

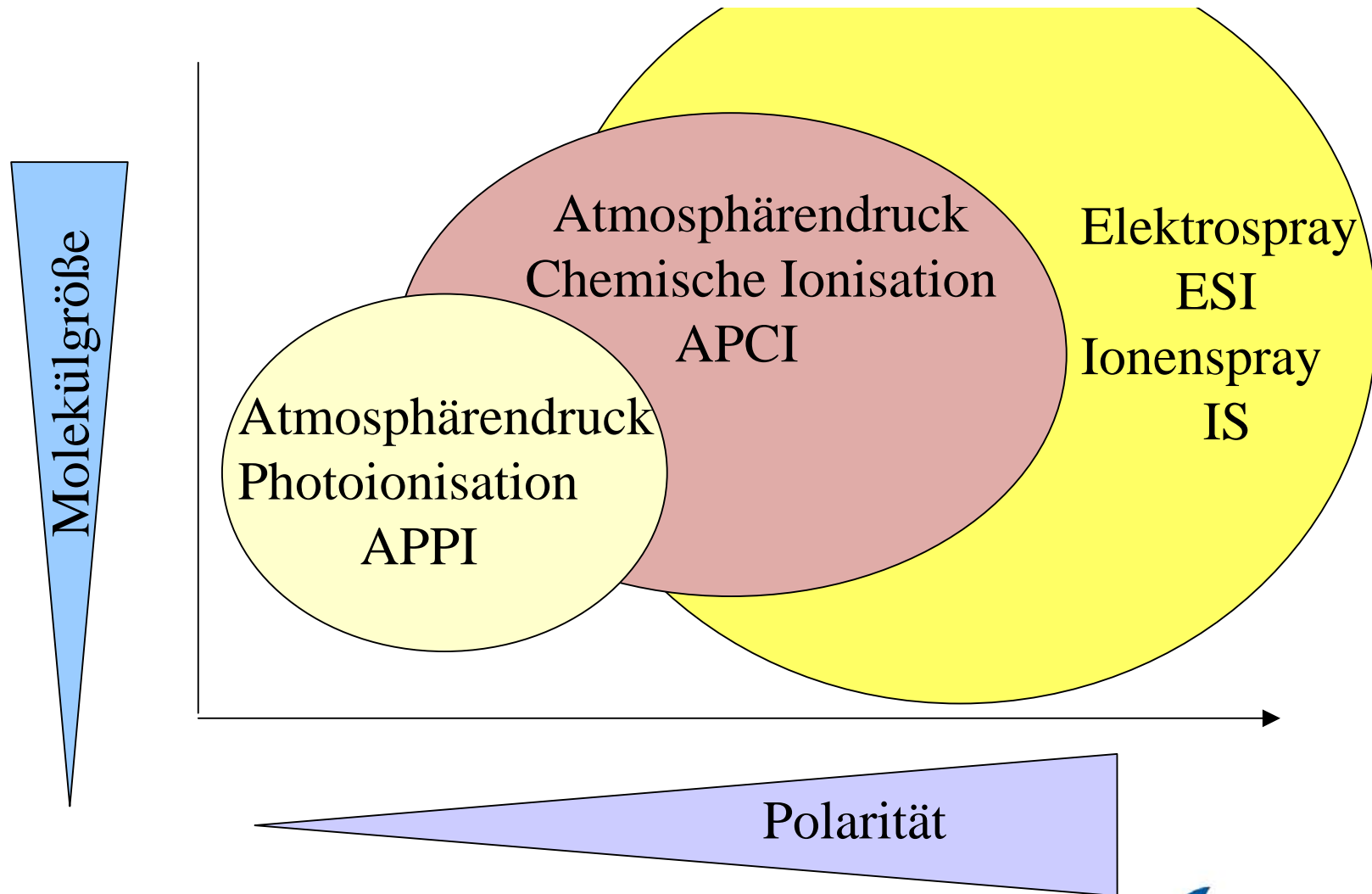
# LC-MS Techniken zur Analyse polarer und



thermolabiler  
Verbindungen in  
Umwelt- und  
Biowissenschaften

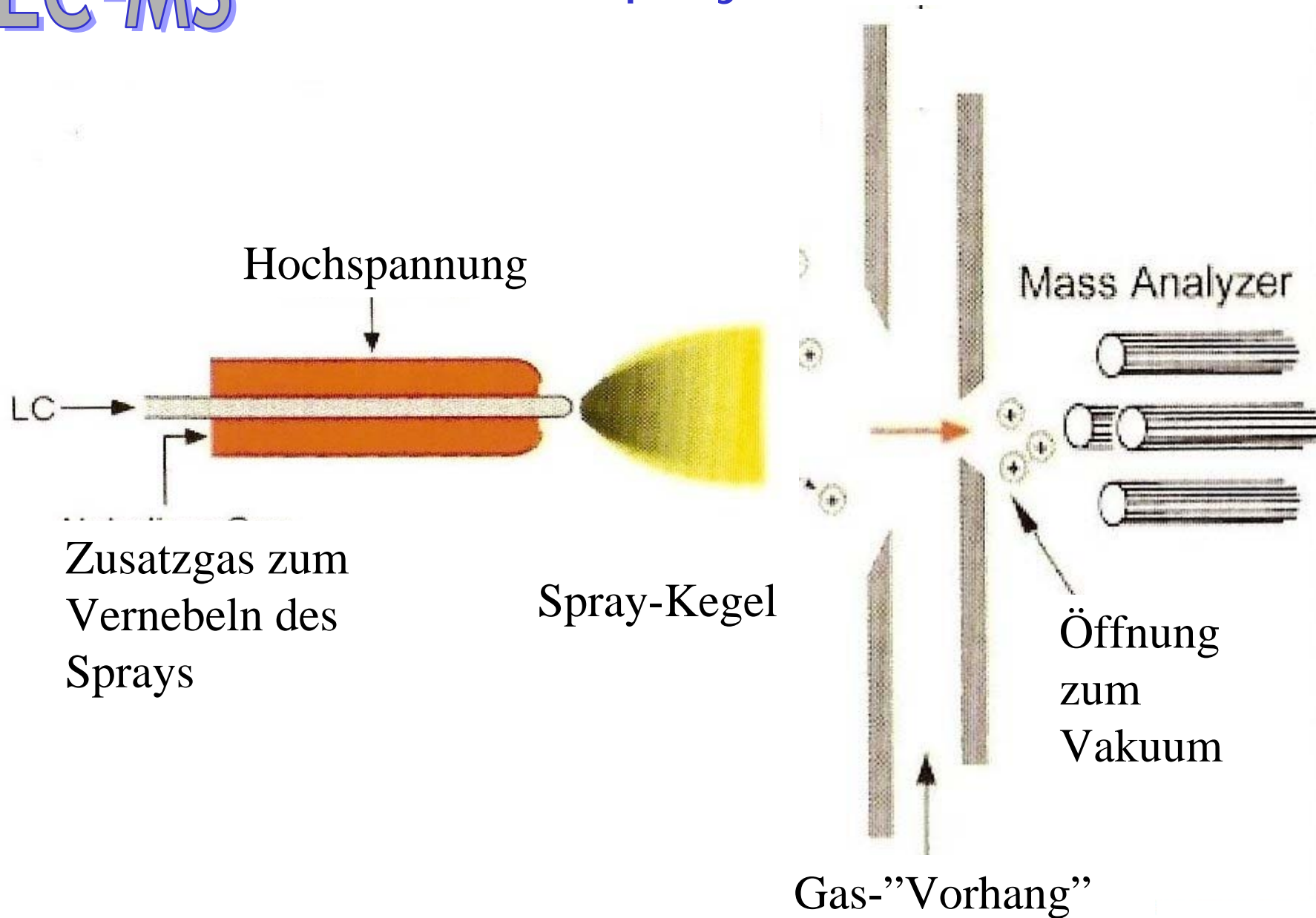
M. Möder, Department Analytik

# Eignung der API-Techniken



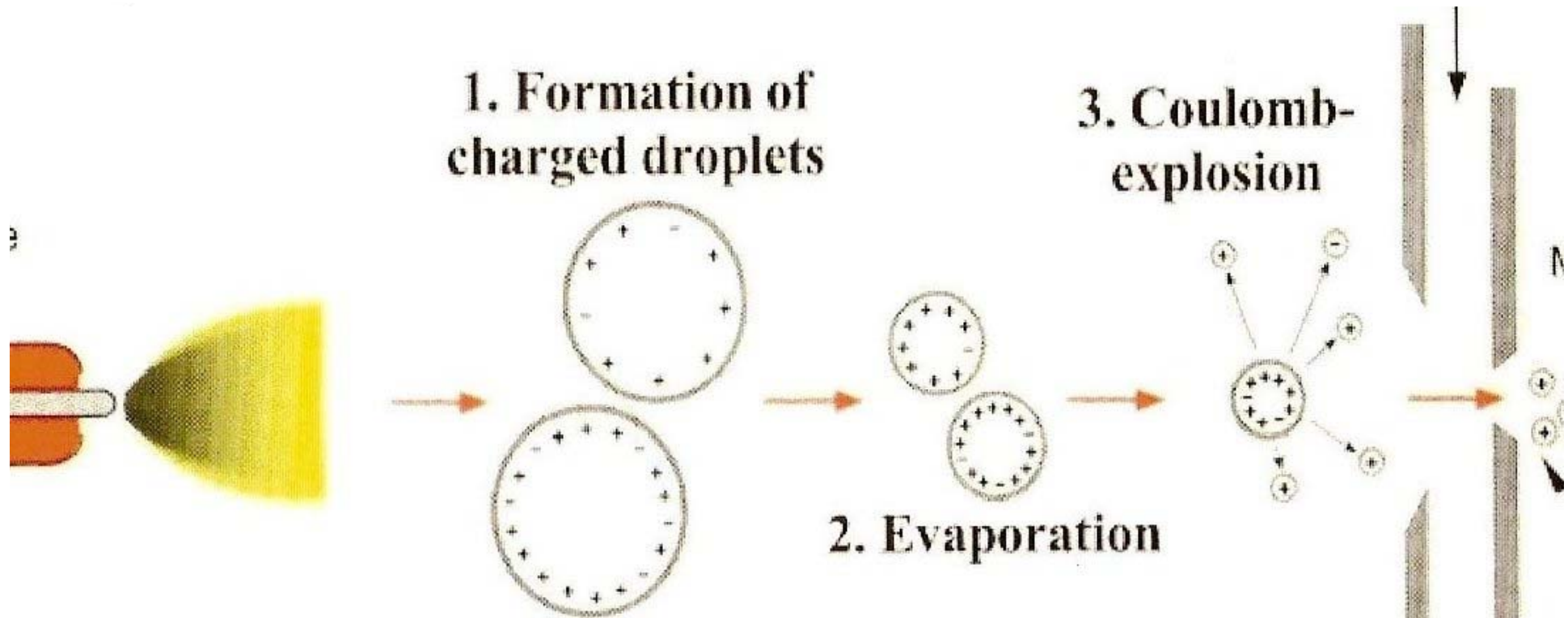
# LC-MS

## Electrospray ionization ESI



# LC-MS

## Ionisierungsmechanismus

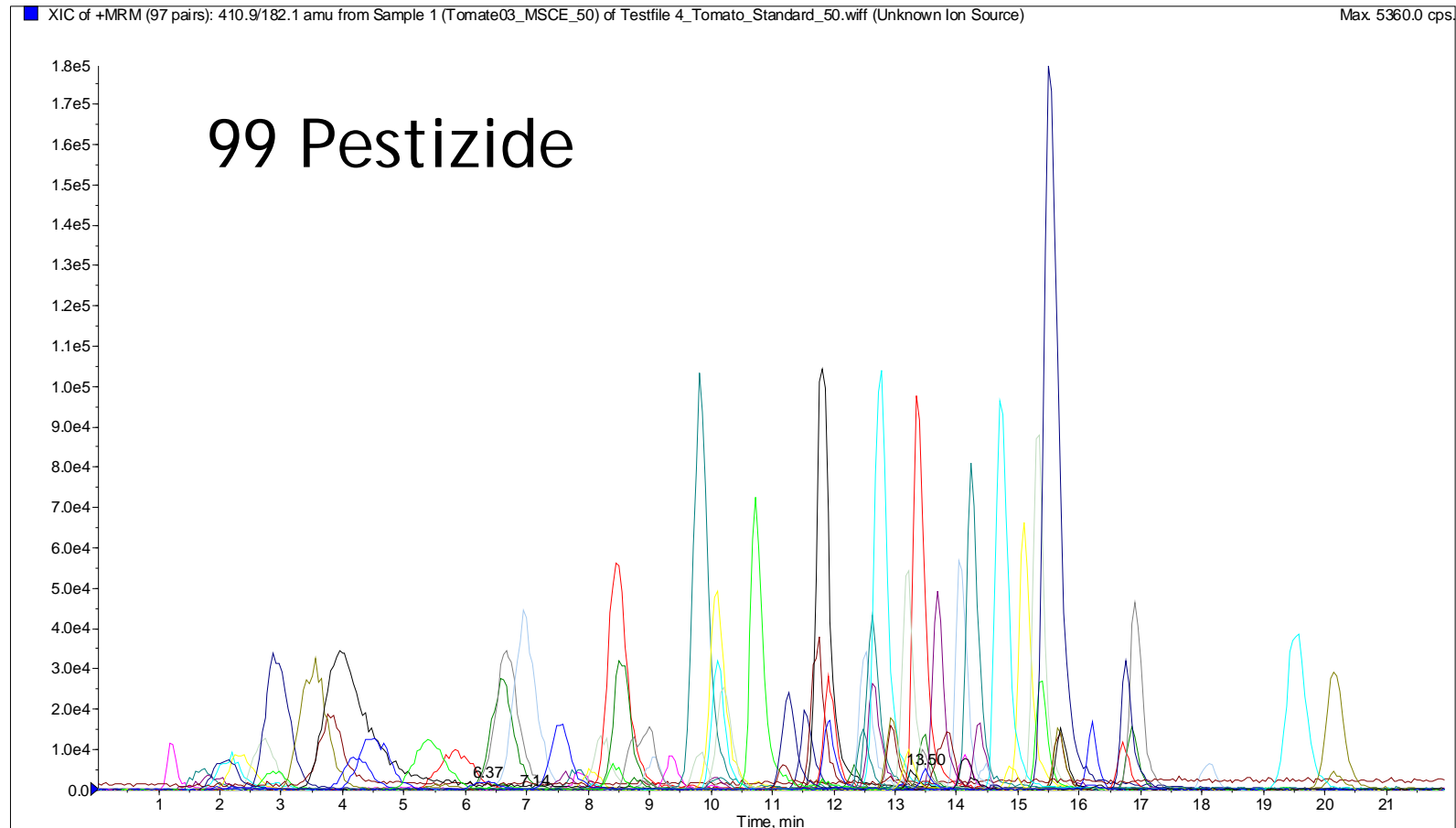


Wenig Energie übertragen  
soft ionization techniques



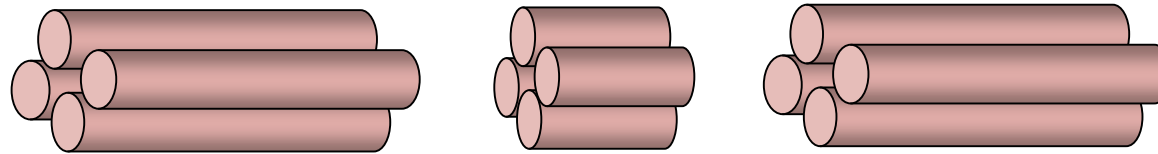
# LC-MS-MS

## Selektiver Nachweis durch MS-MS



# LC-MS-MS

## Tandem-Massenspektrometrie

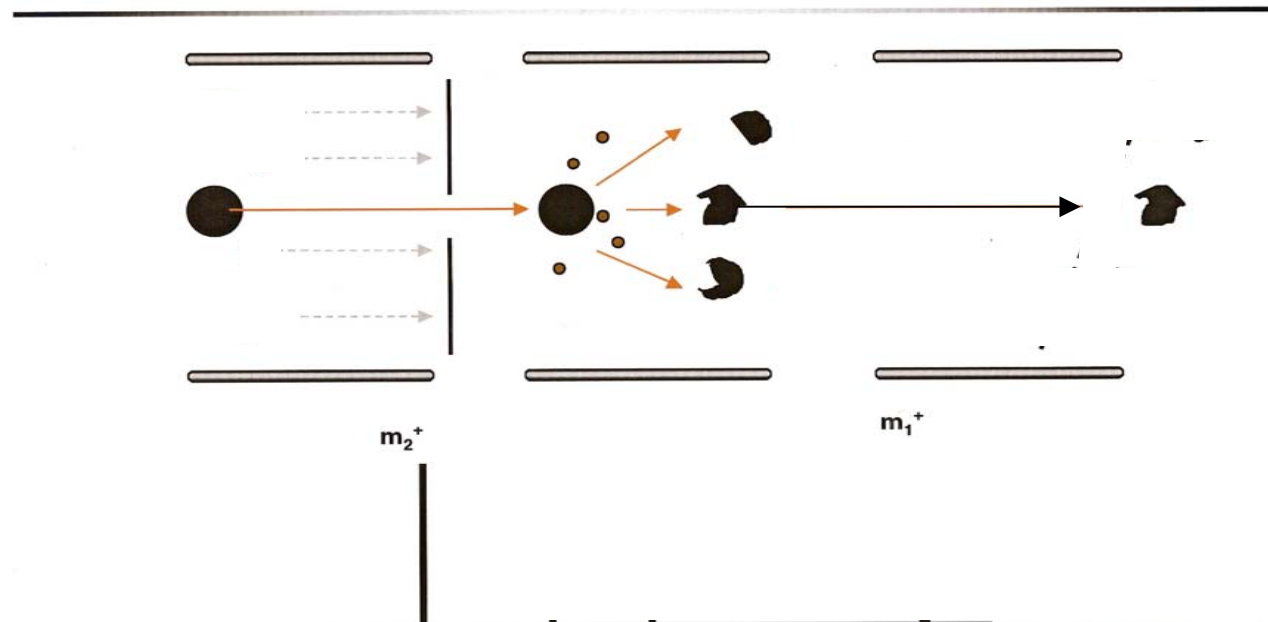


1. Quadrupol

Stoßzelle

2. Quadrupol

*MS/MS - Multiple reaction monitoring MRM*



# LC-MS

## Neugeborenen-Screening

Früherkennung von Stoffwechselerkrankungen

- Phenylketonuria PKU 1: 9000 Neugeborenen
- Hypothyroismus (verminderte Bildung von Thyroidhormon)
- adrenogenitales Syndrom (Steroidhormonbildung in Nebenniere gestört)



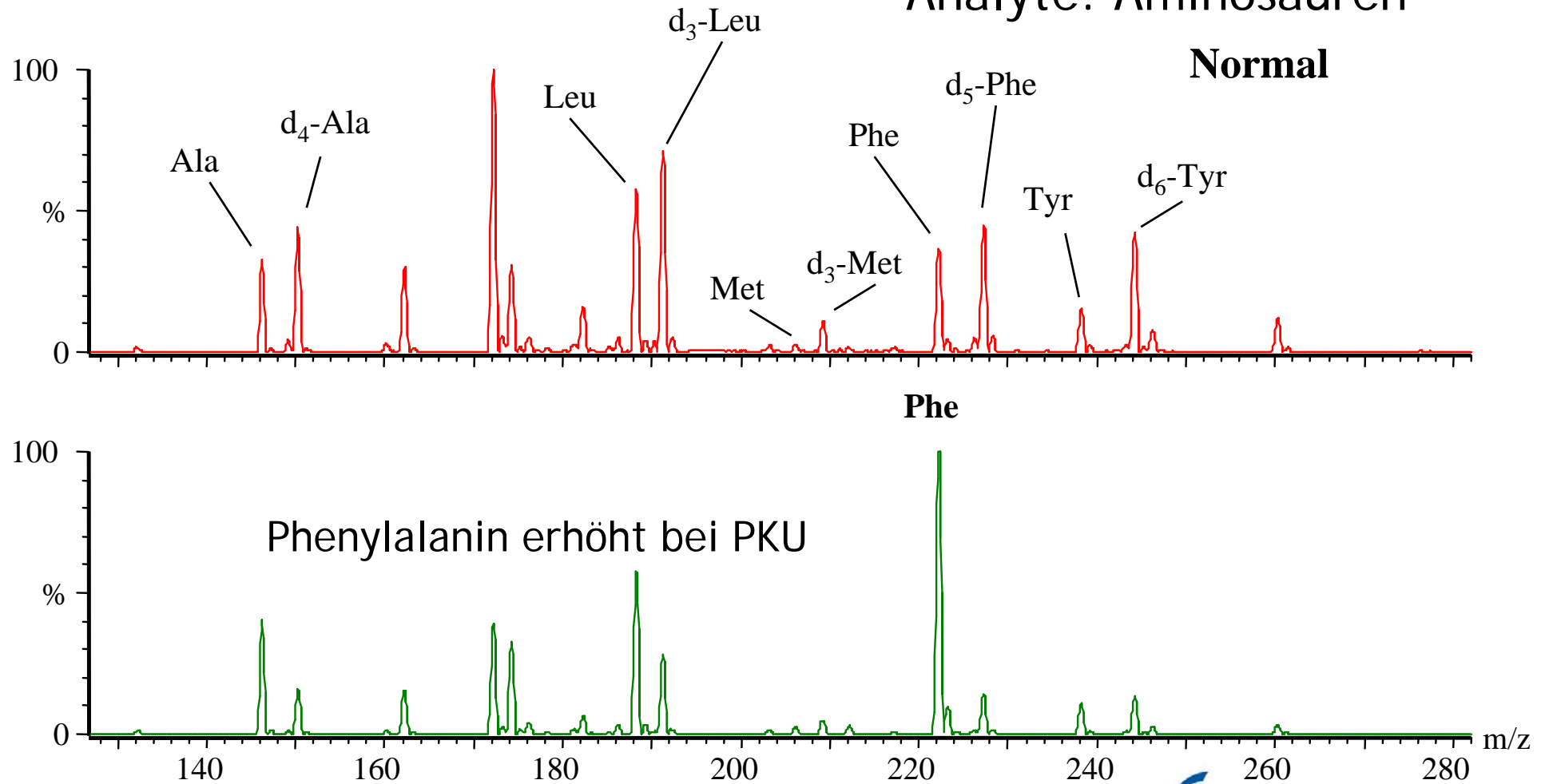
Ursache: Enzymdefekte, reduzierte oder fehlende Enzymaktivitäten > Anreicherung bestimmter toxischer Stoffwechselprodukte -> Organschädigung, schnelle Behandlung erforderlich > dazu schnelle Diagnose

Prozedur: 2-3 µl Blut aus Ferse auf Filterpapier, Methanolextraktion, LC-MS

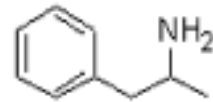
# LC-MS

## Neugeborenen-Screening

Analyte: Aminosäuren

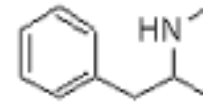






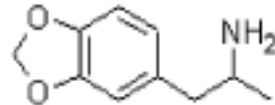
Amphetamine

M.W. 135.10



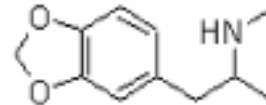
Methamphetamine

M.W. 149.12



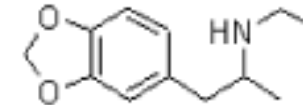
3,4-methylenedioxyamphetamine  
(MDA)

M.W. 179.09



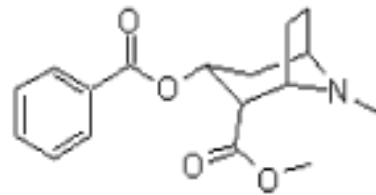
3,4-methylenedioxy-methamphetamine  
(MDMA)

M.W. 193.11



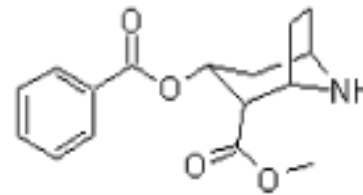
3,4-methylenedioxyethamphetamine  
(MDEA)

M.W. 207.13



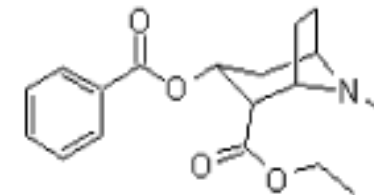
Cocaine

M.W. 303.15



Norcocaine

M.W. 289.13



Cocaethylene

M.W. 317.16

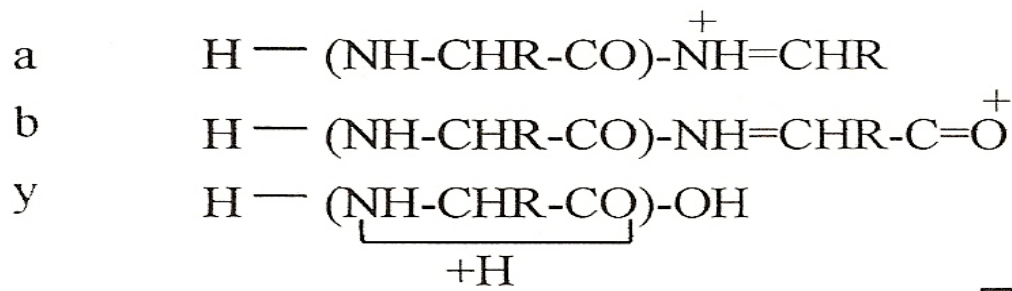
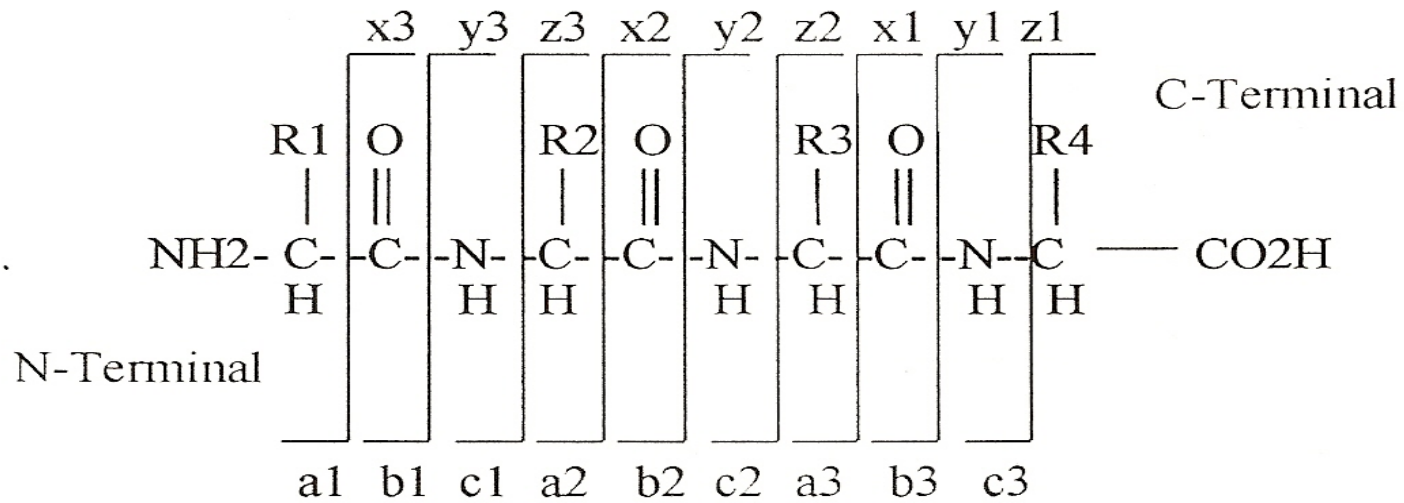
**Table 6. Concentrations (ng/L) of Illicit Drugs and Their Metabolites in Influent and Effluents of the Nosedo (Milan) and Lugano WWTPs**

illicit drugs	Nosedo, February 2006		Lugano, March 2006	
	influent, mean <sup>a</sup> ± SD	effluent, mean <sup>a</sup> ± SD	influent, mean <sup>a</sup> ± SD	effluent, mean <sup>a</sup> ± SD
benzoylecgonine	1132.1 ± 197.2	<LOQ	547.4 ± 169.4	100.3 ± 28.6
norbenzoylecgonine	36.6 ± 7.8	<LOQ	18.8 ± 5.6	7.5 ± 2.9
cocaine	421.4 ± 83.3	<LOQ	218.4 ± 58.4	10.7 ± 3.2
norcocaine	13.7 ± 5.3	<LOQ	4.3 ± 0.9	0.7 ± 0.5
cocaethylene	11.5 ± 5.1	<LOQ	5.9 ± 2.6	0.2 ± 0.5
morphine	83.3 ± 11.8	<LOQ	204.4 ± 49.9	55.4 ± 11.1
6-acetylmorphine	11.8 ± 8.5	<LOQ	10.4 ± 4.8	<LOQ
morphine-3β-D-glucuronide	2.5 ± 7.1	<LOQ	18.1 ± 30	<LOQ
amphetamine	14.7 ± 10.6	<LOQ	<LOQ	<LOQ
methamphetamine	16.2 ± 7.1	3.5 ± 2	<LOQ	<LOQ
MDA	4.6 ± 7.3	1.1 ± 1.5	<LOQ	0.9 ± 1.9
MDMA	14.2 ± 14.5	4.4 ± 3.7	13.6 ± 12.6	5.1 ± 3
MDEA	1.5 ± 3.8	<LOQ	<LOQ	<LOQ
methadone	11.6 ± 1.7	9.1 ± 0.5	49.7 ± 9.6	36.2 ± 2.8
EDDP	19.8 ± 3.1	22.6 ± 0.6	91.3 ± 19.2	72.1 ± 8.7
11-nor-9-carboxy-Δ <sup>9</sup> -THC	62.7 ± 5	<LOQ	91.2 ± 24.7	7.2 ± 3.7

<sup>a</sup> Mean of eight samples collected during 1 week.

*S. Castiglioni et al. Anal. Chem. 78 (2006) 5421*

### Peptide Fragment ions



**PE Biosystems**

# Zusammenfassung

- LC-MS(MS) Methode der Wahl für Untersuchung polarer, thermisch labiler Verbindungen
- durch Mehrfachladungen große Moleküle mit normalen Quadrupol MS analysierbar
- Analyse aus wässrigen Proben möglich
- modernste Geräte mit NWG von ng/L bei Direktinjektion

# Zusammenfassung

- Qualität der Spektren geräteabhängig
- Strukturaufklärung unbekannter Verbindungen schwierig
- Matrixmoleküle (Fette, Tenside, Ionen, Huminstoffe) beeinflussen Ionisierungsprozesse
- keine Spektrenbibliotheken
- Vorsicht mit nicht-flüchtigen Salzen (Phosphate, NaCl...)

LC-MS-MS heute Standardtechnik