



Environmental Trace Analysis by Means of Supersensitive GC-IMS J. W. Leonhardt, H. Bensch, K. Standtke, IUT Ltd. Berlin, Germany

ABSTRACT

A new supersensitive Ion Mobility Sensor was developed and checked by IUT Ltd., which meets new demands. The systems arrives the following technical parameters:

- ionization source: 50 MBq - tritium source
- amplifier: $5 \cdot 10^9$
- resolution: better 50
- sensitivity: $\approx 1 \mu\text{g}/\text{m}^3$ for many compounds
(acetone, ethers, phosphoric acid, esters, nicotine, drugs, halocarbons, etc.)

The use of tritium sources is an advantage in comparison with other IMS being equipped by nickel-63, the application of which is rather critical in respect of the radiation protection. On the other hand an integrated separation column allows to reduce interferences by matrix effects.

The most important applications are as follows:

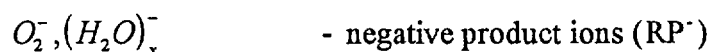
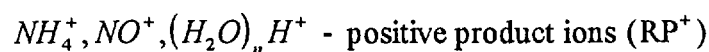
- The detection of nicotine in ambient air .
- The selective on line determination of halogenated compounds.
- The analysis of breath air.
- Chemical warfare agent detection.
- Analysis of S-Lost in mixtures of organic compounds.
- The characterisation of food.
- Explosive detection.

IUT GC-IMS can be used in production control easily. The price is about 2 times lower as other conventional techniques like GC and GC/MS.

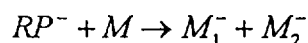
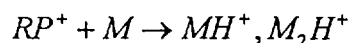
INTRODUCTION

Ion Mobility Spectrometry - IMS - is a new technology in analytical chemistry. The ambient air samples are ionized by means of beta particles. Produced ions at atmospheric pressure are collected after passing a homogenous electrical field. The time of flight - or better time of drift - reflects ion properties like mass, charge, charge distribution, structure, cross section etc. The number of ions at certain drift time is a function of the compound concentration in the sample. In the case of purified air the moisture content should be below 10 ppm.

Thermodynamically stable cluster ions are produced:



These ions are available always in the ion source. The collected ions build up the so named product ion peaks. If electropositive or electronegative compounds (M) enter the ionisation source of an IMS charge transfer reactions take place and new product ions are formed:



These product ions will have their own specific drift times and the spectrum is changed.

Cross sensitivities may arrive in compound mixtures due to quenching processes. Compounds of interest can be masked by other compounds in the mixture. Especially in the case of supertrace determination 10^{-9} to 10^{-10} high concentrations of other compounds in the ranges of ppm do disturb the correct analysis. Therefore the IMS is equipped by a separation column, which separates quenching compounds..

EXPERIMENTAL

The combination of a high resolution IMS cell with a GC separation column was studied to analyse sophisticated mixtures in the trace region. First results of IMS integrated GC-columns in the inner loop of an IMS were reported 1995 [1,2] due to the detection of aromates.

The scheme of the GC IMS is given in fig. 1. The drift cell used has a 10 cm drift length and the electrical field strength of $E = 0.7 \text{ KV/cm}$. A 10 Mbq Tritium source is used as ionisation source. The 50 ml/min carrier gas through the column and the 450 ml/min drift gas is special purified synthetic air or nitrogen. The column the gas sampling system and the detector can be heated up to 100°C . The resolution arrived is about $R \geq 100$. Electronic parts are a special designed amplifier with $5 \cdot 10^9 \frac{\text{V}}{\text{A}}$ and having a rise time better than $50 \mu\text{s}$. The pulser is adapted to the detector, the pulse width is 10 microseconds. The device was tested for compounds, which have to be measured in complicated mixtures especially.

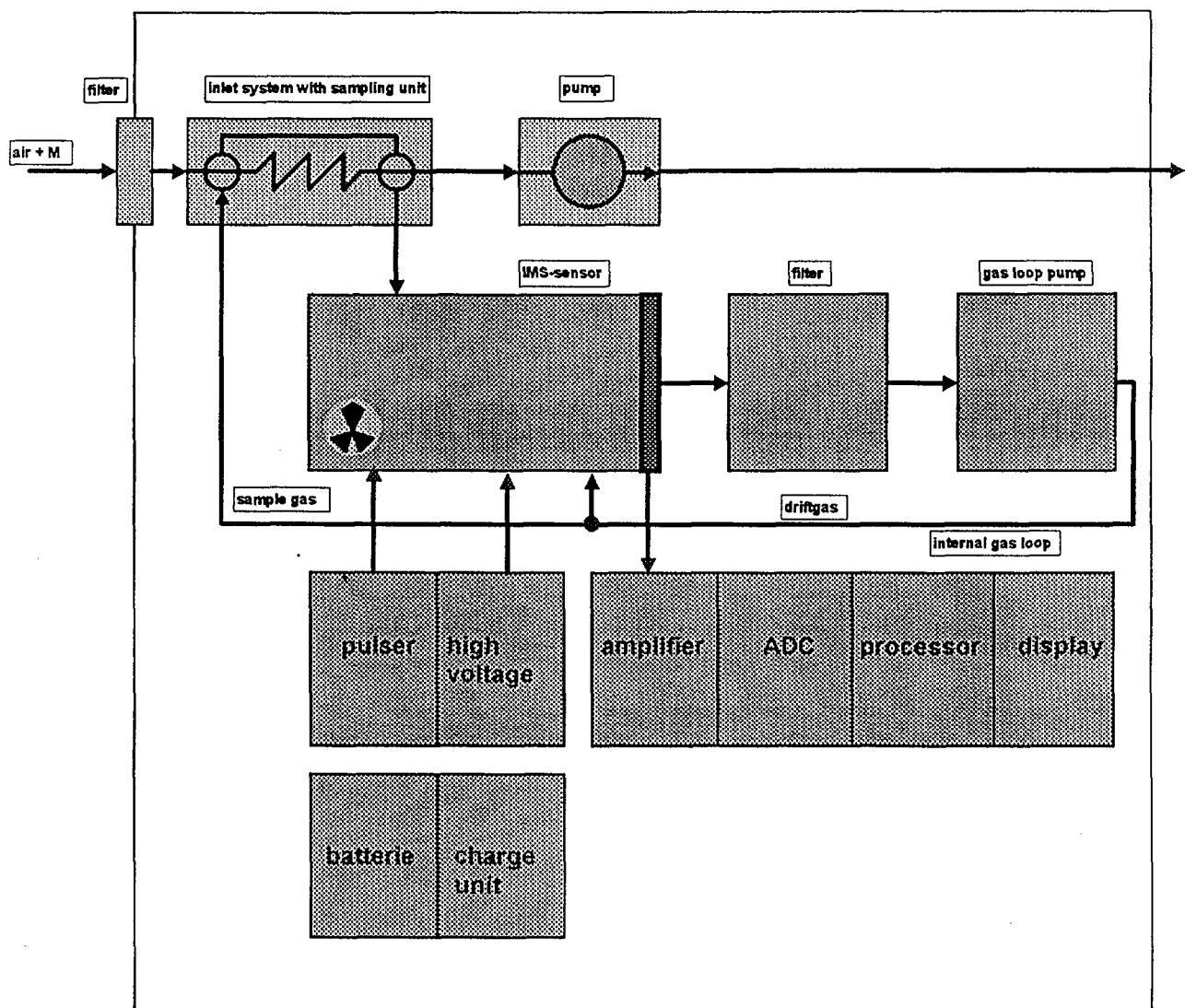


Fig. 1: scheme of the GC-IMS

RESULTS

(1) The detection of nicotine in ambient air

The problem of nicotine detection in ambient air is of high interest for smoking and even more for non-smoking people. Due to the high toxicity there is the need to arrive detection limits of 1 - 2 ppb in mixtures of aerosols and other organic compounds. The gas inlet system and separation columns are heated up to 80°C. As shown in fig. 2 the nicotine has a monomer peak at 10,44 ms and a dimer peak at 15,20 ms. There is a good chance to see the trace concentration. Analysing a smokers breath air there is a mixture of formaldehyde, alcohol's and other compounds of large concentrations, which cover the nicotine Peaks. GC IMS is a very good tool to overcome this situation and separate the nicotine.

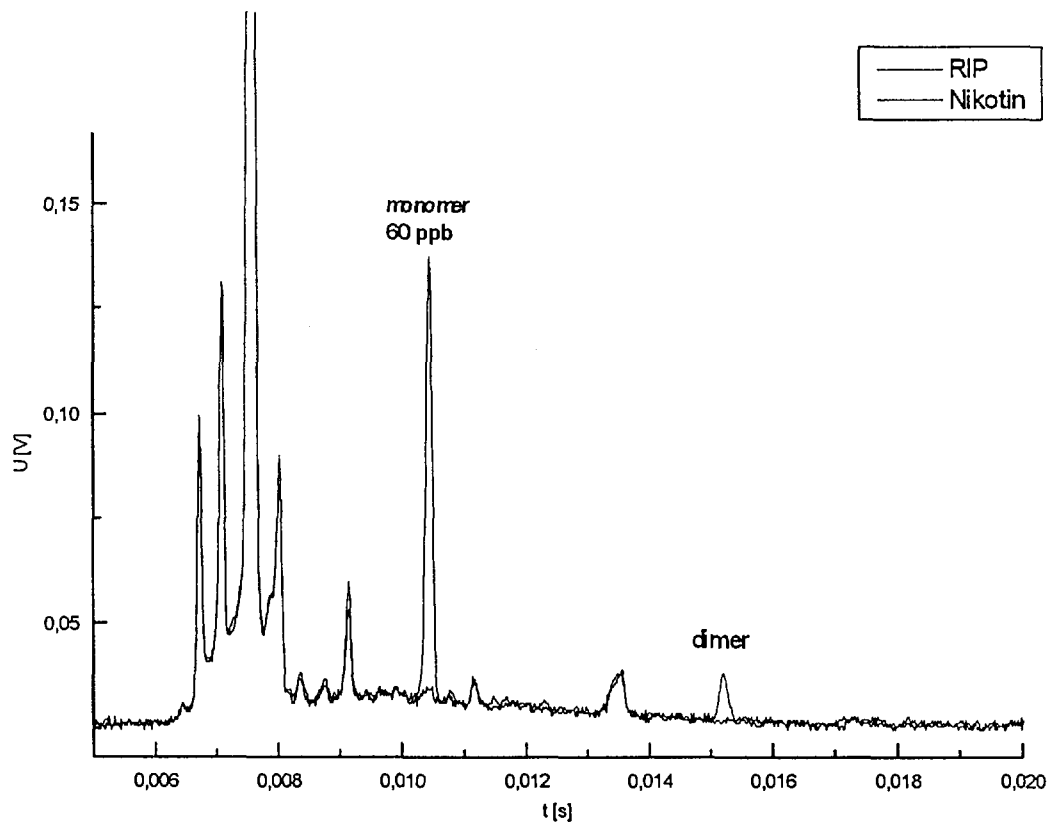


Fig. 2: Detection of nicotine by GC-IMS

(2) The detection of halogenated hydrocarbons

The analysis of these compounds uses the formation of negative ions. One example carried out by means of IMS is the trace termination of ω -Chloracetophenon (teargas) down to 0,5 ppb or 2,5 $\mu\text{g}/\text{m}^3$.

The characteristic spectrum of that are two Chlorine peaks due to Cl^- and Cl_2^- and the main Peak $\text{M}(\text{H}_2\text{O})^-$ and its dimer ion $\text{M}_2(\text{H}_2\text{O})^-$. Using the IUT-GSM sampling unit the delaboration of hand granates of world war II was controlled successfully at 1997.

(3) The analysis of breath air

The group of LINDINGER [3] in Innsbruck have designed a large mass-spec using the proton transfer reaction to produce ions like in the IMS. There were studied the remaining compounds like formaldehyde, alcohol's, acetone and also esters of the fatty acids and showed the correlation between them and possible diseases like diabetes and malfunctions of the liver. Checks of these compounds by means GC/IMS and of living persons of the lab confirmed these results. As an simple example the fig. 3 gives the spectra of 2 persons, who concumend alcohol 5 and 3 days before the check. Some research activities together with medical groups are in progress.

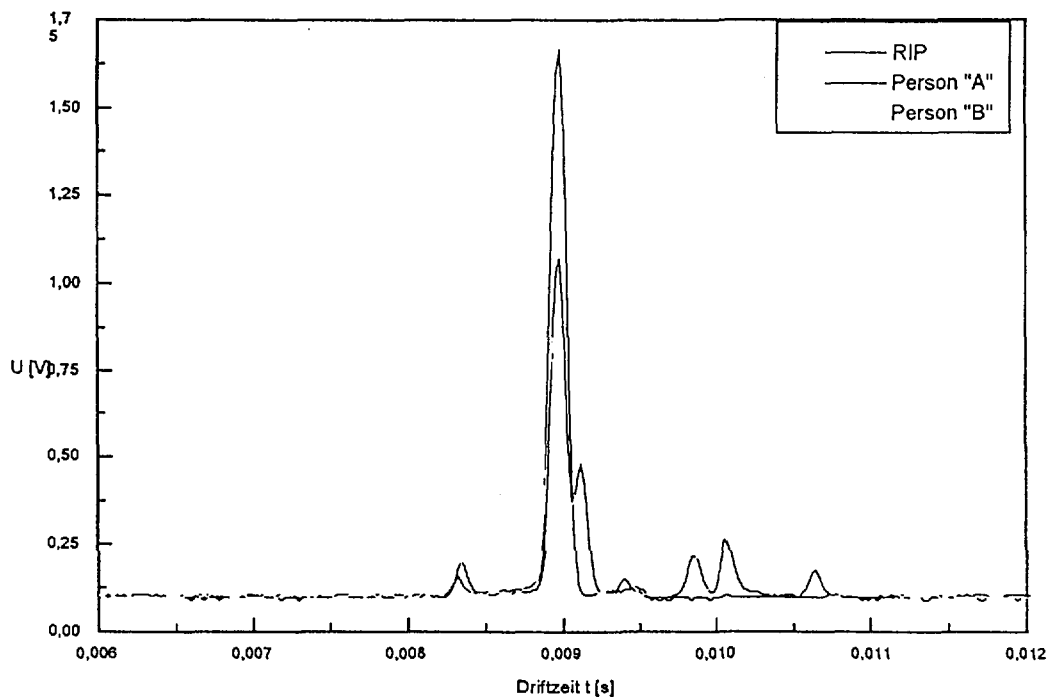


Fig. 3: Direct analyse of breath with GC IMS

(4) Chemical warfare agent detection

First application of IMS is due to CWA detection and Graseby Ionics from UK have available the suitable military equipment. The new designed IUT-GSM often is used in civil clearing of old battle grounds or former production sites. Its good sensitivity is documented by means of the Prince Maurits Laboratory in the Netherlands, which show the sarin detection limit around $\leq 1 \mu\text{g}/\text{m}^3$ that means 0,2 ppb. The absolute mass used in the sample is 0,5 μg . Meanwhile this analysis is done without a separation column. In fig. 4 the sarin peak at the concentration of $7 \mu\text{g}/\text{m}^3$ is demonstrated.

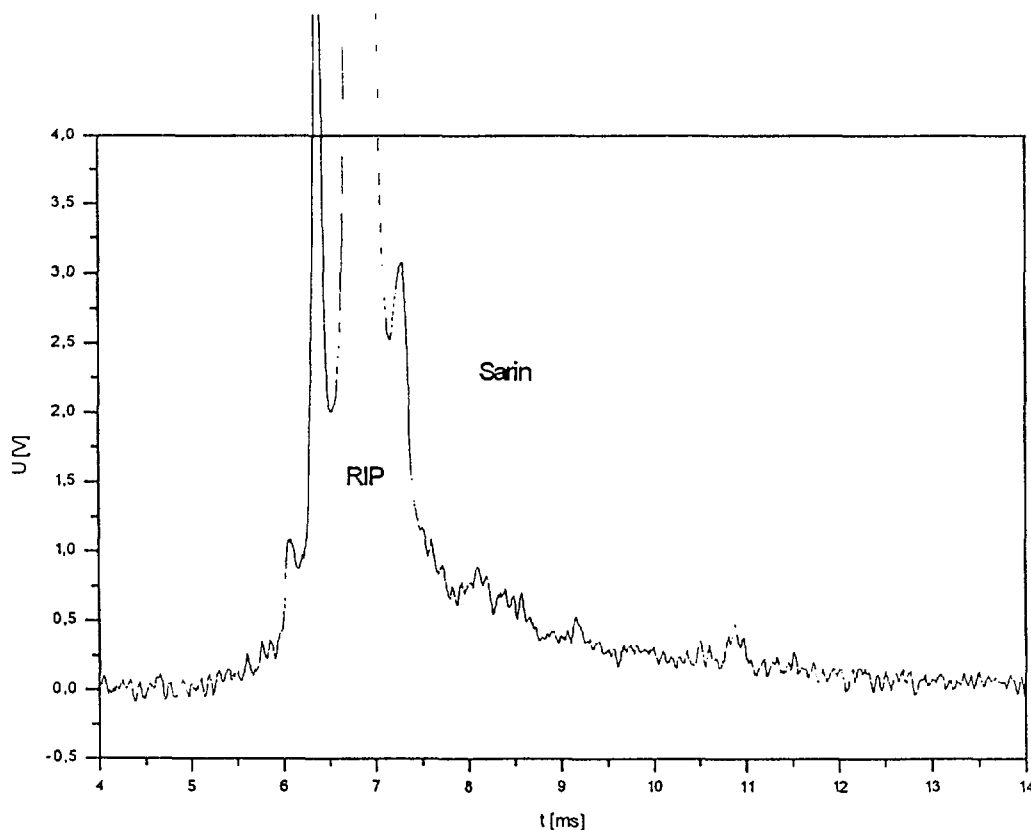


Fig. 4: IMS-spectrum of $11 \mu\text{g}/\text{m}^3$

(5) Analysis of S-Lost in mixtures of organic compounds

The problem of chemical warfare detection in different mixtures has been studied in the Fraunhofer Institute of Environmental Toxicology [4]. Also using a laboratory arrangement of a IUT GC IMS the detection of S-Lost in Trichlorethen, 1,4Oxathian and dithian was studied at 0 and 50 % relative humidity.

The advantage of this system was confirmed. Moisture influence is decreased. S-Lost can be detected in the positive and negative mode. The positive signal seems to give a better sensitivity by a factor of 2 - 3. The fig. 5 gives the S-Lost signal. Unfortunately the used GC/IMS has a reduced sensitivity in consequence of the sample dilution by the carrier gas passing the separation column, which is to be estimated a factor of 10 - 20. Also the ionization source is relatively weak, which could be increased if necessary.

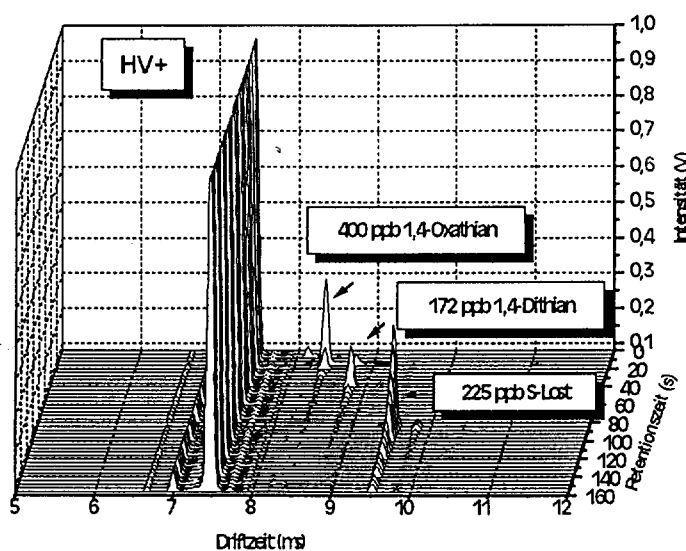


Fig. 5: S-Lost in a mixture of 1,4 ocathian and 1,4 Dithian

(6) The characterisation of food

The GC/IMS opened up a new dimension to identify the quality of food and products of gallantry by means of their three dimensional IMS spectra as fingerprints. There was studied the applications of common interest at least of our secretary in the IUT: coffee quality, mushroom, spices.

(7) Explosive detection

Many questions we had due to the sniffing techniques for fast explosive identical monitoring. Not only the costumes control and airport security are interested - mainly people from the pioneers and similar service is concerned to find landmines not having any metal. By the way we did some studies by labelled compounds to determine the TNT vapour pressure about a personal land mine covered by some 5 cm of earth. The was to find them directly besides dogs noses, which may be sensitive enough to sense some thousand molecules. We think that one other way is the application of neutron gauges, which we developed successfully [5].

The best result we had was to sense a little bit from the TNT from a German missile V2, which was delaborated by our help [6].

CONCLUSIONS

The IMS application in Analytical Chemistry is slowly growing. IMS does complete other analytical techniques in industry and in the consumption sphere. The large potential of IMS is not really touched yet. But IMS is the best portabel analytical instrument today, which provide us with specific analytical information about chemical compounds in ambient air, which concentrations are in the range of microgram/m³. In table I relative drift times and minimal detectable concentrations are listed for selected organic compounds.

References

- [1] J.W. Leonhardt, W. Rohrbeck, H. Bensch: A High Resolution IMS For Environmental Studies, Proc. Int. Spec. Workshop, August 95, Cambridge
- [2] DP
- [3] Lindinger
- [4] H. Sohn, J. Steinhansens: Internal Report on Huse of the IMS for Workersprotection, IUCT, Mai 1997
- [5] W.Katzung, G. Harfst: ECSTASY Informationsschrift WIRD, Verlag Deutsche Polizeiliteratur GmbH, 2. Aufl. 1994
- [6] J.W. Leonhardt: Landmine By Means of Gas Sensors, Proc.Int.Conf. RRAI 1996, Berlin, in preparation

Table I gives some selected examples:

Remarks:

- 1) About 200 chemical compounds are measured at IUT GmbH and their spectra are available here.
- 2) Any other compound may be measured in the IUT-lab.

Compound	$\frac{T_M}{T_{RP}}$	$\frac{T_D}{T_{RP}}$	$\frac{T_T}{T_{RP}}$	MDC in ppb	Ionization
Alcohols					
Methanol	0.97	1.03		20	$\beta(+)$
Ethanol	1.06	1.15		10	$\beta(+)$
Butanol	1.19	1.41	1.68	10	$\beta(+)$
Heptanol	1.42	1.81		10	$\beta(+)$
Tetrahydrofurfuryl alcohol	1.16	1.43		10	$\beta(+)$
Cyclohexanol	1.28	1.35	1.58	10	$\beta(+)$
Cresol	1.14			10	$\beta(+)$
Alkanes					
Heptane	1.12			50	$\beta(+)$
Nonane	1.55			50	$\beta(+)$
Isooctane	1.03	1.11	1.16	50	$\beta(+)$
Cyclohexane	1.04	1.09	1.13	50	$\beta(+)$
Aldehyde					
Formaldehyde	0.99			10	$\beta(+)$
Butylaldehyde	1.13	1.22	1.30	10	$\beta(+)$
Heptylaldehyde	1.35	1.72		10	$\beta(+)$
Propionaldehyde	1.04	1.16	1.33	10	$\beta(+)$
Amines					
Amphetamine	1.13	1.67		1	$\beta(+)$
Hydrazine	1.04	1.14		10	$\beta(+)$
Nicotine	1.38	2.12		2	$\beta(+)$
Diaminopropane	0.86	0.91	1.31	10	$\beta(+)$
Diaminopropane	0.93	1.34	1.75	10	$\beta(-)$
Diaminobutane	0.86	0.92	1.26	10	$\beta(+)$
Diaminobutane	0.91	1.34	1.75	10	$\beta(-)$
Hexamethylmethylen- tetraamine	0.96	1.17		10	$\beta(+)$
Nonafluorobutylamine	1.44			1	$\beta(-)$
Hexylamine	0.86	0.92	1.29	1	$\beta(+)$
Dimethylformamide	1.04	1.26		1	$\beta(+)$
Dimethylurea	0.91	0.94	1.10	1	$\beta(+)$
Methylhydrazine	1.24			1	$\beta(-)$
Methylhydrazine	0.85	0.92	1.05	1	$\beta(+)$
Aromates					
Benzene	1.00			5	UV
Toluene	1.02			5	UV
p-Xylene	1.08			5	UV
Cumene	1.15	1.17		5	UV
Ethylbenzene	1.20	1.60		5	$\beta(+)$
Phenol	1.27			10	$\beta(-)$
Nitrobenzene	1.26	1.55		10	$\beta(-)$
Chlorophenol	1.33	1.69		10	$\beta(-)$
Jodbenzene	0.95			10	$\beta(-)$
Dimethoxybenzene	1.16	1.29	1.61	10	$\beta(+)$
Arsine	1.03	1.16		10	UV

Carbon acids					
Acetic acid	1.06	1.17		10	$\beta(+)$ ($\beta(-)$)
Esters					
Ethylacetate	1.11	1.36		1	$\beta(+)$
Ethylacetoacetate	1.18	1.39	1.62	1	$\beta(+)$
Aceticacidethylester	1.11	1.36		1	$\beta(+)$
Ammoniumacetate	0.85	0.91	0.95	1	$\beta(+)$
Phthalsäurediethylester	1.05	1.15		1	$\beta(+)$
Phthalsäuredibutylester	1.19	1.40		1	$\beta(+)$
Diocylester	1.11	1.28	1.36	1	$\beta(+)$
Ethers					
Diethylether	1.08	1.25		1	$\beta(+)$
Divinylether	1.20	1.69	1.75	1	$\beta(+)$
Halogenated Hydrocarbons					
Dichlorethane	0.91	0.98		5	$\beta(-)$
Trichlorethylene	0.93	0.96	1.44		$\beta(-)$
Dibromomethane	0.93	0.96	1.05		$\beta(-)$
Dibromoethane	0.93	0.96	1.05		$\beta(-)$
Dibromopropane	0.93	0.96	1.05		$\beta(-)$
Dibromobutane	0.93	0.96	1.05		$\beta(-)$
N-Butylchloride	0.91	0.98	1.04		$\beta(-)$
Isobutylchloride	0.91	0.96	1.34		$\beta(-)$
Trichlorfluoromethane	0.97	1.03			$\beta(-)$
Amylchloride	0.91	0.98	1.04		$\beta(-)$
Amylchloride	1.29	1.75			$\beta(+)$
Chlorbromomethane	0.93	1.03	1.50		$\beta(-)$
Chloroacetonitryl	0.91	0.98	1.14		$\beta(-)$
Chlorotrimethylsilane	1.21	1.36			$\beta(-)$
Ketons					
Acetone	1.12			1	$\beta(+)$
Acetophenone	1.20	1.58		1	$\beta(+)$
Benzophenone	1.36	1.95			$\beta(+)$
Hexanone	1.21	1.47	1.50		$\beta(+)$
Acethylacetone	1.12	1.34	1.46		$\beta(+)$
Acethylacetone	1.05	1.26			$\beta(-)$
Ethylmethylketone	1.07	1.27		1	$\beta(+)$
Phosphororganic compounds					
Malathion	1.13	1.37		1	$\beta(+)$
Trikresylphosphate	1.69	2.49		3	$\beta(+)$
tert-Dibutylmalonate	1.04	1.27			$\beta(+)$
Dibutylsulfite	1.32	1.84			$\beta(+)$
Tributylphosphite	1.19	1.41	1.56	1	$\beta(+)$
Pyridine					
Pyridine	1.02	1.27		10	$\beta(+)$
2-Dimethylpyridine	1.67	1.40		10	$\beta(+)$