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ANALYTICAL APPLICATIONS OF ION MOBILITY SPECTROMETRY

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ABSTRACT. Ion Mobility Spectrometry is, first at all, a vapors' identification technique by measuring their ionic mobilities in the gaseous phase and at atmospheric pressure, under the influence of a weak electric field. The applications of Ion Mobility Spectrometry (IMS) could be separated into the use of IMS instrument as stand-alone spectrometer and its use in hyphenated technologies (as a detector following chromatographic techniques or as a separator before a mass spectrometer). By using the IMS technology a wide range of chemical compounds (both organic and inorganic) at trace detection levels can be detected, but the most spectacular applications of the Ion Mobility Spectrometry are the military/security ones (chemical warfare agents, explosives and illicit drugs). However, there is an increasing trend towards the civilian applications, like the industrial process monitoring and the detection of the pollutants. This paper's goal is to summarize the applications of Ion Mobility Spectrometry, which is definitely one of the most powerful trace detection techniques available today.

1. Introduction

In Ion Mobility Spectrometry (IMS), a powerful and promising trace detection technique that appeared in 1970 *[1,2]*, the two main steps that occur are ionization of a gas (or vapors), followed by separation of ionic species resulted in a drift tube, under the driving influence of an electric field with low intensity (under 300 V/cm), at or near atmospheric pressure *[3,4,5]*.

It can be emphasized that because of the versatility of Ion Mobility Spectrometry, detectors based on its principle promise to satisfy a wide range of practical applications, from explosives, chemical warfare agents and drugs detection to monitoring air pollutants *[3,4]*. Many IMS applications are not laboratory applications but field applications, who have totally different specifications. For instance, IMS has became attractive as a field technique due to its physical and mechanical simplicity of instrumentation and also to its low cost electronics, comparing with other bulk and complex systems (such as vacuum pumps used in mass spectrometers).

Using an ion mobility spectrometer one can made some separations very easily, but the other are impossible; for example, some anestezic gases were

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separated (even the isomers), but hexane can't be separated from carbon dioxide (because none of them is "seen" in IMS).

It is worthy to say that Ion Mobility Spectrometry is practically the backbone of defense systems against chemical warfare agents in all NATO armies, that it helps real-time detection of explosives and illicit drugs and that, last but not least, it contributes to industrial hygiene standards observance and to environment protection *[3,4]*.

Usually the IMS spectrometer can be used as a chemical analyzer only if the target analyte has very different ionization characteristics as compared with the other sample components, because of the competitive charge exchange in the ionization region of the ion mobility spectrometer cell. Currently the IMS technology has not predictive or interpretative properties when mixtures which contain compounds with similar ionization parameters have to be analyzed *[4,6]*.

The advantages of Ion Mobility Spectrometry are:

- ☺ analytical flexibility, because it can be applied to analyze both organic and inorganic vapors, and also can be monitored both positive and negative ions.
- ☺ very fast response (the drift times are in the millisecond range, up to several dozens ms); so, a complete analysis cycle will take only several seconds, and consequently we can speak here about real-time response
- ☺ very good sensitivity, in the parts-per-billion (ppb) and even parts-per-trillion (ppt) range without any preconcentration
- ☺ good selectivity; it can be improved by using dopants and/or different ionization sources
- ☺ the analysis is done at (or near) atmospheric pressure, and not in vacuum like in mass spectrometry
- ☺ the instrumentation is very robust and can be easily miniaturized *[3]*.

Of course, IMS has a number of major disadvantages:

- ☹ the theoretical concepts concerning ion mobility spectrometry were not yet perfectly defined
- ☹ there are not comprehensive models for the response characteristics
- ☹ the dynamic range is quite limited, which in turn don't encourage the quantitation.

2. Coupling IMS with other analytical techniques

Hyphenated analytical techniques are now more and more used because of their great advantages. In the most common case, the first step is a separation one, and the second gives spectral information about separated substances *[4]*.

The molecular ions generated in the IMS instrument can be injected directly into a quadrupole mass spectrometer. It is very important to say at this point that in almost all the cases the identification of the ions generated in the IMS spectrometer is performed by using mass spectrometry *[3,4]*. So, the IMS/MS tandem is a very powerful analytical tool, widely used to analyze/ identify the ions that are formed by atmospheric pressure chemical ionization *[4,7]*. Since the analytical applications of IMS will certainly reflect also the effects due to contaminants/matrix of the sample, only the use of the IMS/MS tandem can prove with a high degree of confidence if a given IMS response is generated by the target analyte *[7]*.

The ion mobility spectrometer can be used also as an interface between a gas chromatograph and a mass spectrometer, and so it is obtained a complex analytical chain: GC/IMS/MS. In this particular situation, the sample analyzed by IMS is just a specific GC peak, and using mass spectrometry the identification of ions is made.

It is interesting to note that the first use of an ion mobility spectrometer was in a GC/IMS chain, when some disadvantages due to chemical ionization were reduced *[8,9]*. In such a chain, the chromatographic column serves as sample introduction system for IMS spectrometer, and this will avoid the competitive charge exchange between 2 or many chemical compounds (of course, only if we don't have some GC peak co-elution) and also will avoid sample overloading.

The possibilities for using ion mobility spectrometer as a chromatographic detector are:

☺ the tandem IMS spectrometer - gas chromatograph (GC/IMS) *[10,11]*
☺ the tandem IMS spectrometer - liquid chromatograph (LC/IMS) *[12,13]*
☺ the tandem IMS spectrometer - supercritical fluid chromatograph (SFC/IMS) *[14]*.

3. Detection of vapors using IMS

3.1. Basic concepts

Since its appearance in 1970, IMS spectrometer was quickly seen as an useful sensor for trace vapor analysis and it is not at all surprising that the military used this new technology to detect chemical warfare agents *[4]*. However, IMS instruments were evaluated as environmental sensors or used in the industrial processes control only since 1980 *[15]*.

It is important to emphasize here that by neglecting the IMS spectrometers used by armed forces to detect and monitor chemical warfare compounds, the number of IMS units used as field monitoring instruments is still low. The good news is that the situation tends to a change, due to several reasons:

☺ IMS instrumentation is better and cheaper
☺ the need to protect the environment is continuously increasing
☺ threshold values in the regulations are lower, and consequently the old analytical techniques can't help the user *[3,4]*.

As any other analytical technique, the usefulness of IMS for a particular application is to be judged on an individual basis; the factors that must be considered include detection limits, response time, matrix interferences, the cost and the portability.

3.2. Applicability fields of IMS technology

Ion mobility spectrometer can be set to detect a great diversity of chemicals, both organic and inorganic. This device has been considered for a long time as an ideal detector for organic vapors monitoring, but it can also be used to detect many inorganic gases. In the bibliographic reference *[3]* can be found an exhaustive list (with about 170 bibliographic references) of practical applications of Ion Mobility Spectrometry.

There are many applications, but with a minimum systematization these can be classified as follows:

- alkanes, alkenes (at extremely low water vapor levels) *[16]*
- organophosphoric compounds: insecticides (of type Malathion, Parathion, Dichlorvos) *[17]* and chemical warfare agents (nerve gases likeTabun, Sarin, Soman, VX and others) *[18]*
- organic compounds with nitro functional group: explosives (nitroglycerin, TNT, EGDN, ammonium nitrate, RDX, PETN, etc.) *[19,20]*
- isocyanates: MDI, TDI *[21]*
- metalcarbonyls: nickel tetracarbonyl *[22]*
- inorganic compounds: halogens (Cl_2, Br_2, I_2) *[23]*; acid gases (HCN, HCl, HF, HI, HNO_3) *[24]*, ammonia *[25]*, phosgene *[7,26]*, NO_2/N_2O_4, ClO_2 *[27]*
- organic amines, aliphatic and aromatic: aniline *[28]*, diethylamine, triethylamine *[29]*
- aromatics: benzene, toluene, xylenes, ethylbenzene *[30]*, PAHs (policyclic aromatic hydrocarbons) *[31]*
- solvents: furan, cyclohexanone, phenols, alcohols >C3, acrylonitrile, DMF, DMSO *[32,33]*
- chlorinated solvents: dichloromethane, Me bromide, Me chloride, $CHCl_3$, CCl_4, $C_2H_4Cl_2$, CH_3I *[34]*
- freons and CFCs (chlorofluorinated hydrocarbons) *[35]*
- anesthetics (Halothane, Enflurane, Isoflurane, Desflurane, Methoxy-flurane) *[36]*
- chlorinated alkenes: vinyl chloride, alyl chloride, tetrachloroethylene *[37]*
- aldehydes and ketones *[33,38]*
- organic acids & their esters *[39]*
- chlorinated pesticides *[40]*
- propelants/rocket fuels: hydrazine, monomethylhydrazine, dimethyl-hydrazine, N_2O_4 *[41]*
- drugs: analgesics; illicit drugs (cocaine, heroine, amphetamines, ephedrine, THC from cannabis) *[42,43]*
- water and soil monitoring: PAHs and VOCs in water *[44]*; amines and chlorinated solvents in waste water; pesticides in soils
- applications in semiconductor industry: arsine, diborane, NF_3, PCl_3; contamination of Si wafers and their QC; N-methylpyrolidone *[45]*
- chlorinated phenols (used as wood preservatives) *[46]*
- perfumes, flavors and aromatic oils *[47]*
- some “exotic” applications: wood species characterization *[48]*; exobiology studies *[49]*; pheromone detection; monitoring the degree of freshness of fish or other organic matters (by monitoring aliphatic amines); micro-organisms detection, in particular detection of biological warfare agents (using pyrolysis or enzymatic techniques) *[50,51]*; nicotine detection in cigarette factories *[52]*.

3.3. Industrial and environmental applications

These categories of applications use two classes of IMS spectrometers:

1. Fixed-point monitors, used to detect, monitor and measure the concentration of an analyte (or a chemical class of compounds). The

measurements are performed continuously, and the instrument keep the same location; this way will result a concentration vs. time profile.

2. Hand-held portable instruments, which are used especially to detect gas/vapor leaks. These instruments will generate concentration vs. location profiles.

A very suggestive example for industrial hygiene applications is the list from the company *ETG (Environmental Technology Group) Inc. [3]* and presented here in Table 1.

Table 1.

Application groups of the IMS in industrial hygiene and air monitoring

Compound	*M.D.L. [ppm]*	*Compound*	*M.D.L. [ppm]*
ACID AND STACK GASES/VAPORS:			
HCN	0.1	Phosgene $COCl_2$	0.1
HCl	0.1	HNO_3	0.1
HF	0.1	NH_3	0.1
HI	0.1	NO_2	0.1
HALOGENS:			
Chlorine Cl_2	0.1	Iodine I_2	0.005
Bromine Br_2	0.1		
ORGANIC AMINES:			
Aliphatic amines	0.005	Aniline	0.005
Aromatic amines	0.005	Methylenedianiline	0.010
ISOCYANATES:			
TDI	0.005	NDI	0.005
1,6-Diisocyatohexane	0.1	H12MDI	0.1
TDA	0.005	TXMDI	0.1
SOLVENTS:			
Alcohols	0.1	Phenols	0.1
Furans	0.1	Ketones	0.01
Ethers	0.1	Esters	0.01
Acetonitrile	0.01	Acrylonitrile	0.01
Cyclohexanone	0.01	Toluidine	0.1
Chlorinated solvents	1.0		
GASES IN THE SEMICONDUCTOR INDUSTRY:			
NF_3	0.1	PCl_3	0.1
OTHER CHEMICALS:			
Aldehydes	0.1	Vinyl acetate	0.1

Nitrobenzene	0.005	PCBs	0.1
H_2S	1.0	Mercaptans	0.1

where M.D.L. is the Minimum Detectable Limit.

Major applications (industrial and environmental) deal with many toxic compounds and industrial emissions that are dangerous to people or environment *[15]*.

3.4. Drugs, explosives and chemical warfare agents detection

Currently there is a considerable current of interest for the detection of illicit drugs, explosives and chemical warfare agents. In fact, IMS systems were and still are intensively used as screening devices for persons and baggages/goods.

Concerning the IMS detection of illicit drugs (and explosives), a serious problem is the "collection" of enough molecules to obtain a response, because most drugs and explosives have very low vapor pressures. As a matter of fact, the key word is here the preconcentration sampling *[53-55]*.

A typical military application is field detection of the chemical warfare agents. IMS spectrometers are extremely sensitive in the positive operation mode to organophosphoric compounds (nerve agents); in the negative mode, IMS instruments detect easily blister agents (like mustard gas) *[56,57]*.

4. Laboratory applications of IMS

4.1. Ionic mobility measurement

The reduced mobility K_0 of an ion represents a qualitative parameter useful for its identification, quite like is the retention time in gas chromatography.

It is interesting to note that the use of some "reference ions" (from compounds called *calibrants*) with well known mobilities would lead to obtain sets of "universal" reduced mobilities. Until now, such a standard compound fully accepted does not exist yet, but 2,4-lutidine (proposed by Karpas, having K_0 = 1,95 cm^2/Vxs *[58]*), DMF (dimethylformamide) and nonanone in the positive mode of operation, and bromide ions, phenol, trinitrotoluene and methylsalicylate *[7]* in the negative mode of operation appear to be serious candidates.

The methodology used to measure the reduced mobilities is quite simple: instrumental and operational parameters are set, the sample is introduced and finally drift times are measured. Of course, mass spectrometric identification of IMS product ions is the unique procedure that can certify the assignment of a product ion peak *[29,59]*.

4.2. Studies of ions' structure

Isomers separation and identification using IMS was observed very soon (in 1974), in a study concerning mono- and di-halogenated nitrobenzenes *[60]*.

Some typical examples for isomers detection are:

1. the isomers of aliphatic amines *[58]*
2. anilines *[61]*
3. diamines and aminoalcohols *[62]*
4. geometric isomers E/Z *[63]*.

Collision section measurements. Using IMS studies on isomers or on homologous series of compounds one can obtain structural information, and specifically one can calculate the transversal collision integral Ω_D of the ion-molecule pair *[64]*.

Large atomic clusters and biomolecule studies. As well as reduced mobilities information, drift tube studies can also supply valuable information about the kinetics of ion-molecule reactions and about the equilibria involved in these processes *[65,66]*.

5. Future trends in IMS

In the last two decades Ion Mobility Spectrometry has developed in an explosive manner, so that it is now a powerful and quite less expensive tool for the detection and quantitation of a very large number of chemical compounds at trace levels, directly or after a chromatographic preseparation. Currently IMS is extensively used to monitor directly several chemical categories, such as chemical warfare agents, explosives and illicit drugs *[3,4]*.

Latest significant trends in Ion Mobility Spectrometry regarding its applications are:

- ➲ use of selective techniques for sampling and dynamic range broadening
- ➲ use and implementation of new signal processing techniques for IMS signal, such as Fourier transform and neural networks
- ➲ the emerging of biological applications
- ➲ manufacturing of portable GC/IMS and IMS/MS instrumentation
- ➲ use on a larger scale of the non-radioactive ionization sources.

An increasing interest is currently directed towards atmospheric pollutants monitoring, but also towards analyzing directly, with little if any sample preparation, liquid and even solid samples.

Although IMS could be seen today as a mature technology, it still remains in many fields and application niches a brand new technique. Its low detection limits, speed and simplicity of the instrumentation reserve to IMS a strategic place in analytical chemistry between the universal non-specific detectors (like ECD and FID detectors) and more powerful qualitative techniques (like mass spectrometry).

BIBLIOGRAPHY

[1] Karasek, F.W., Res. Dev. 1970, 21(3), 34.

[2] Cohen, M.J.; Karasek, F.W., J. Chromatogr. Sci. 1970, 8(6), 330.

[3] Bocoş-Binţinţan, V., "Spectrometria de mobilitate ionică", Editura Presa Universitară Clujeană, Cluj-Napoca, 1998.

[4] Eiceman, G.A.; Karpas, Z., "Ion Mobility Spectrometry", CRC Press, Boca Raton, FL, 1994.

[5] Carr, T.W. (Ed.), "Plasma Chromatography", Plenum Press, New York, 1984.

[6] Siegel, M.W., "Atmospheric pressure ionization", in "Plasma Chromatography", Plenum Press, New York, 1984, 95.

[7] Bocoş-Binţinţan, V., "Studies on phosgene and chlorine by ion mobility spectrometry and mass spectrometry", PhD Thesis, "Babeş-Bolyai" University, 2000.

[8] Rokushika, S.; Hatano, H.; Hill, H.H., Jr., Anal. Chem. 1987, 59, 8.

[9] Campbell, D.N.; Vora, K.N.; Davis, R.C., U.S. Patent 4.597.299: "Ion gate sample gas inlet control for gas chromatograph analyzer", July 1, 1986.

[10] Shumate, C.; Hill, H.H., Jr., Anal. Chem. 1989, 61, 601.

[11] StLouis, R.H.; Siems, W.F.; Hill, H.H., Jr., J. Chromatogr. 1989, 479, 221.

[12] McMinn, D.G.; Kinzer, J.; Shumate, C.B.; Siems, W.F.; Hill, H.H., Jr., J. Microcolumn Sep. 1990, 2, 188.

[13] Geniec, J.; Mack, L.L.; Nakamae, K.; Gupta, C.; Kumar, V.; Dole, M., Biomed. Mass Spectrom. 1984, 11, 259.

[14] Tarver, E.; Hill, H.H., Jr., "ECD-like response after supercritical fluid chromatography", West ACS Conf., Los Angeles, 1988.

[15] Roehl, J., Appl. Spectrosc. Rev. 1991, 26, 1.

[16] Bell, S.E.; Ewing, R.G.; Eiceman, G.A.; Karpas, Z., J. Am. Soc. Mass Spectrom. 1994, 5(3), 177.

[17] Eiceman, G.A.; Wang, Y.F.; Garcia-Gonzales, L.; Harden, C.S.; Shoff, D.B., Anal. Chim. Acta 1995, 306(1), 21.

[18] Adler, J.; Doering, H.-R., Zfl.-Mitt. 1990, 154, 75.

[19] Christophorou, L.G.; McCorkle, D.L.; Sauers, I., Anal. Chim. Acta 1982, 135(2), 179.

[20] Cohen, M.J.; Wernlund, R.F.; Stimac, R.M., J. Inst. Nucl. Mater. Manage. 1984, 13, 220.

[21] Brokenshire, J.L.; Dharmarajan, V.; Coyne, L.B.; Keller, J., J. Cell. Plast. 1990, 29, 123.

[22] Wernlund, R.F.; Cohen, M.J., Res. Dev. 1975, 26(7), 32.

[23] Karpas, Z.; Pollevoy, Y.; Melloul, S., Anal. Chim. Acta 1991, 249(2), 503.

[24] Bacon, A.T.; Reategui, J.A., U.S. Patent 5.095.206: "Method and apparatus for improving the specificity of an ion mobility spectrometer utilizing sulfur dioxide dopant chemistry", Mar. 10, 1992.

[25] Przybylko, A.R.M.; Thomas, C.L.P.; Anstice, P.J.; Fielden, P.R.; Brokenshire, J.L.; Irons, F., Anal. Chim. Acta 1995, 311(1), 77.

[26] Adler, J.; Doering, H.-R., Zfl.-Mitt. 1990, 154, 97.

[27] Bacon, A.T.; Getz, R.C., U.S. Patent 5.283.199: "Chlorine dioxide monitor based on ion mobility spectrometry with selective dopant chemistry", Feb. 1, 1994.

[28] Karasek, F.W.; Kim, S.H.; Rokushika, S., Anal. Chem. 1978, 50(14), 2013.

[29] Karpas, Z., Anal. Chem. 1989, 61(7), 684.

[30] Lubman, D.M., Anal. Chem. 1984, 56(8), 1298.

[31] Eiceman, G.A.; Anderson, G.K.; Danen, W.C.; Ferris, M.J.; Tiee, J.J., Anal. Lett. 1988, 21(4), 539.

[32] Karasek, F.W.; Cohen, M.J.; Carroll, D.I., J. Chromatogr. Sci. 1971, 9(7), 390.

[33] Karasek, F.W.; Kilpatrick, W.D.; Cohen, M.J., Anal. Chem. 1971, 43, 1441.

[34] Baim, M.A.; Hill, H.H., Jr., J. High Resolut. Chromatogr. Chromatogr. Commun. 1983, 6(1), 4.

[35] Cram, S.P.; Chesler, S.N., J. Chromatogr. Sci. 1973, 11(8), 391.

[36] Sacristan, E., U.S. Patent 5.455.417: "Ion mobility method and device for gas analysis", Oct. 3, 1995.

[37] Simpson, G.; Klasmeier, M.; Hill, H.H., Jr.; Atkinson, D.; Radolovich, G.; Lopez-Avila, V.; Jones, T.L., J. High Resolut. Chromatogr. 1996, 19(6), 301.

[38] Benezra, S.A., J. Chromatogr. Sci. 1976, 14(3), 122.

[39] Kim, S.H.; Karasek, F.W., J. Chromatogr. Sci. 1982, 234(1), 13.

[40] Louis, R.S.H.; Hill, H.H., Jr., J. High Resolut. Chromatogr. 1990, 13(9), 628.

[41] Eiceman, G.A.; Salazar, M.R.; Rodriguez, M.R.; Limero, T.; Beck, S.W.; Cross, J.H.; Young, R.; James, J.T., Anal. Chem. 1993, 65(13), 1696.

[42] Lawrence, A.H.; Elias, L., Bull. Narc. 1985, 37(1), 3.

[43] Lawrence, A.H., Anal. Chem. 1986, 58(6), 1269.

[44] Vandiver, V.J.; Leasure, C.S.; Eiceman, G.A., Int. J. Mass Spectrom. Ion Processes 1985, 66(2), 223.

[45] Budde, K.J.; Holzapfel, W.J., Proc.-Electrochem. Soc. 1992, 92-7, 271.

[46] Jones, D.; Brenton, A.G.; Games, D.E.; Brittain, A.H.; Taylor, S.; Kennedy, D.; Smith, P., Rapid Commun. Mass Spectrom. 1993, 7(6), 561.

[47] Karasek, F.W.; Keller, R.A., J. Chromatogr. Sci. 1972, 10(10), 626.

[48] Lawrence, A.H., J. Pulp. Pap. Sci. 1989, 15(5), J196.

[49] Kojiro, D.R.; Cohen, M.J.; Stimac, R.M.; Wernlund, R.F.; Humphry, D.E.; Takeuchi, N., Anal. Chem. 1991, 63(20), 2295.

[50] Smith, G.B.; Eiceman, G.A.; Walsh, M.K.; Critz, S.A.; Andazola, E.; Ortega, E.; Cadena, F., Field Anal. Chem. Technol. 1997, 1(4), 213.

[51] Dworzanski, J.P.; McClennen, W.H.; Cole, P.A.; Thornton, S.N.; Meuzelaar, H.L.C.; Arnold, N.S.; Snyder, A.P., Field Anal. Chem. Technol. 1997, 1(5), 295.

[52] Eiceman, G.A.; Sowa, S.; Lin, S.; Bell, S.E., J. Hazard. Mater. 1995, 43(1-2), 13.

[53] Garofolo, F.; Marziali, F.; Migliozzi, V.; Stama, A., Rapid Commun. Mass Spectrom. 1996, 10(11), 1321.

[54] Rodacy, P., SANDIA Natl. Lab. Report 1993, SAND-92-0229.

[55] Karasek, F.W.; Kim, S.H., Anal. Chem. 1975, 47(7), 1166.

[56] Doering, H.-R.; Hartmann, E., U.S. Patent 5.510.268: "Method and device for detecting substances in an ambient substance, in particular for detecting chemical warfare agents", Apr. 23, 1996.

[57] Allinson, G.; McLeod, C.W., J. Forensic Sci. 1997, 42(2), 312.

[58] Karpas, Z.; Stimac, R.M.; Rappoport, Z., Int. J. Mass Spectrom. Ion Processes 1988, 83, 163.

[59] Karpas, Z.; Cohen, M.J.; Stimac, R.M.; Wernlund, R.F., Int. J. Mass Spectrom. Ion Processes 1986, 74, 153.

[60] Karasek, F.W.; Kane, D.M., Anal. Chem. 1974, 46(6), 780.

[61] Karpas, Z.; Berant, Z.; Stimac, R.M., Struct. Chem. 1990, 1, 201.

[62] Karpas, Z., Struct. Chem. 1992, 3, 139.

[63] Carr, T.W., J. Chromatogr. Sci. 1977, 15(2), 85.

[64] Karpas, Z.; Berant, Z., J. Phys. Chem. 1989, 893, 3021.

[65] Clemmer, D.E.; Jarrold, M.F., J. Mass Spectrom. 1997, 32(6), 577.

[66] Giles, K.; Grimsrud, E.P., J. Phys. Chem. 1992, 96(16), 6680.