ANALYSIS OF GASES BY FOURIER TRANSFORM INFRARED SPECTROMETRY

Summary of PhD thesis

by

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INTRODUCTIONS, AIMS

The analysis of trace gases in the atmosphere has gained a special significance since the mankind has realised that global warming and stratospheric ozone depletion, acid rains and photochemical smog showed close correlation with the increasing amount of atmospheric pollutants. The study of physical and chemical processes, the understanding of the ways of interactions requires the knowledge of the composition, the spatial and the time distribution of the pollutants. For protection of human health, it is important to know the influence of toxic compounds existing in minor concentrations in our microenvironment. Due to these demands the various measurement techniques applicable in environmental protection have exhibited a tremendous progress. These technical achievements can be fruitfully adopted to solve many other problems of life and science.

In gas spectroscopy, the requirements toward suitable analytical tools are as follows: high sensitivity, selectivity, easiness of use, capability for *in-situ* measurements, etc. A number of methods have been developed from chemiluminescence to gas chromatography, as early developments, that are still in use in detection of gaseous pollutants. I the last decade special attention has been paid to spectroscopic techniques, since their use is favourable in many applications due to relatively low cost, fast and reliable detection. One of the most promising methods is the continuously progressing Fourier-transform infrared (FTIR) spectrometry.

The basic advantage of the FTIR technique is due to the fact that all atmospheric gaseous species (except homonuclear diatomic molecules) exhibit infrared absorption bands, therefore in addition to excellent selectivity it offers the possibility of simultaneous analysis of complex mixtures. It is a non-destructive method, it does not need complicated sample preparations, and by means of open-path field methods it offers the possibility of *in-situ* monitoring, providing continuous information on the concentration of pollutant gases.

The literature survey clearly demonstrates that FTIR gas spectrometry has been widely used in the last 15 years in the developed western countries, and some specific measurements are already standardised. In spite of these facts, the method still cannot be considered as fully developed; problems of quantitative analysis, automation, further developments of methodology and new analytical applications are still the subjects of contemporary research publications.

The first modern FTIR-based instruments of gas analysis (long path, 32 to 360-m gas cells, dynamically aligned spectrometers) were installed in Hungary about 10 years ago at the Analytical Chemistry Research Group of (Veszprém) Pannon University. An open path FTIR system capable of solving even more complex analytical problems was purchased at the

beginning of our research activity. (Due to economical considerations, the open path FTIR system is used jointly with the Chemical Institute of West Hungarian University).

After the installation of this modern and well equipped laboratory, a number of complex analytical problems have been solved at high scientific level.

The author of this Thesis joined this laboratory at the beginning of these developments, where his primary task was to organize a well operating experimental unit capable of solving practical problems of spectroscopic gas analysis. Our scientific efforts may soon gain a special significance, as a European Union Standard is expected to appear in the near future about applications of open path methods, which will stimulate full acceptance and widespread use of these methods in Hungary as well.

According to the above considerations, the aim of my work can be summarised as follows:

- installation of the instruments, learning the ways of their complex applications, and introduction of the methodology in Hungary;
- adaptation of the methods of sampling and sample preparation to specific techniques,
- practical realisation of qualitative and quantitative analysis using the existing computer softwares;
- professional survey of the published result, in order to formulate new and important research program;
- development of new and internationally acceptable FTIR gas analytical methods;
- solution of practical analytical problems which favour the application of FTIR spectrometry.

THESES

I. The basis for research in the field of FTIR gas spectrometry has been established.

I/1. The state of the art in the research field has been assessed and evaluated by two review articles published by us (the reviews amount to 130 pages and include 400 cited references).

I/2. The method of quantitative analysis has been developed based on the existing instruments and software and the problems and their solutions have been discussed. As a final goal a successful laboratory of FTIR gas spectrometry has been built up to adopt complex analytical applications.

II. A new method has been developed to collect a background spectrum for long path extractive FTIR measurements. It was named by us "shadow spectroscopy".

II/1. With the aid of the new method, a background spectrum can be collected in a fast manner, whereby the absorption of atmospheric water vapor and carbon dioxide in the sample spectrum can be compensated to such a high degree which cannot be reached by traditional methods (e.g. by using evacuated cell background followed by subtraction of reference library spectra of water vapor and carbon dioxide, or by using a "clean air" background).

II/2. The method was applied to detection of six volatile organic compounds and the detection limits have been strongly improved. On the other hand, the limitations of shadow spectroscopy have also been described.

II/3. The disturbing absorption of ozone in the sample spectra generated by the UV radiation has been compensated successfully by subtraction of own ozone reference.

III. The relationship between pressure and the shape of infrared spectral features of gases has been studied.

III/1. It has been shown that the difference between the pressure of the sample and reference can cause serious errors in quantitative analysis. New methods (CLS and half-width methods) have been developed to determine the total pressure by means of FTIR spectrometry at moderate spectral resolution of 0.5 cm^{-1}. These methods are applicable to the determination of total pressure in enclosed spaces (cavities) within any kind of infrared transparent material where a gaseous compound is present and shows resolvable rotational fine structure.

III/2. The CLS method was successfully applied to measure carbon monoxide concentrations and the total pressure in extremely small bubble-like gas cavities (with a diameter of about 1 mm) in the silica glass body of gas discharge light bulbs.

IV. The open-path FTIR field technique was applied in Hungary the first time to measure the concentration of gases (or vapours) originated from diffuse sources of pollution.

IV/1. The open-path measurements require totally different approaches as compared to those of conventional spectrometry. The spectral subtraction method was found to be the most suitable method for quantitative analysis in case of unknown situation when the open-path measurements were performed at relatively high (0.5 cm^{-1}) resolution, in contrast to the generally used CLS method which method is very sensitive to the presence of water vapour and carbon dioxide bands.

IV/2. The detection limits of each molecule have been determined according to the noise level of the residual spectra, since the method based on these experimental values are more realistic than those based on the noise level of the detectors.

IV/3. A tabulated comparison between open-path and extractive FTIR techniques has been performed on the basis of our own experimental experiences and of the available literature. The tabulated summary offers a great help in selection of the appropriate method of measurement, in proper judgement of the results and in identifying the incidental sources of errors and their elimination.

IV/4. A new method was developed for calibration of the open-path spectrometer by using a simple 10 cm pathlength gas cell in the beam, containing vapours of the pure reference sample. The concentration (or vapour pressure) in the cell has been calculated from the known heat of enthalpy of the solid sample.

IV/5. The critical technological processes and the places of distribution of 2,4-dichlorophenol in a chemical factory have been established by open-path FTIR monitoring.

V. The analysis of cigarette smoke and smoky air have been investigated by means of extractive and open-path FTIR spectrometry.

V/1. It was proved by the analysis of cigarette smoke for 11 toxic gaseous compounds by means of extractive FTIR spectrometry that the composition of mainstream cigarette smoke inhaled by the smoker shows no correlation with the strength of the cigarette i.e. with its nominal content of nicotine and tar.

V/2. A modified open-path FTIR system was successfully applied for investigation of smoky room air. It could be established that the main source of pollution in a room is the side-stream cigarette smoke, whereas the concentration of pollutants in the exhaled smoke is much smaller due to the reactions between the compounds and to retentive and filtering effects of the human lung.

VI. To optimise the operation (ideal temperature and flow rate, etc.) of catalysts used for degradation of air pollutants, an experimental set-up has been built to investigate the efficiency of the catalyst by continuous analysis of the reactor inlet and outlet gas streams.

PUBLICATIONS RELATED TO THE DISSERTATION

1. **Z. Bacsik**, J. Mink, G. Keresztury
   FTIR Spectroscopy of the Atmosphere. I. Principles and Methods
   Applied Spectroscopy Reviews **39** (3), (2004) 295-363.

2. **Z. Bacsik**, J. Mink, G. Keresztury
   FTIR Spectroscopy of the Atmosphere. II. Applications
   Applied Spectroscopy Reviews **40** (4), (2005) 327-390.

3. **Z. Bacsik**, V. Komlósi, T. Ollár, J. Mink
   Comparison of Open Path and Extractive Long Path FTIR Techniques in Detection of Air Pollutants
   Applied Spectroscopy Reviews **41** (1), (2006) 77-97.

4. **Z. Bacsik**, A. Gyivicsán, K. Horváth, J. Mink
   Determination of carbon monoxide concentration and total pressure in gas cavities in silica glass body of light bulbs by FTIR spectrometry
   Analytical Chemistry **78** (7), (2006) 2382-2387.

5. **Z. Bacsik**, J. Mink
   Photolysis-assisted, Long-Path FT-IR Detection of Air Pollutants in the Presence of Water and Carbon Dioxide
   Talanta (2006) (in press, available online 27 April 2006 at www.sciencedirect.com)

6. **Z. Bacsik**, J. McGregor, J. Mink
   FTIR analysis of gaseous compounds in the mainstream smoke of regular and light cigarettes
   Food and Chemical Toxicology, (submitted)

OTHER PUBLICATION

1. **Z. Bacsik**, J. N. Canongia Lopes, M. F. Costa Gomes, G. Jancsó, J. Mink, and A. A. H. Pádua
   Solubility isotope effects in aqueous solutions of methane
   Journal of Chemical Physics **116** (24), (2002) 10816-24.

PRESENTATIONS

(The name of presenter is underlined)

[1] **Z. Bacsik**, A. Herczeg, J. Mink (oral)
FT-IR Investigation of Atmospheric Pollutants by Photolysis Assisted Long Path Gas Cell
1st North-African and Middle Eastern Symposium on Environmental and Sanitary Analytical Chemistry
Hammamet, Tunisia, March 7-11,1999

[2] **Z. Bacsik**, A. Herczeg, J. Mink (poster)
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7th Austrian-Hungarian International Conference on Vibrational Spectroscopy
Balatonfüred, Hungary, April 7-9, 1999

[3] J. Mink, **Z. Bacsik**, A. Herczeg (plenary)
Problems and Solutions in FTIR Study of Atmospheric Pollutants
5th International Austro-Tunisian Meeting on Analytical Chemistry of the Environment
Graz, Austria, March 23-24, 2000

[4] **Z. Bacsik**, T. Ollár, J. Mink (poster)
Open path FTIR Study of Atmospheric Pollutants in Industrial Environment
5th International Austro-Tunisian Meeting on Analytical Chemistry of the Environment
Graz, Austria, March 23-24, 2000

[5] **Z. Bacsik**, A. Herczeg, T. Ollár, J. Mink (oral)
Légköri szennyezők nagyérzékenységű FT-IR spektroszkópiája
MTA Spektrokémiai Munkabizottságának Ülése
Veszprém, Hungary, March 19-20, 2000

[6] J. Mink, J. Mihály, **Z. Bacsik**, A. Herczeg (oral)
New Possibilities in FTIR Spectroscopic Detection of Atmospheric Pollutants
3rd Mediterran Basin Conference on Analytical Chemistry,
Antalaya, Turkey, June 4-9, 2000

[7] J. Mink, **Z. Bacsik**, A. Herczeg, V. Komlósi, T. Ollár (oral)
New Developments in FTIR Study of Atmospheric Pollutants
Euroanalysis XI
Lisbon, Portugal, September 3-5, 2000

[8] J. Mink, **Z. Bacsik**, T. Ollár, V. Komlósi (poster)
Field FTIR Monitoring of Atmospheric Pollutants in Industrial Environment
Eouroanalysis XI
Lisbon, Portugal, September 3-5, 2000

[9] E. Farnady, **Z. Bacsik**, Gy. Gyulai, J. Mink (poster)
FTIR Detection of Gas Phase Pollutants Originated from PVC Pyrolysis
4th Euroconference on Environmental Analytical Chemistry
Visegrád, Hungary, September 14-19, 2000

[10] **Z. Bacsik**, J. Mink, T. Ollar, V. Komlosi (poster)
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[11] V. Komlosi, **Z. Bacsik**, J. Mink (poster)
Open Path FTIR Spectroscopic Study of Air Pollutants
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Visegrád, Hungary, September 14-19, 2000

[12] J. Mink, **Z. Bacsik**, A. Herczeg, V. Komlósi, T Ollár (oral)
Advanced Methods in FTIR study of Atmospheric Pollutants
4th Euroconference on Environmental Analytical Chemistry
Visegrád, Hungary, September 14-19, 2000

[13] J. Mink, **Z. Bacsik**, V. Komlósi, A. Gelencsér, (invited)
Advances in environmental infrared and Raman spectroscopy
Enviromin 2001 (Post-CSI XXXII Conference)
Skukuza, South Africa, July 14-18, 2001

[14] J. Mink, **Z. Bacsik**, V. Komlósi, (plenary)
New Trends in FTIR Spectroscopic Detection of Atmospheric Pollutants
IUPAC International Congress on Analytical Sciences
Tokyo, Japan, August 6-10, 2001

[15] J. Mink, **Z. Bacsik**, V. Komlósi (oral)
Légköri szennyezők nagy érzékenységű FT-IR spektroszkópiai detektálása
MKE Környezetvédelem Analitikája Konferencia
Hajdúszoboszló, Hungary, October 10-12, 2001

[16] J. Mink, **Z. Bacsik**, V. Komlósi (invited)
A korszerű infravörös spektroszkópia, a légkör tisztaságának őre
Magyar Tudomány Napja, MTA
Budapest, Hungary, October 19, 2001

[17] J. Mink, **Z. Bacsik** and V. Komlósi, (invited)
Advantages and problems in FTIR monitoring of atmospheric pollutants
Fourth International Symposium on Modern Principles of Air Monitoring
Lillehammer, Norway, February 3-7, 2002

[18] **Z. Bacsik** and J. Mink, (poster)
Validation of experimental results obtained by open path FTIR monitoring of atmospheric pollutants.
Fourth International Symposium on Modern Principles of Air Monitoring
Lillehammer, Norway, February 3-7, 2002

[19] **Z. Bacsik**, A. Görög, J. Mink, V. Komlósi (oral)
Légköri szennyezők FT-IR spektroszkópiai detektálása.
45. Magyar Spektrokémiai Vándorgyűlés
Siófok, Hungary, July 1-3, 2002

[20] **Z. Bacsik**, J. Mink V. Komlósi and T. Ollár (poster)
Extractive and Open Path FTIR Detection of Atmospheric Pollutants in Industrial Environment
EUROANALYSIS-12
Dortmund, Germany, September 8-13, 2002

[21] J. Mink and **Z. Bacsik** (oral)
FTIR Detection of air Pollutants
4th Mediterranean Basin Conference on Analytical Chemistry
Portorož, Slovenia, September 15-20, 2002

[22] **Z. Bacsik**, A. Görög and J. Mink (poster)
FTIR Detection of air Pollutants Interfering by Water and Carbon Dioxide
4th Mediterranean Basin Conference on Analytical Chemistry
Portorož, Slovenia, September 15-20, 2002

[23] **Z. Bacsik** and J. Mink (invited)
Légköri szennyezők FT-IR spektroszkópiai detektálása
IX. Anyagszerkezet-kutatási Konferencia, MTA Kémiai Kutatóközpont
Budapest, Hungary, December 18, 2002

[24] **Z. Bacsik**, N. Balogh and J. Mink (poster)
Detection of Chlorine and Bromine Molecules by FTIR Spectroscopy
6th Austro-Tunisian Meeting on Analytical Chemistry
Tunis, Tunisia, May 2-3, 2003

[25] J. Mink and **Z. Bacsik** (lecture)
Extractive and Open Path Detection of Air Pollutants by FTIR Spectroscopy
6th Austro-Tunisian Meeting on Analytical Chemistry
Tunis, Tunisia, May 2-3, 2003

[26] **Z. Bacsik**, J. Mink, (oral)
Diffúz légszennyező források vizsgálata *in situ* és extraktív FTIR spektrometriával
46. Magyar Spektrokémiai Vándorgyűlés,
Szeged, Hungary, June 30 – July 2, 2003

[27] **Z. Bacsik**, L. Hajba, G. Jancsó, J. Mink, (poster)
Detection of 2,4-dichlorophenol by open path Fourier transform infrared spectrometry
ICAVS-2,
Nottingham, UK, August 24-29, 2003

[28] **Z. Bacsik**, J. Mink (poster)
A practical background spectrum technique for long path FTIR detection of organic air pollutants
ICAVS-2,
Nottingham, UK, August 24-29, 2003

[29] **Z. Bacsik**, N. Balogh and J. Mink (poster)
Indirect Determination of Molecular Chlorine by FTIR Spectrometry
XXVII European Congress on Molecular Spectroscopy,
Krakow, Poland, September 5-10, 2004

[30] **Z. Bacsik**, A. Gyivicsán and J. Mink (poster)
Determination of Carbon Monoxide Content of Gas Cavities in Silica Glass Body of Light Bulbs by FTIR Spectrometry
XXVII European Congress on Molecular Spectroscopy,
Krakow, Poland, September 5-10, 2004

[31] **Z. Bacsik** and J. Mink (poster)
Investigation of Cigarette Smoke by Extractive and Open Path FTIR Spectrometry
Fifth International Symposium on Modern Principles of Air Monitoring
Loen, Norway, June 12-16, 2005

[32] J. Mink and **Z. Bacsik** (invited)
FTIR Spectrometry – a Versatile Technique in Environmental Analysis
Fifth International Symposium on Modern Principles of Air Monitoring
Loen, Norway, June 12-16, 2005

[33] R. Kállai, **Z. Bacsik**, M. Bernsten, Y. Thomassen and J. Mink (poster)
FTIR Study of Heat and UV Degradation Processes of Different Paints
Fifth International Symposium on Modern Principles of Air Monitoring
Loen, Norway, June 12-16, 2005

[34] Gyivicsán, **Z. Bacsik**, J. Mink (poster)
Kisméretű gázzárványok szén-monoxid tartalmának meghatározása kvarcüvegben FT-IR spektrometriával
46. Magyar Spektrokémiai Vándorgyűlés,
Hajdúszoboszló, Hungary, July 4-6, 2005

[35] **Z. Bacsik**, A. Gyivicsán and J. Mink (poster)
Determination of Carbon Monoxide Concentration and Total Pressure in Gas Cavities in Silica Glass Body of Light Bulbs by FTIR Spectrometry
The third International Conference on Advanced Vibrational Spectroscopy
Delavan, USA, August 14-19, 2005