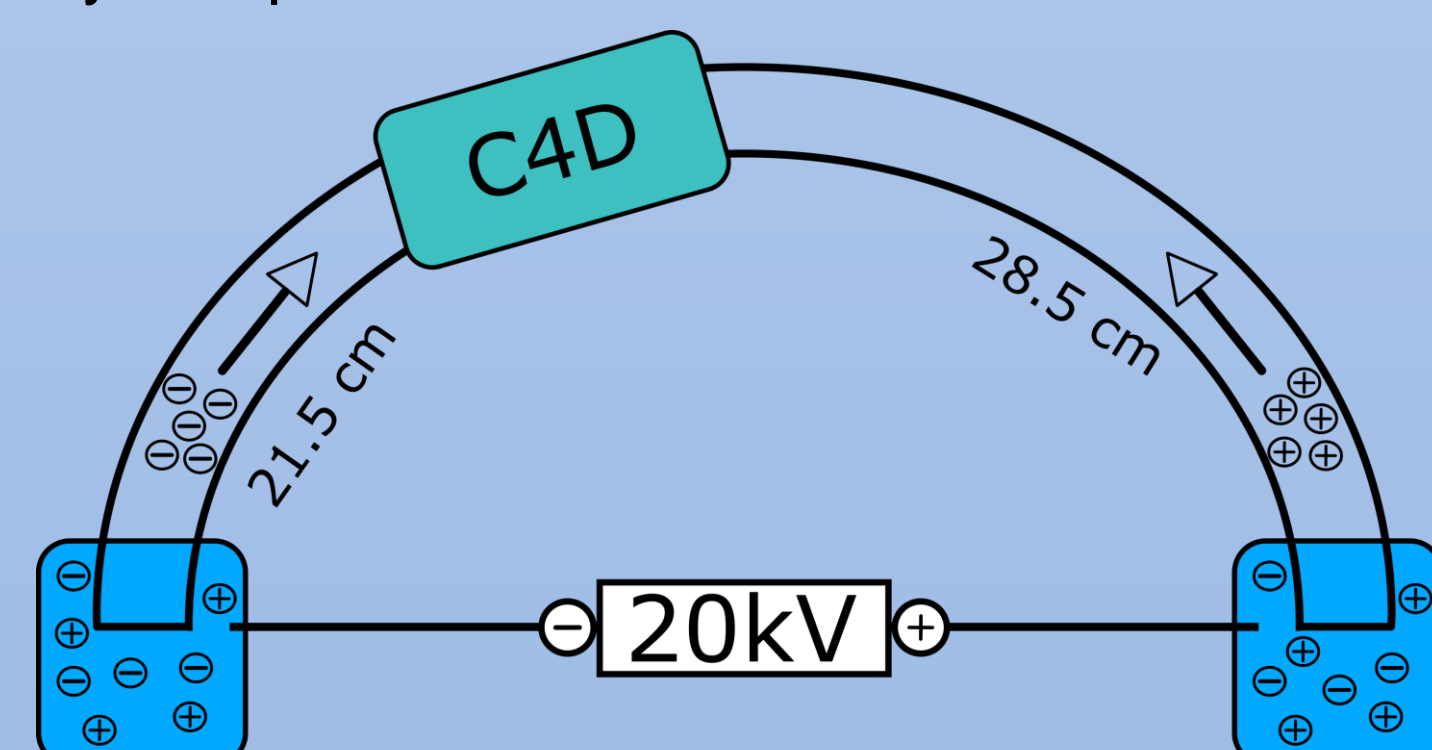
- Aqueous waste samples were taken after each step of an amphetamine synthesis
- SPE sample preparation was performed using Oasis HLB cartridges as shown above
- 1  $\mu$ L of methanolic extract was directly injected into GC system without dilution
- GC runtime was 34 minutes with a temperature gradient from 65 – 300 °C
- Mass spectra were used to identify key compounds which show a high intensity and cover the whole synthesis procedure

### HPLC/DAD

- Five key compounds were identified and references of them were either bought or synthesised
- Deionised water was saturated with these compounds by adding a small amount to a vial with water
- Three replicates were prepared and analysed using a HPLC-DAD method
- Mobile phase was a mixture of ammonium formate buffer (pH 6.8) and acetonitrile
- Using an external calibration the solubility of the key compounds was calculated

### CE/C4D

- Waste was diluted up to 1:50000
- Simultaneous separation of anions and cations was performed from both capillary ends
- External calibration with mixed anion/cation standard was used for quantification
- Separation buffer was made of 8mM L-histidine and 2.8mM 2-hydroxyisobutyric acid at pH 4.25
- Contactless conductivity measurement (C4D) was used for detection

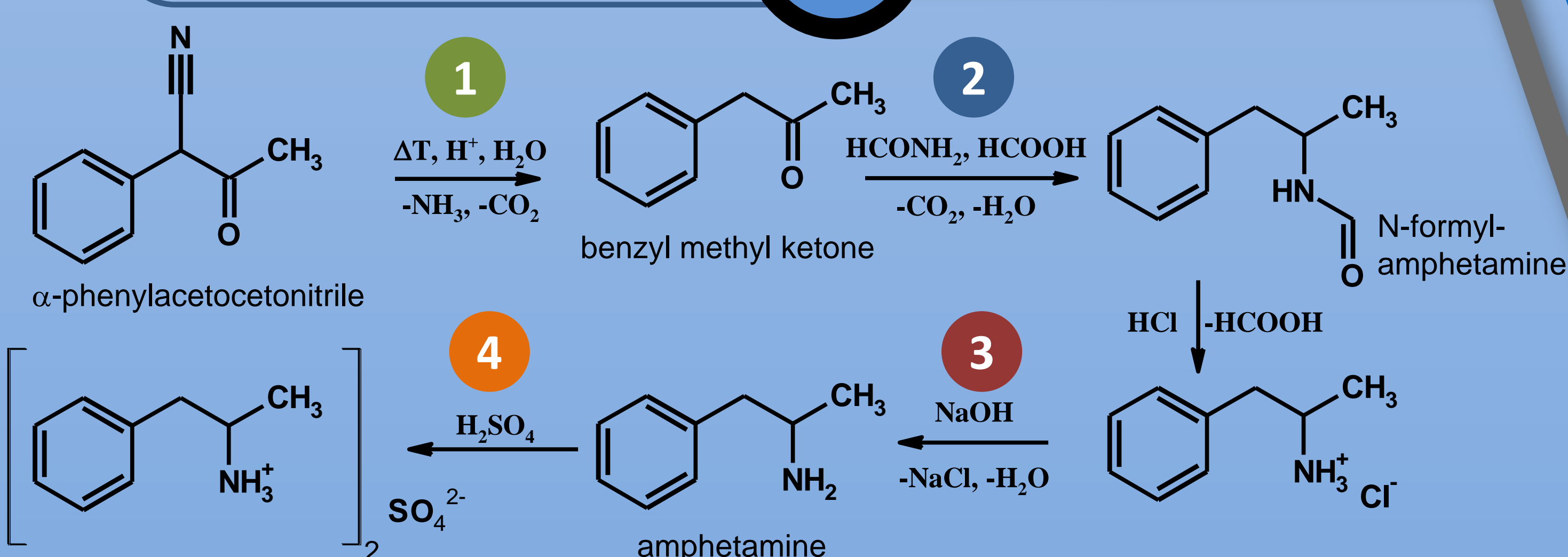


### pH/cond.

- Physical parameters were determined using pH and conductivity electrodes
- Parameters were measured directly in undiluted waste samples after collection

## Synthesis

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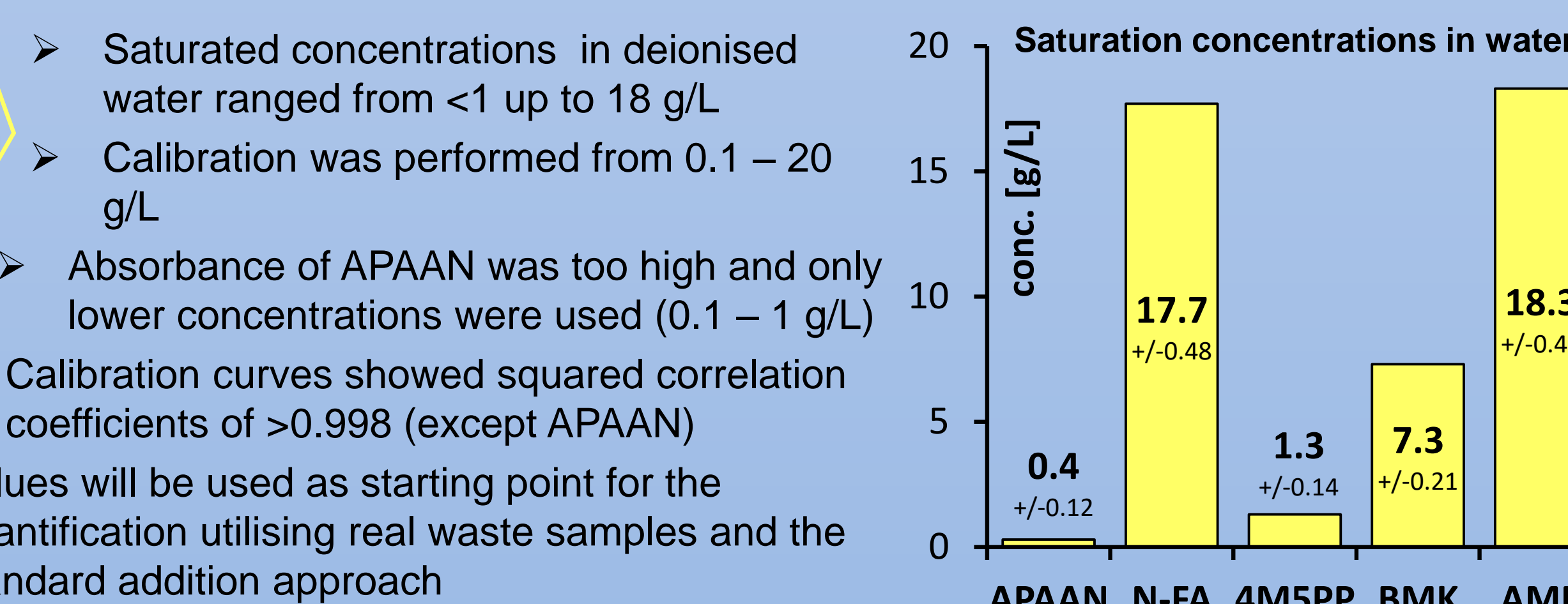
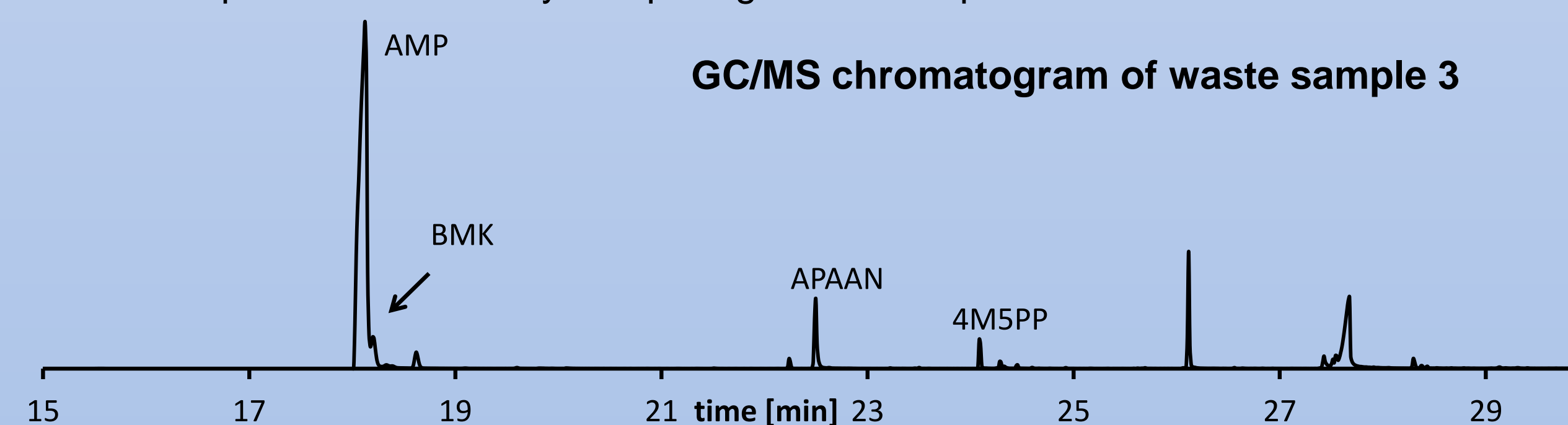


APAAN is converted to BMK under acidic conditions. BMK then undergoes the Leuckart reaction. The formed amphetamine base is finally precipitated as sulphate. Steps where waste was collected are numbered from 1 – 4.

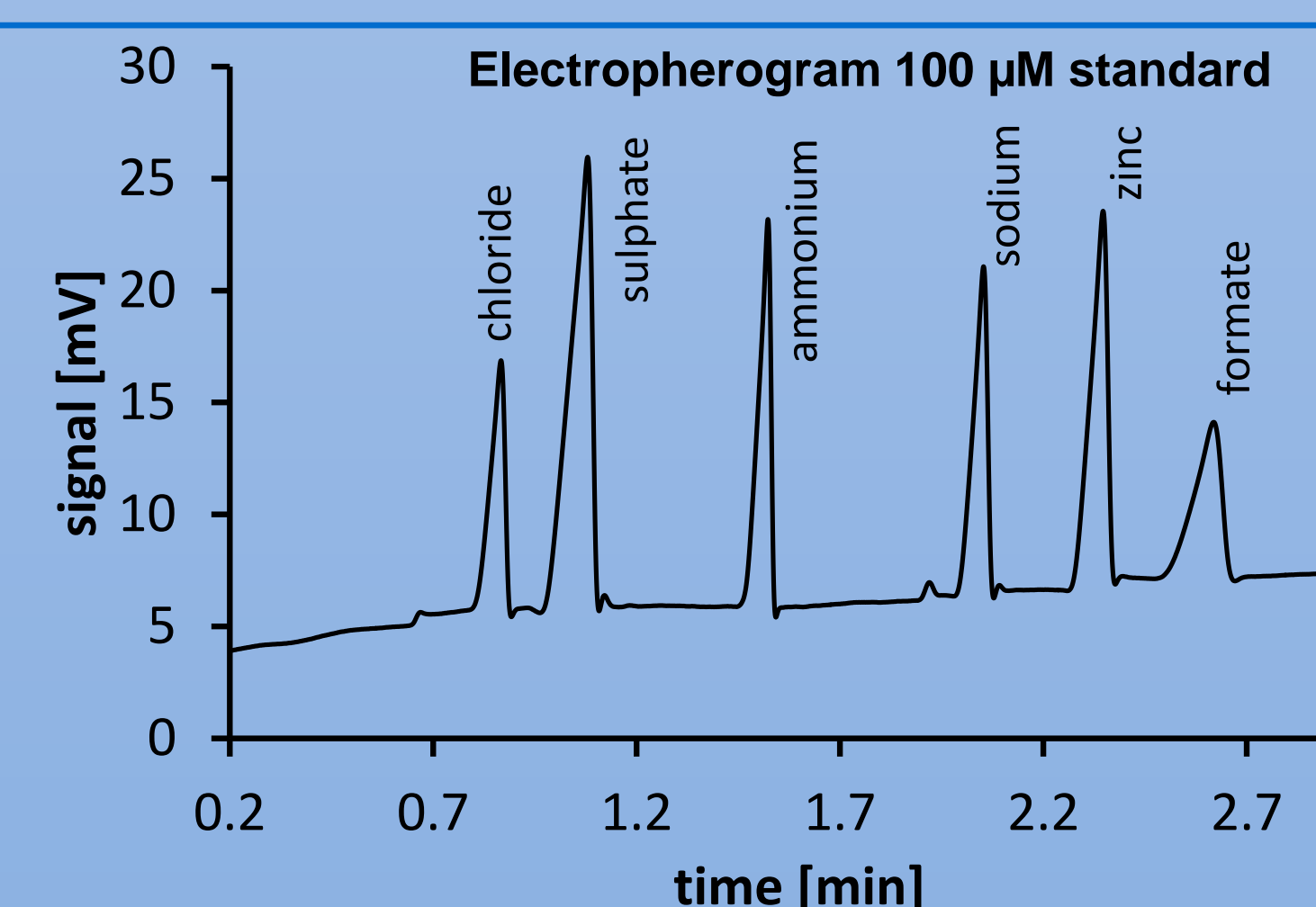
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## Results

- Key compounds were benzyl methyl ketone (**BMK**),  $\alpha$ -phenylacetoacetonitrile (**APAAN**), N-formylamphetamine (**N-FA**), amphetamine (**AMP**) and 4-methyl-5-phenylpyrimidine (**4M5PP**)
- These five compounds were chosen because they either showed a high signal intensity and/or were present in wastes from different steps (see table below)
- BMK and AMP were difficult to separate but mass spectra allowed for differentiation
- Identification of peaks was done by comparing the mass spectra with our database



- Ion concentrations ranged from 0.03 – 6.2 M
- Calibration was performed from 10 – 300  $\mu$ M
- Correlation coefficients were above 0.999
- Total analysis time is 7.5 min including a capillary washing step before each run
- Method could be used to quickly differentiate between wastes from different synthesis steps (see table below) and get information about the synthesis process



	Waste 1	Waste 2	Waste 3	Waste 4
Organic compounds (main signal)	BMK; APAAN	N-FA; 4M5PP Benzyl nitrile	AMP; BMK APAAN; 4M5PP	BMK; 4M5PP APAAN
Ions [conc. in mol/L]	SO <sub>4</sub> <sup>2-</sup> [6.2]	Na <sup>+</sup> [4.9] NH <sub>4</sub> <sup>+</sup> [2.3] HCOO <sup>-</sup> [5.0]	Cl <sup>-</sup> [3.6] Na <sup>+</sup> [5.8] NH <sub>4</sub> <sup>+</sup> [1.1] HCOO <sup>-</sup> [1.9]	Cl <sup>-</sup> [0.06] SO <sub>4</sub> <sup>2-</sup> [0.07] HCOO <sup>-</sup> [0.03]
Conductivity [mS/cm]	> 200	35 - 60	35 - 130	-
pH	< 1	10 - 12	12 - 14	4 - 6