Determination of arsine and phosphine in ethane with GC-ICP-MS

Peter Johansson
Erica Andersson

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Head Office
Borealis AG
Wagramer Strasse 17–19
A-1220 Vienna, Austria
Tel. +43 1 22 400 300
Fax +43 1 22 400 333
www.borealisgroup.com

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Austria, Belgium, Brazil, Finland, Turkey, United States

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Site Stenungsund

Stenungsund site

– Fully integrated complex comprising one of Europe's most flexible cracker (four feedstock options), and three polyethylene plants

– Home to ca 950 employees

Feedstock supply to the cracker plant

- Propane
- Butane
- Ethane
- Virgin Naphta

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The Journey to success

In the autumn of 2012 the cracker laboratory was involved in the project of new feedstock candidates for the cracker.

The target of the project was to analyze contaminates as Arsine, AsH3, and Phosphine, PH3, in feedstock.

Methods for AsH3 and PH3 in gas and liquefied gas are usually based on collection of the sample in different filters or solvents. These methods are time consuming and also only give the result of total As and total P.

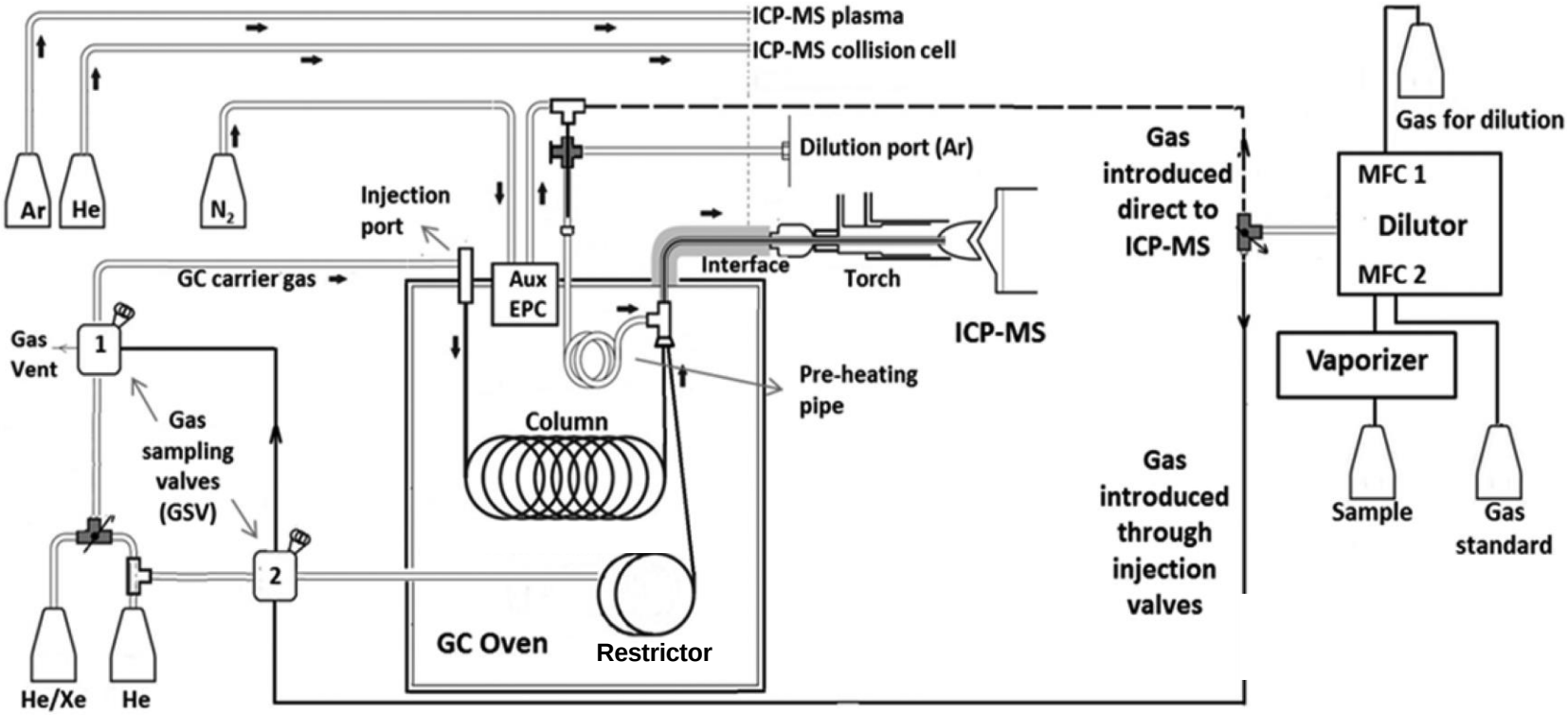
During this work many different technics have been tested. A lot of suppliers of instruments have been evaluated. Some part of the method development in cooperation with different universities.

- University of Graz in Austria
- University of Oviedo in Spain
- University of Umeå in Sweden

The Journey to success

A GC-ICP-MS instrument was modified for simultaneous total and speciation analysis of gas and liquefied gas samples.

A diagram of the new GC-ICP-MS configuration is shown below.



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GC-ICP-MS Instrument

Vaporizer

- Liquefied samples are vaporized in the vaporizer.

Diluter

- Standards, samples and the gas used for dilution are connected to the gas dilutor.
- The diluter have five channels with mass flow controllers, were two are heated.
- It is possible to connect up to 12 different channels in the diluter

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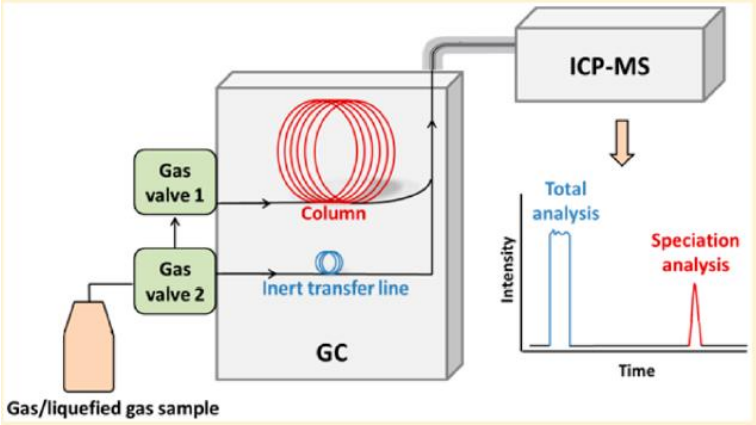
GC-ICP-MS Instrument

GC

- A three-way valve allows to direct the dilutor outlet gas flow to the GC through the gas sampling valves (GSV) 1 and 2. GSV1 and GSV2 are internally connected, so they are loaded at the same time.

- From GSV1 volume is injected through the injection port of the GC to the analytical column. In that way, speciation analysis of the different target species is carried out.

- Simultaneously, GSV2 volume is introduced directly into the GC-ICP-MS, total analysis is carried out



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GC-ICP-MS Instrument

Ethane, Propane and Butane is analyzed using vaporizer-dilutor-GC-ICP-MS

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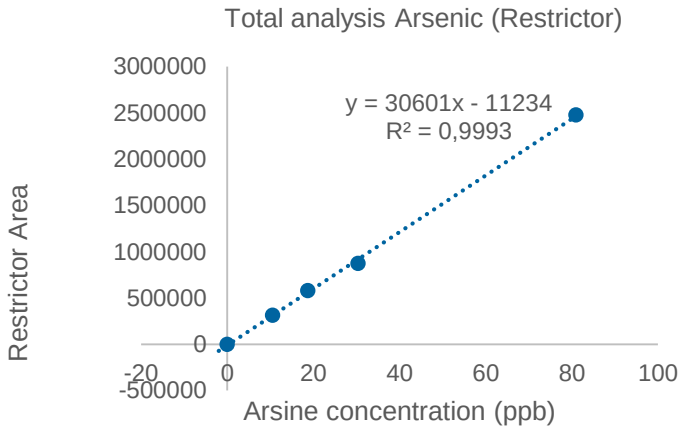
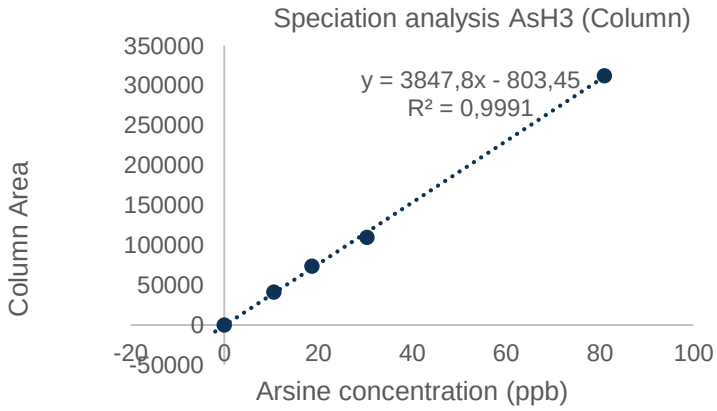
The method – external calibration

From the beginning we did a external calibration with a gas standard, AsH_3 in N2

Arsine in nitrogen standard			81	ppb
AsH3 flow	Ar flow	ppb AsH3	Area rest	Area col
0	100	0	0	0
30	200	11	313578	41106
30	100	19	579941	73821
30	50	30	874621	109717
30	0	81	2479214	312466
AsH3 flow	Ar flow	ppb AsH3	Area rest	Area col
13.675	1122.725	1	101544	9710
13.675	1122.725	1	112306	10783
13.675	1122.725	1	117619	11565
		Mean	110489.6667	10686
		Deviation	8190	931
		RSD (%)	7	9
			DL (ppt)	DL (ppt)
			70.31	231.16





Matrix effects were observed when we added hydrocarbons to the plasma.

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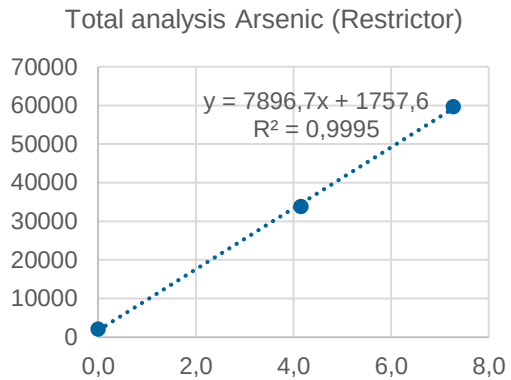
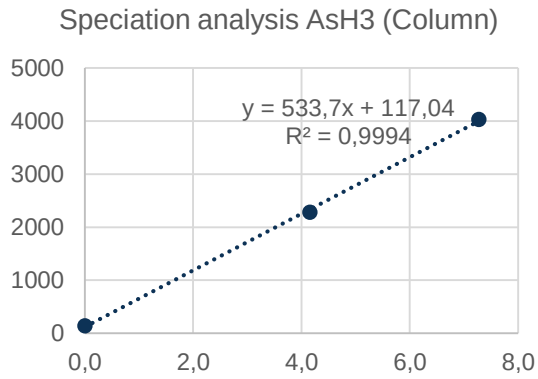
The method –Standard addition calibration

- Changed the method to standard addition calibration
- The diluter made this possible. We use two different gas standards.
  - AsH_3 in Nitrogen
  - PH_3 in Argon

		Arsine in nitrogen standard		83.1						
	GasMix	#2	#3	#4						
	Replicat	AsH3/N2 flow	Ar flow	Sample flow	Total flow	ppb AsH3	Area rest	Area col		
	Blank	0	385	15	400	0.0	2086	141	0.06773	
	Add 1	20	365	15	400	4.2	33802	2278	0.06739	
	Add 2	35	350	15	400	7.3	59614	4030	0.06760	
						Restrictor		Speciation		
TK 2bb				Interception		1757.6		117.0		
Förgasare 3.2 bar				Slope		7896.7		533.7		
Dil. 0.25				Amount		0.2		0.2		
				Amount * Dilfactor		5.9		5.8		
				Sample: Propane from US (Houston)						





Result AsH_3 Calibration

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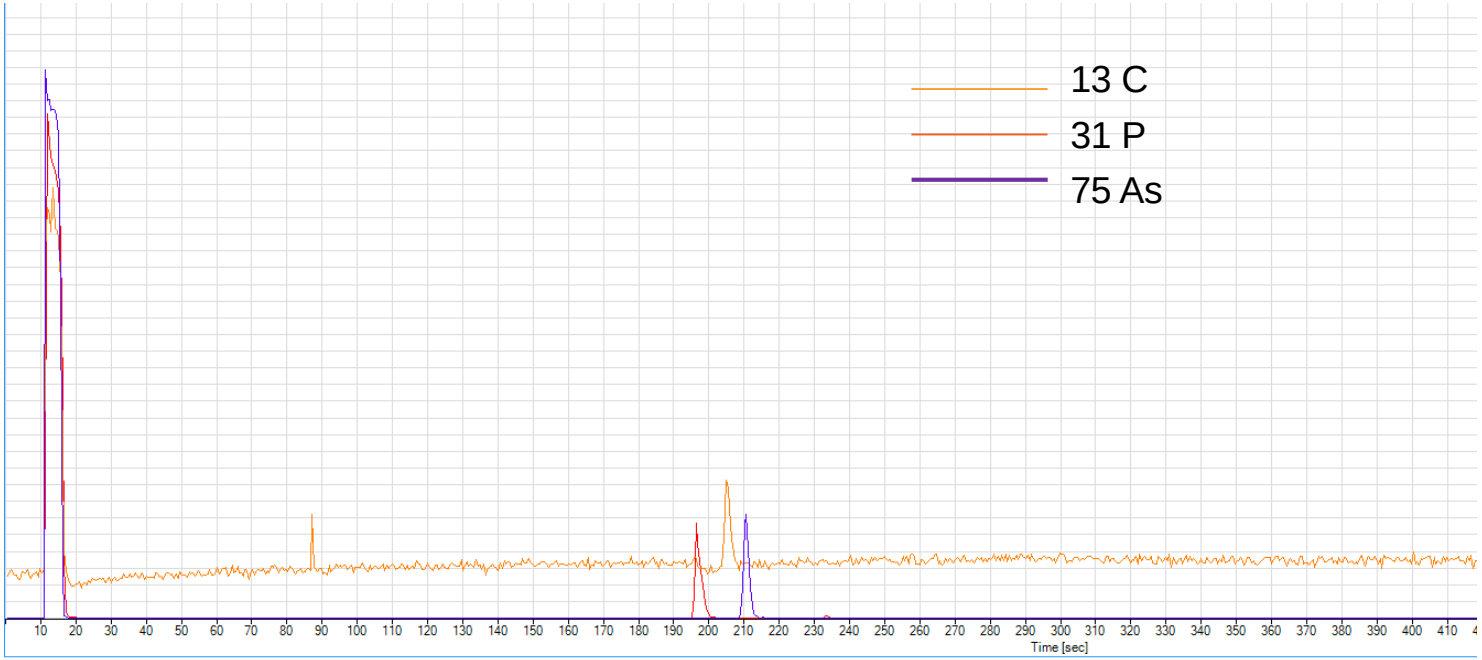
Analyses in Ethane

– Result from 2,4 wt-ppb AsH3 and 2,5 wt-ppb PH3



Color	Display	Mass	Range	Count	Avg Count
	☐	TIC	2.0E7	52332	
	☑	13	2.0E7	2582	
	☐	23	500	136	
▶	☑	31	5000	88	
	☐	39	5.0E4	654	
	☑	75	2.0E4	0	
	☐	124	1.0E5	48870	

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Conclusions

- To use GC-ICP-MS as a technic for direct measuring of Arsine and Phosphine in Liquefied Feedstock rather unique.
    - Compared to other laboratories using SPM or Super C we can analyze all elements with one instrument.
    - We are able separate Arsine and Phosphine which the other technics don´t.
    - We need no sample preparation
    - The method is really time saving.
    - The diluter can be programed to automatic sample sequence and injections.

- We have validated our method with calibration mixtures.
    - A proficiency test was made with other laboratories in Europe. A sample of propylene with Arsine was tested.
    - The result showed that our method and the university of Graz could measure Arsine while all the other laboratories found nothing.

Thank you

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