

# Mass Spectrometry

## I. Introduction

Mass spectrometry is an important tool in modern analytical techniques and in isotope separation. In this experiment, you will learn how to use a vacuum apparatus and perform qualitative and quantitative analyses on a commercial quadrupole mass spectrometer. This type of dynamic mass spectrometer is widely used due to its compact design in vacuum technology and residual gas analysis.

For the preparation and execution of the experiment, this manual contains in the appendix all necessary literature excerpts, operating instructions, and tables. The theoretical principles will not be discussed in this section. Further literature is given at the end under section V.

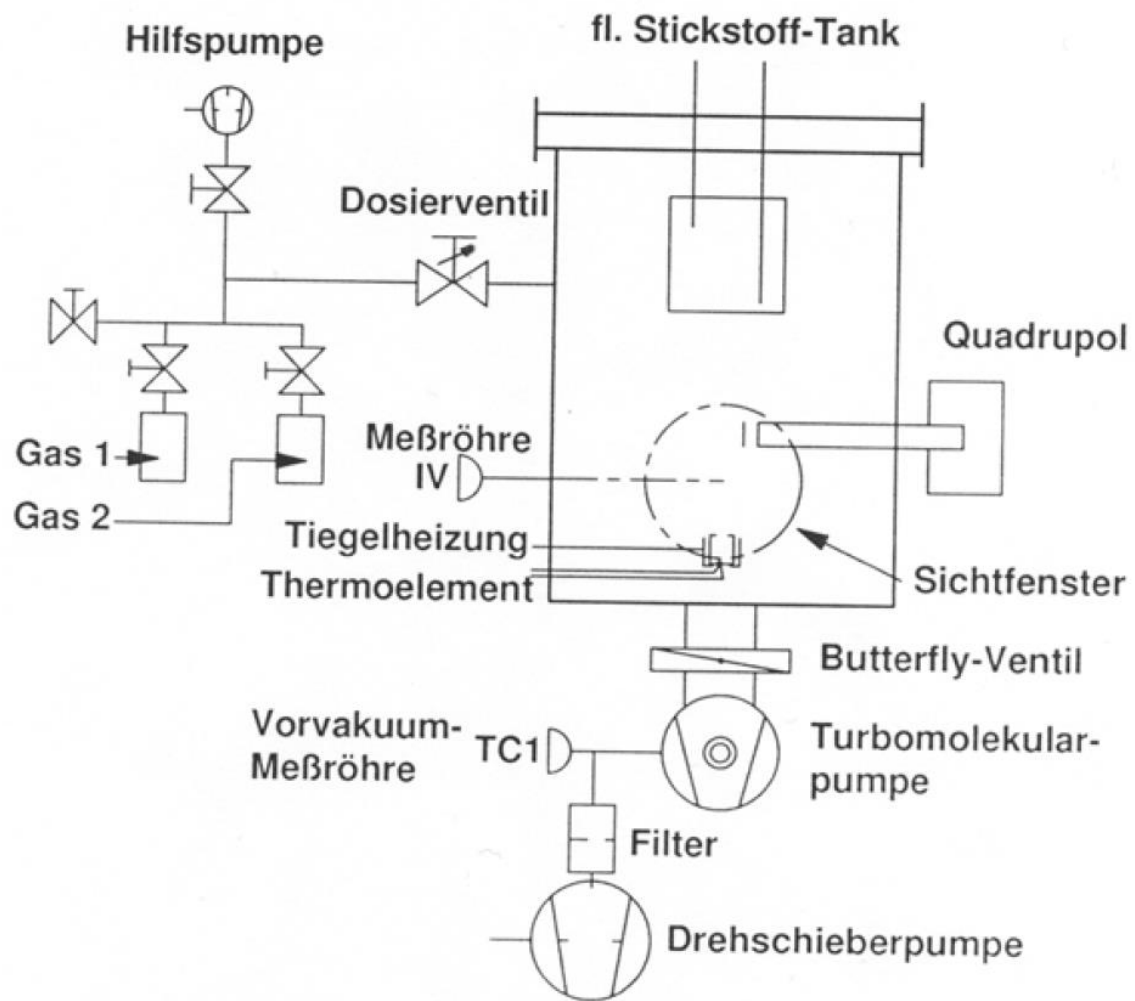
## II. Experimental setup

### 1. Vacuum system

A rotary vane pump is initially used to generate a high vacuum in the range of  $10^{-7}$  mbar, which generates a vacuum pressure of about  $3 \times 10^{-2}$  mbar. The second stage is a turbomolecular pump (70,000 rpm) flanged to the stainless steel recipient via a small butterfly valve. Due to the high rotation frequency the steel frame of the vacuum system should not be bumped when the turbopump is running! To prevent a backflow of oil vapor from the backing pump, an adsorption trap is installed between the turbopump and the rotary pump.

All elements of the high vacuum system are flanged with Cu metal gaskets. The quadrupole mass spectrometer, a heatable crucible with temperature control, and a stainless-steel tank for liquid nitrogen are inserted in the vacuum chamber. Various gases from pressurized cans or room air can be introduced via a dosing valve. The interior can be viewed through a window at the window at the front.

For total pressure measurement in the high-vacuum chamber, a Bayard- Alpert gauge is attached clearly visible in a glass bulb (IV). Please do not touch the glass bulb as fingerprints will be burned in. The forepump pressure is determined with a heat conduction manometer (Pirani type TC1). Both gauges are measured with a common control unit. This control unit also includes safety switches when the turbopump is switched on ( $p_1 < 1$  mbar) or the filament of the mass spectrometer is switched off ( $p > 2 \times 10^{-5}$  mbar).



## 2. The mass spectrometer

The quadrupole mass spectrometer MASSTORR FX operates in the mass range 1 - 200 amu. The instrument should only be operated in the pressure range  $p < 10^{-5}$  mbar! The partial pressures measured at the set mass can be read directly from the instrument in the unit "mbar". In the scan mode, a spectrum is run through in the set mass range and displayed on an xy-recorder or oscilloscope. In addition, two potentiometers have been installed for setting the electron energy and the electron current to generate the ions. The acceleration energy of the electrons can be read directly from a digital voltmeter. To determine the ion current please use the dependence on the potentiometer setting given in appendix. Standard spectra are run with  $E = 65$  eV and  $I_e = 1$  mA.

## 3. Crucible heating

A small boron nitride (BN) crucible is located below the ionization chamber of the spectrometer for evaporation of solid substances. The crucible (10 mm diameter) is closed with a lid. Evaporating material can escape into the vacuum system through a small opening in the lid. For thermal heating, the crucible is wrapped with a thin tantalum foil, which is attached to a current feedthrough and can be heated with an ac current (0 - 40 A). An iron-constantan thermocouple (Fe-CuNi) is inserted into the crucible for temperature determination. The resulting thermoelectric voltage is read out directly

via a digital voltmeter. It should be noted that the room temperature value must be added to the measured thermoelectric voltage.

#### **4. Gas inlet**

The selected gas is introduced via a dosing valve. Prior to this, the gas line should be cleaned of residual gases by pumping and flushing several times. The gases from the connected pressure cans (argon,  $C_xH_y$ ) are introduced via small fine-dosing valves. Room air can be admitted via a needle valve.

The fine-dosing valve allows precise adjustment of the gas pressure in the vacuum chamber over the entire pressure range. When introducing gas for the first time, operate it carefully in order to get a feeling for the handling of the valve. When closing the valve, make sure that the zero marks match again!

### **III. Experimental procedure**

#### **1. Introduction**

Familiarize yourself with the vacuum system and the mass spectrometer! Record a residual gas spectrum (or several sub-ranges) in the mass range 1 - 200 amu. Note: All spectra should be recorded under standard conditions ( $E = 65$  eV,  $I_e = 1$  mA)! Use different sensitivities to make smaller components visible. Explain the dominant lines, especially at  $m = 28, 32, 44$ .

Measure the dependence of the ion current or partial pressure on the electron current  $I_e$  for one line.

What is the behaviour of  $p(I_e)$ ? In which range should the emission current be set for further measurements?

Determine the mass resolution by measuring the line width at one line each in the range of small and large mass numbers. According to which definition can a resolution be given in a meaningful way? How does the resolution depend on  $m$ ?

#### **2. Emergence energy of argon**

Consider beforehand the gas supply to the vacuum chamber, possibly the filaments of the measuring tube and spectrometer should be switched off for a short time!

With the turbopump connected, let argon gas ( $m = 40$ ) flow into the chamber by using the dosing valve up to a constant maximum pressure  $p = 5 \times 10^{-6}$  mbar. Measure the emergence energies (ionization energies) of  $Ar^+$  and  $Ar^{++}$  up to about 100 eV. In the energy range of interest, choose small measurement intervals (0.5 eV). Compare your measurement result with values from literature. Possibly the electron energy should be readjusted for further measurements (?).

#### **3. Quantitative analysis**

For further measurements first determine the residual gas background at  $m = 14$  and  $m = 28$  as a function of the electron energy. Record a spectrum. Let room air into the chamber via the dosing valve up to the mentioned maximum pressure (!). Record a spectrum again. Index the spectrum with the aid of the cracking patterns and separate it down into its components. Consider only meaningful

air components! Use the maximum line from each group and determine the partial pressures by taking into account the relative sensitivities of the spectrometer for different ions. Determine the composition of air. Is the result reasonable? What are the possible sources of error? Compare the sum of the partial pressures (total pressure) with the pressure of the ionization gauge and discuss the result.

#### 4. Dissociation energies of nitrogen

First explain the reaction pathways for nitrogen ( $N_2$ ) under electron bombardment with respect to the lines at  $m = 14$  and  $m = 28$ . Measure both energies of dissociation and discuss possible influences of the background measured before.

Knowing the ionization energy for the nitrogen atom  $E_i(N \rightarrow N^+ + e^-) = 14.5 \text{ eV}$ , determine now the dissociation energies for the nitrogen molecule ion and for the neutral nitrogen molecule. Compare your result with values from the literature.

#### 5. Qualitative analysis

Allow an unknown gas  $C_xH_y$  to enter the chamber up to the maximum pressure and record three different spectra at excitation energies  $E = 15 \text{ eV}$ ,  $30 \text{ eV}$ , and  $65 \text{ eV}$ . With the aid of the cracking patterns determine the gas species. After identification, name characteristic lines after the assignment of the fragments. How can the formation of certain lines be qualitatively explained? What influence does the excitation energy have on the intensities?

#### 6. Thermal decomposition

First, record a residual gas spectrum!

Slowly heat the  $CaCO_3$  in the boron nitride crucible up to about  $500^\circ\text{C}$ . Correct the temperature determined from the thermoelectric voltage with the room temperature value.

What conclusions can be drawn about the decomposition of the  $CaCO_3$  from comparing the spectra?

During slow cooling, measure the partial pressure of the gaseous component as a function of temperature. Determine the enthalpy of decomposition from a suitable plot of  $p(T)$ . Compare the results with values from the literature.

#### 7. Residual gas analysis

Record a spectrum and determine a typical composition of the major components of the residual gas. Again, compare the total pressure with the value of the ionization gauge. Fill liquid nitrogen into the upper tank of the chamber. Wait a few minutes until the total pressure has stabilized. Take a spectrum again. How did the cold nitrogen tank ( $T = 77 \text{ K}$ ) change the composition of the residual gas?

### IV. Important notes

To evacuate the system, make sure that the venting valve of the turbopump is closed! If possible, the rotary vane pump and the turbopump should be switched on simultaneously. The turbopump starts

automatically when the set switching point of 1 mbar is reached. The turbopump and mass spectrometer can only be operated when the two measuring tubes are operating as these actuate the corresponding switching points of the pressure control unit.

After the turbopump has been switched off, it must be carefully vented immediately via the venting valve on the high vacuum side! If the recipient is not to be vented in the process the butterfly valve must be closed hand-tight beforehand.

If the measurement of the decomposition of calcium carbonate shows large deviations or an incorrect  $p(T)$ , it is possible that the crucible contents have completely decomposed. In this case the crucible must be removed and reloaded.

If the dosing valve no longer seals when closed, turn it a few scale divisions further. The zero mark should be readjusted with an Allen key. When the zero mark (engraved) specified by the manufacturer is reached the metal seal in the valve must be replaced.

## V. Literature

H.E. Duckworth, R.C. Barber, The Late V.S. Venkatasubramanian, Mass Spectroscopy, 2. Ed. Cambridge University Press, 1986 (FBC library, chem 3.6, 83A/784)

H. Budzikiewicz, Massenspektrometrie, 3. Aufl., Verlag Chemie Weinheim, 1992 (FBC library, chem 3.6, 81A/403)

Jürgen H. Gross, Mass Spectrometry, Springer 2017, DOI: [10.1007/978-3-319-54398-7](https://doi.org/10.1007/978-3-319-54398-7)  
K10plus-PPN: 1659355850, PPN: 490767753 ([Direktlink](#))

James M. Thompson, Mass Spectrometry, K10plus-PPN: 1014255643, PPN: 518073408 ([Direktlink](#))

## VI. Appendix

	Methan	Ammoniak	Wasser	Neon	Acethylen	Ethylen	Kohlenmonoxid	Stickstoff	Ethan	Stickstoffmonoxid	Methanol	Sauerstoff	Schwefelwasserstoff	Argon	Propen	Propan	Kohlendioxid	Distickstoffdioxid	Acetaldehyd	Ethanol
m/e	16 CH <sub>4</sub>	17 NH <sub>3</sub>	18 H <sub>2</sub> O	20 Ne	26 C <sub>2</sub> H <sub>2</sub>	28 C <sub>2</sub> H <sub>4</sub>	28 CO	28 N <sub>2</sub>	30 C <sub>2</sub> H <sub>6</sub>	30 NO	32 CH <sub>3</sub> O	32 O <sub>2</sub>	34 H <sub>2</sub> S	40 A	42 C <sub>3</sub> H <sub>6</sub>	44 C <sub>3</sub> H <sub>8</sub>	44 CO <sub>2</sub>	44 N <sub>2</sub> O	44 C <sub>2</sub> H <sub>4</sub> O	46 C <sub>2</sub> H <sub>5</sub> O
2	3.0		0.7										0.2							
12	2.4				2.5	2.1	4.5									0.4	6.0			
13	7.7				5.6	3.5										0.5	0.1			
14	18.6	2.2			0.2	6.3	0.6	7.2	3.4	7.5					3.9	2.5		12.9		
15	35.8	7.5							4.6	2.4					5.9	3.9		0.1		
16	100.0	80.0	1.1				0.9			1.5		11.4					8.5	5.0		
17	1.2	100.0	23.0																	
18		0.4	100.0								1.9									5.5
19			0.1																	2.3
20			0.3	100.0										10.7						
21				0.3																
22				9.9																
24					5.6	3.7											1.2			
25					20.1	11.7			4.2							0.7			1.6	
26					100.0	62.3			23.0						11.3	7.6			4.8	
27					2.8	64.8			33.3						38.4	37.9			9.1	8.3
28					0.2	100.0	100.0	100.0	100.0		6.4					59.1	11.4	10.8	4.5	23.9
29						2.2	1.1	0.6	21.7		64.7					100.0	0.1	0.1	2.7	6.9
30							0.2		26.2	100.0	0.8					2.1		31.1		6.0
31										0.4	100.0							0.1		100.0
32										0.2	66.7	100.0	44.4							
33											1.0	0.1	42.0							
34												0.4	100.0							
35													2.5							
36													4.2	0.3		0.4				
37																				
38															13.4	3.1				
39														0.1	20.3	4.9				
40															74.0	16.2				
41														100.0	29.0	2.8				
42															100.0	12.4		3.9		
43															69.6	5.1		9.2	2.9	
44																22.3		26.7	7.6	
45															26.2	100.0	100.0	45.7		
46															0.8	1.3	0.7		34.4	
																0.4	0.2		16.5	

	Stickstoffdioxid	Ameisensäure	N-Butan	Aceton	Isopropanol	Essigsäure	Ethylenglykol	Vinylchlorid	Schwefeldioxid	Schwefelkohlenstoff	Benzol	Toluol	O-Xylol	Trichlorethylen	Schwefelhexafluorid	Tetrachlorkohlenstoff	Alcatel Öl 200	Santovac Öl 5	Alcatel Öl 215	Vorpumpöl
m/e	46 NO <sub>2</sub>	46 CH <sub>2</sub> O <sub>2</sub>	58 C <sub>4</sub> H <sub>10</sub>	58 C <sub>3</sub> H <sub>6</sub> O	60 C <sub>3</sub> H <sub>8</sub> O	60 C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	62 C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	62 C <sub>2</sub> H <sub>4</sub> Cl	64 SO <sub>2</sub>	76 CS <sub>2</sub>	78 C <sub>6</sub> H <sub>6</sub>	92 C <sub>7</sub> H <sub>8</sub>	106 C <sub>8</sub> H <sub>10</sub>	130 C <sub>7</sub> HCl <sub>3</sub>	146 SF <sub>6</sub>	152 CCl <sub>4</sub>	430	446	546	500
2																				
12		3.3																		
13		2.9																		
14	9.6									1.0										
15			5.3				17.9													
16	22.3	5.2							5.2											
17		17.1																		
18					6.6		3.0													
21																				
22																				
24								0.8												
25								13.2												
26			6.3	8.3				33.7												
27			37.1	8.0	13.7		5.3	100.0				6.0	11.0							
28		17.2	32.6			5.6		36.5		5.4										
29		100.0	44.2	4.3	10.1	13.6	17.4										15.1			
30	100.0	1.6					2.8													
31					5.6	4.3	100.0													
32								10.4	21.8						5.1					
33							28.6													
34								0.4	1.0											
35							7.9							39.9	4.6	6.4				
36							4.5								2.0					
37				2.1										12.8		2.2				
38				2.3						6.4	5.6	5.7								
39			12.5	3.0	5.7					14.2	20.6	17.4						9.9		
40																				
41			27.8	2.1	6.6	4.5											39.1		32.8	
42			12.2	7.0	4.0	14.5	2.3										18.3		6.0	
43			100.0	100.0	16.6	100.0	6.7										68.2		73.3	
45		10.0				4.9	2.5		17.3											
46		47.6			100.0	93.6													1.9	
47	37.0	60.9																		
48								4.8						25.0		12.7				
49								49.9												
50								0.4								4.3				
51								2.3		13.7	7.1							7.7		
52										10.6	10.7	16.1		7.6			29.3	2.5		
53										19.4								7.1		
54														7.4				5.2		
55																		3.2		
56																	100.0		72.7	
57																			22.4	
58			12.5	27.1													25.6		100.0	
59					3.4												94.1		4.7	
60						57.7							64.9							
							62 (83.5)	64 (100) (27.4)	76 (100) (100)	77 (14.4) (10.1)	63 (10.1) (10.1)	77 (12.7) (12.7)	62 (20.9) (5.3)	70 (5.3) (19.4)	82 (19.4) (19.4)	69.70 (71) (64)	62.63 (71) (64)	77.78 (77) (81)		
							64 (27.4)	66 (4.9)	77 (100) (100)	78 (13.8) (8.4)	65 (13.8) (8.4)	78 (8.4) (8.4)	95 (100) (26.3)	89 (12.7) (12.7)	54 (12.7) (12.7)	81.83 (85) (85)	77 (79.0) (79.0)	81 (106) (106)		
								78 (8.9)	90 (9.1) (100)	91 (100) (100)	90 (9.1) (100)	91 (100) (100)	105 (24.1) (69.9)	130 (100) (100)	127 (94.7) (100)	119 (94.7) (100)	ETC (127.129) (129)	137 (139.140) (149)		
									92 (75.5)	92 (75.5)	92 (75.5)	92 (75.5)	134 (26.0)				ETC (160)	130 (130)		

Craig & Harden, Vacuum **16**, 67 (1966) The Interpretation of Mass Spectra in Vacuum Measurement  
 Ch. Biguenet, Spectrométrie de masse. Index des spectres LE VIDE n° 159-160 p. 161-175 - Mai 1972.  
 "Compilation of Mass Spectral Data" by A. Cornu and R. Massot, published by Heyden & Son Limited, London.

# RELATIVE SENSITIVITIES OF VARIOUS GASES COMPARED TO NITROGEN (1.0)

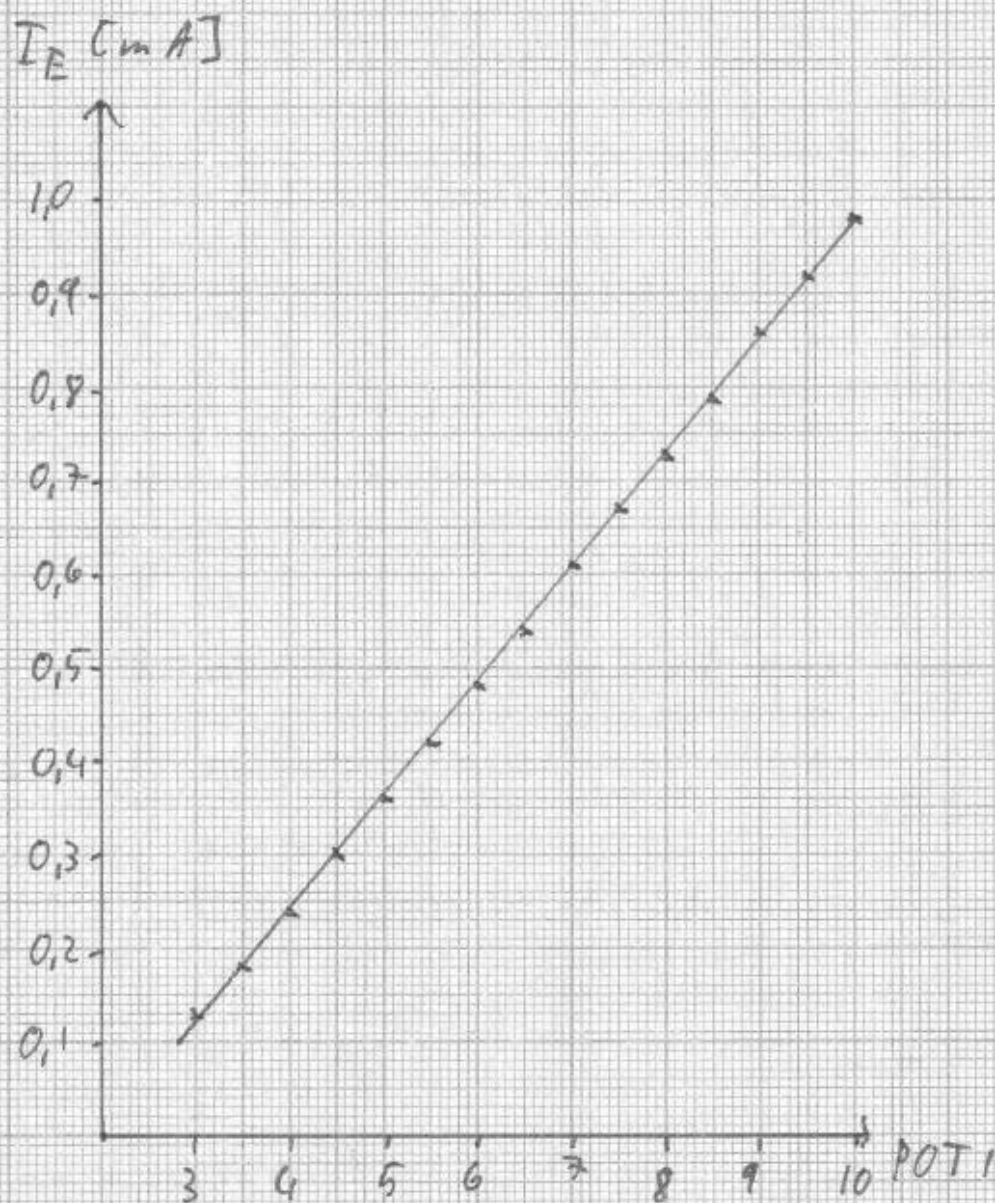
Gas	H <sub>2</sub>	He	CH <sub>4</sub>	H <sub>2</sub> O	Ne	CO	N <sub>2</sub>	O <sub>2</sub>	Ar	CO <sub>2</sub>	Kr	Xe	Hg
Relative Sensitivity	0.7	0.23	1.08	1.17	0.24	1.09	1.00	0.62	1.16	0.9	0.8	1.56	1.3

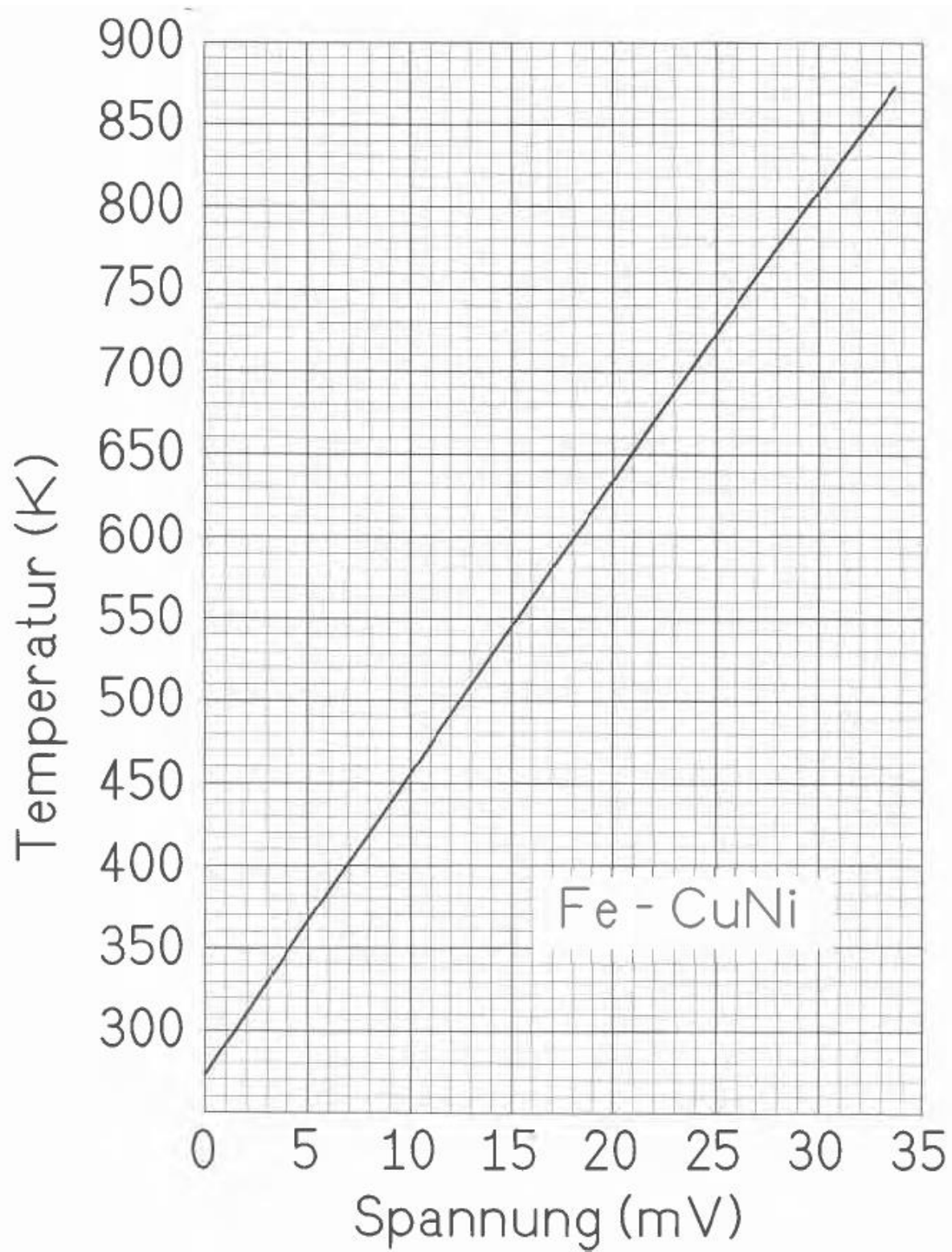
The approximate total hydrocarbon partial pressure may be obtained by dividing the 43-peak by a relative sensitivity factor of 1.4 \*\*  
The approximate split of the 28-peak between nitrogen and carbon monoxide may be calculated using the 12 and 14 peaks, together with the cracking pattern data given in 01.611.

\*\*see Craig, R. D. and Harden, E. H. Vacuum 17, p 67 (1966)



### Emissionsstrom in Abhängigkeit von der Potentiometerstellung





Thermopaar	Eisen – Konstantan (Eisen – Kupfernickel)		
Kurzzeichen	Fe – Konst (Fe – CuNi)		
Grundwert- reihe nach	DIN 43 710		
Kennzeichen	blau		
Temperatur °C	Grundwert mV	zulässige Abweichung °C    mV	
0	0		
20	1,05		
50	2,65	3,0	0,17
100	5,37	3,0	0,17
200	10,95	3,0	0,17
300	16,56	3,0	0,17
400	22,16	3,0	0,17
500	27,85	3,8	0,22
600	33,67	4,5	0,27
700	39,72	5,3	0,33
800	46,22	6,0	0,40
900	53,14	6,7	0,48
-20	-1,02		
-40	-2,03		
-60	-2,98		
-80	-3,89		
-100	-4,75		
-120	-5,53		
-140	-6,26		
-160	-6,93		
-180	-7,56		
-200	-8,15		

# DISSOCIATION PRESSURE OF CALCIUM CARBONATE

Temp. °C	mm/Hg	Temp. °C	mm/Hg	Temp. °C	mm/Hg	Temp. °C	mm/Hg	Temp. °C	mm/Hg
550	0.41	727	44	819	235	894	716		
587	1.0	736	54	830	255	898	769 atm.		
605	2.3	743	60	840	311	906.5	1.151		
671	13.5	748	70	852	381	937	1.770		
680	15.8	749	72	857	420	1082.5	8.892		
691	19.0	777	105	871	537	1157.7	18.687		
701	23.0	786	134	881	603	1226.3	34.333		
703	25.5	795	150	891	684	1241	39.094		
711	32.7	800	183						