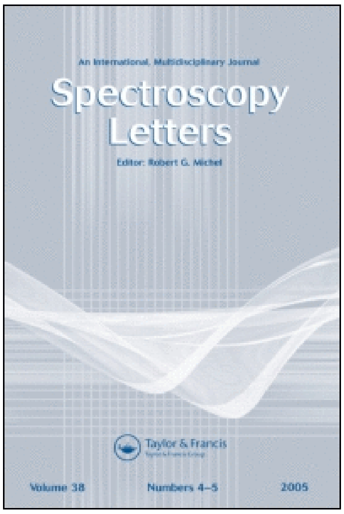

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Quantitative Vibrational Spectrometry in the 21st Century: A Scientometric Evaluation

S. Armenta[a]; S. Garrigues[a]; M. de la Guardia[a]
[a] Department of Analytical Chemistry, University of Valencia, Valencia, Spain

To cite this Article Armenta, S. , Garrigues, S. and de la Guardia, M.(2005) 'Quantitative Vibrational Spectrometry in the 21st Century: A Scientometric Evaluation', Spectroscopy Letters, 38: 6, 665 — 675
To link to this Article: DOI: 10.1080/00387010500315751
URL: http://dx.doi.org/10.1080/00387010500315751

Spectroscopy Letters, 38: 665–675, 2005

ISSN 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010500315751

Taylor & Francis
Taylor & Francis Group

Quantitative Vibrational Spectrometry in the 21st Century: A Scientometric Evaluation

S. Armenta, S. Garrigues, and M. de la Guardia
Department of Analytical Chemistry, University of Valencia, Valencia, Spain

Abstract: The state of the art of research on vibrational spectrometry–based quantitative methodologies was evaluated from the literature compiled in Analytical Abstracts from 1980. Medium and near infrared, Raman spectrometry, and photoacoustic methods of analysis were considered. The evolution of the number of published papers, the distribution of the literature as a function of the different application fields in which the vibrational methods were employed, and a study of the impact on this area of chemometric and automation studies clearly shows that, from the 1990s until now, the importance of vibrational spectrometry in application analysis has grown to reach maturity. This field provides alternative methods for industrial, environmental, and food analysis and in clinical studies. The most active research groups on these subjects have been identified from their scientific production in the first years of this century and from the journals in which this research is commonly published.

Keywords: FTIR, NIR, photoacoustic, quantitative analysis, raman, scientometric, vibrational spectrometry

INTRODUCTION

Scientometrics is a discipline devoted to the quantitative study of the scientific literature. From the pioneering study of Price,[1] it has been shown that, based

Received 20 December 2004, Accepted 24 May 2005
This paper was by special invitation as a contribution to a special issue of the journal entitled "Quantitative Vibrational Spectrometry in the 21st Century." This special issue was organized by Professor Miguel de la Guardia, Professor of Analytical Chemistry at Valencia University, Spain.
Address correspondence to M. de la Guardia, Department of Analytical Chemistry, University of Valencia, Edificio Jeroni Muñoz, 46100 Valencia, Spain. E-mail: miguel.delaguardia@uv.es

on a study of published papers in a field and their evolution with time, various indicators can be identified, including the state of the art and level of activity of a discipline or technique, the main research lines, for the future, the relevant research teams, and the most appropriate journals in which to follow the future perspectives in a research area.

Scientometrics has been applied to the evaluation of scientific disciplines,[2,3] national scientific production,[4] and bibliographic databases,[5,6] and it provides valuable tools to describe the scientific activity and to orient future research.

Vibrational spectrometry covers a series of well-established analytical methodologies suitable to be employed for both qualitative and quantitative purposes. However, in the main part of textbooks on vibrational techniques, the qualitative aspects are discussed in detail, reducing the quantitative applications to a short notice.[7,8]

It is true that, compared to ultraviolet-visible spectrometry, the infrared range of the spectrum offers reduced sensitivity, and that the problems related to the lack of transparency of water and glass in the middle infrared region, together with problems arising from the compatibility between transparent materials and solvents and the adequate solubilization of analytes, create additional troubles in routine analysis, thus limiting the use of vibrational techniques to the academic field.[9]

However, in the past decades, advances in both instrumentation and software control and the popularization of Fourier transform–based equipment have increased interest in vibrational spectrometry. The tremendous development of chemometrics[10] and automation[11,12] have improved the capabilities of vibrational techniques to process complex samples without requiring long and tedious pretreatments. Also, chemometrics offers an excellent sample throughput and a reduced consumption of reagents and toxic solvents. So, nowadays we can expect a popularization of quantitative vibrational spectrometry in quality control analysis.

In the current study, the evolution of the scientific literature on quantitative analysis through Fourier transform infrared (FTIR), near infrared (NIR), Raman, and photoacoustic methods has been evaluated from papers compiled in Analytical Abstracts. The period from 1980 to 2004 has been used to evaluate the evolution of the literature in this field, and the most relevant research groups on this area were identified from their production in the first years of the century.

EVOLUTION OF THE LITERATURE ON QUANTITATIVE VIBRATIONAL SPECTROMETRY

Figure 1 depicts the evolution of the accumulated number of published papers on quantitative vibrational spectrometry, including the evolution of the literature of the four main techniques; such as middle infrared (MIR), NIR, Raman, and

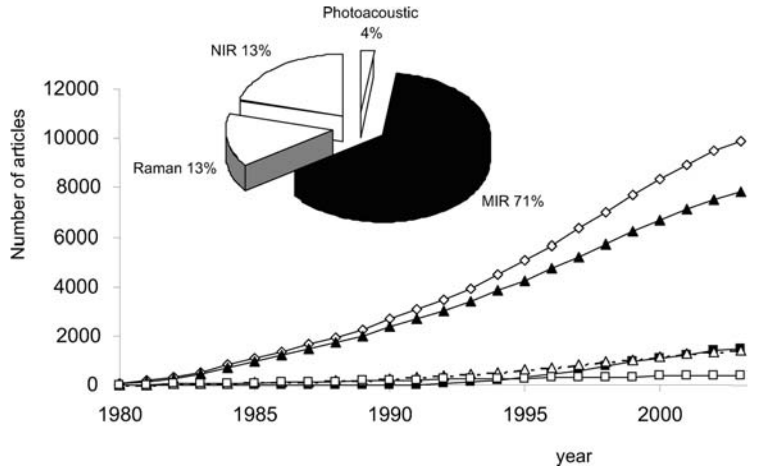

Figure 1. Evolution of the published literature on quantitative vibrational spectrometry: 9879 total published papers –◇–: FTIR –▲–, NIR –■–, Raman –△–, and photoacoustic –□–. Inset: Distribution of the literature on quantitative vibrational spectrometry as a function of the techniques employed (source: *Anal. Abstr.* 1980–2004).

photoacoustic analysis, from the references compiled in Analytical Abstracts for the period 1980–2004. A clear change can be identified in the rate of scientific literature production at the end of the 1980s, which could be described as 251 papers per year until the 586 papers per year published from the beginning of the 1990s until today. This dramatic modification of the productivity in the field can be identified in the papers related to FTIR and Raman, but also strength depends on the development of quantitative NIR, which expands in 1993 and grows to a current frequency of about 142 papers per year, thus indicating that the last decade of the 20th century can be considered as the starting point of a second golden age for vibrational spectrometry.

On considering the quantitative applications of vibrational spectrometry–based scientific papers, it can be seen in the inset of Fig. 1 that 70.7% of the total published papers correspond to FTIR, 12.6% to Raman, 13.1% to NIR, and 3.6% to photoacoustic techniques, which is close to the real situation of the market of vibrational instrumentation but also reflects the tremendous impact of the academic studies clearly reflected by the reduced weight of NIR studies as compared with Raman-based ones.

IDENTIFICATION OF THE MOST PRODUCTIVE RESEARCH GROUPS

Twenty-two percent of the scientific literature published from 1980 until now on quantitative vibrational spectrometry has been reported in the past 4½ years, thus it seems cogent to try to identify the most active research groups for near future developments from those who have reported their contributions in the new century.

Table 1 indicates a probably incomplete list of the authors identified in Analytical Abstracts from their productivity on quantitative applications on vibrational spectrometry from 2000 till now. These authors are organized as a function of the number of published papers and from which could be identified a first group composed of three research teams who have published between 23 and 26 papers, the Sun team in China, Ozaki in Japan, and Lendl in Austria, followed by a second group composed of authors who published between 14 and 18 papers in this period. This group is composed of the teams of Ozaki and Sun and the teams of de la Guardia and Garrigues from Spain, Massart from Belgium, Blanco and co-workers also from Spain, and Small and Mizaikoff, both from the United States. A third group is composed of the teams of Wang from China, Heise from Germany, Li also from China, Hasegawa from Japan, and Wilson also from the United States, in addition to members of the research team of Blanco. Also, there is a member of the group of Small with 9 published papers, 4 authors with 8 papers, followed by 11 authors with 7 papers, 7 authors with 6 publications, and 14 teams with 5 published papers in the past 4½ years (data not shown). So, it can be concluded that there are many active research teams on this field who guarantee a critical mass of scientific knowledge and the continuity of the effort to look for new advances.

As complementary information, it must be noticed that the papers published by Kawansei-Gakuin University are focused on chemometrics including NIR, MIR, and, to a lesser extent, Raman. Those produced in Beijing University are related to MIR and chemometrics, including some studies on Raman and NIR. Those of Vienna University of Technology are based on MIR and flow techniques including studies on Raman and some chemometric-based procedures.

THE MAIN SOURCES FOR THE LITERATURE

The 2115 research papers published from 2000 on the field of quantitative vibrational spectrometry appeared in 185 scientific journals, but only 27 journals have been published with 20 or more articles in this period (Fig. 2).

It turns out that 48 journals only published a single paper on this field during the first years of the century, 24 published 2 papers, 17 journals 3 contributions, and 14 published 4 papers. Only 3 journals concentrate 24.3% of the literature on the field, *Applied Spectroscopy*, *Analytical Chemistry*, and *Analytica Chimica Acta* being these general journals on spectroscopy and analytical chemistry, respectively, which shows the relatively low percentage of quantitative studies in vibrational spectrometry, which indicates that specific journals devoted to these techniques published more qualitative studies than quantitative ones.

Table 1. Identification of the most productive research groups on quantitative vibrational spectrometry at the beginning of the 21st century

Author	Number of papers	Co-workers	Institution
Ozaki, Y	26		Dept. Chem., School Sci., Kwansei Gakuin Univ., Nishinomiya 662-8501, Japan
Sun, SQ	26		Dept. Chem., Qinghua Univ., Beijing 100084, China
Lendl, B	23		Inst. Chem. Technol. and Anal., Vienna Univ. Technol., 1060 Vienna, Austria
de la Guardia, M	18		Dept. Anal. Chem., Univ. Valencia, 46100 Valencia, Spain
Garrigues, S	18	with de la Guardia, M	
Blanco, M	17		Dept. Quim., Unidad Quim. Anal., Univ. Autonoma Barcelona, 08193 Bellaterra, Barcelona, Spain
Massart, DL	17		ChemoAC, Pharm. Inst., Vrije Univ. Brussel, Brussels 1090, Belgium
Sasic, S	16	with Ozaki, Y	
Zhou, Q	16	with Sun, SQ	
Small, GW	15		Center Intelligent Chem. Instrumentation, Dept. Chem. and Biochem., Ohio Univ., Athens, OH 45701, USA
Mizaikoff, B	14		Georgia Inst. Technol., School Chem. and Biochem., Applied Sensors Lab., Atlanta, GA 30332-0400, USA
Wang, JD	12		Dalian Inst. Chem. Phys., Chinese Acad. Sci., Dalian 116012, China
Maspoch, S	10	with Blanco, M	
Wilson, ID	10		Dept. Drug Metabolism and Pharmacokinetics, AstraZeneca, Macclesfield, Cheshire SK10 4TG, UK
Heise, HM	10		Inst. Spectrochem. and Applied Spectroscopy, Univ. Dortmund, 44139 Dortmund, Germany
Li, Y	10		Lab. Advanced Spectroscopy, Nanjing Univ. Sci. and Technol., Nanjing 210014, China
Hasegawa, T	10		Kobe Pharm. Univ., Kobe 658-8558, Japan

(*continued*)

Table 1. Continued

Author	Number of papers	Co-workers	Institution
Arnold, MA	9	with Small, GW	
Buydens, LMC	8		Lab. Anal. Chem., Univ. Nijmegen, 6525 ED Nijmegen, The Netherlands
Schulz, H	8		Fed. Centre Breeding Res. Cultivated Plants, Inst. Plant Anal., 06484 Quedlinburg, Germany
Combs, RJ	8	with Small, GW	
Niessner, R	8		Inst. Hydrochem., Tech. Univ. Munich, 81377 Munich, Germany
Poppi, RJ	8		Inst. Quim., Univ. Estadual Campinas, Sao Paulo, Brazil
Brown, SD	7		Dept. Chem., Univ. Delaware, Newark, DE 19716, USA
Haaland, DM	7		Sandia Nat. Lab., Albuquerque NM 87185-0886, USA
Handley, A	7	with Wilson, ID	
Huvenne, JP	7		Lab. Spectrochim. Infrarouge et Raman, Univ. Sci. et Tecnol. Lille, 59655 Villeneuve d'Ascq, France
Jee, RD	7		Centre Pharm. Anal., School Pharm., Univ. London, London WC1N 1AX, UK
Lenz, E	7	with Wilson, ID	
Louden, D	7	with Wilson, ID	
Reeves, JB	7		AMBL, ANRI, ARS, USDA, BARC East, Beltsville MD 20705, USA
Siesler, HW	7	with Ozaki, Y	
Smith, WE	7		Dept. Pure and Applied Chem., Univ. Strathclyde, Glasgow G1 1XL, UK
Taylor, S	7	with Wilson, ID	

CHEMOMETRICS AND VIBRATIONAL SPECTROMETRY

Chemometrics forms the basis of quantitative studies published recently on vibrational spectrometry (Fig. 3), and on comparing this figure with the evolution of the vibrational applications (Fig. 1), it can be concluded that

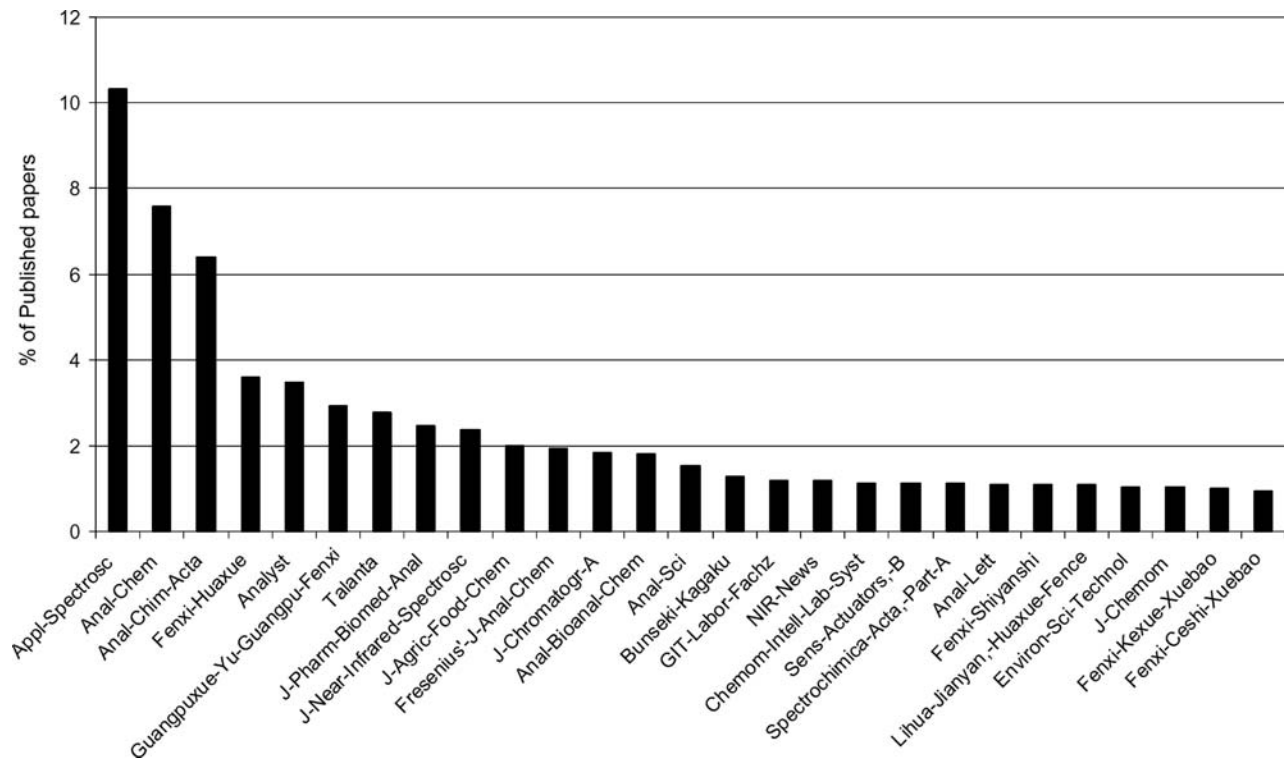

Figure 2. Distribution of the research papers published on the 21st century [2000–2004 (June)] as a function of the journal in which they were published (source: *Anal. Abstr.* 1980–2004. Note: only journals with 20 or more published papers in this period have been represented).

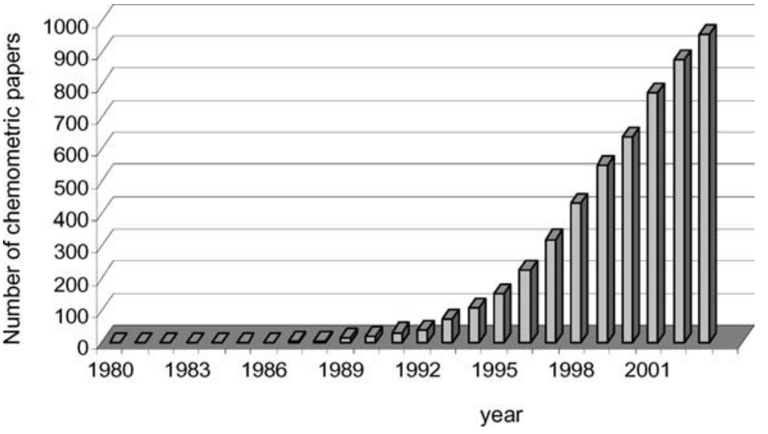

Figure 3. Evolution of the literature published on the chemometric study of infrared data for quantitative purposes (source: *Anal. Abstr.* 1980–2004).

NIR and chemometrics provided a synergistic combination and that the tremendous possibilities explored today by this approach would be impossible without tools like principal component analysis (PCA), partial least squares (PLS), or neuronal networks, which have been applied to evaluate both the analytical composition[13] and physical or practical properties[14] of actual samples of different types. Additionally, it must be noticed that in many cases, the chemometrics studies of vibrational spectra provide quantitative data without requiring a previous sample treatment. Nowadays, we cannot dissociate the tremendous information involved in the absorption or emission spectra in the IR range from their capabilities of multielemental determination through a multiparametric exploitation of spectral data in both the middle IR[15] and NIR.[16]

VIBRATIONAL SPECTROMETRY AND AUTOMATION

Flow injection analysis (FIA) and Fourier-transform infrared spectrometry are synergistic.[17] The use of FTIR as detector for FIA offers (i) fast monitoring of the whole spectrum, (ii) high resolution and a wide wavenumber range, (iii) many bands useful for the determination of a single compound or several compounds in the same sample, (iv) the simultaneous detection of several sample components, and (v) the possibility of elimination of band overlap through the use of derivative spectrometry.

On the other hand, FIA improves quantitative measurements in FTIR through (i) fast sampling and cleaning of the measurement cells, (ii) fast analytical control of the spectral baseline, (iii) easy and fast standardization, (iv) improved repeatability, (v) considered reduction of reagent and solvent consumption and waste generation, and (vi) possible enhancement of the analytical sensitivity through the on-line coupling of preconcentration techniques.

So, it is evident that advances in flow injection and, in general, automation have been extremely popular for the quantitative use of IR spectrometry, both in the middle[18] and NIR range[19] and in Raman spectrometry.[20]

In recent years, new flow approaches, like sequential injection analysis SIA[21] and multiconmutation[22] have been incorporated in vibrational techniques in order to reduce waste generation and to improve analytical productivity.

As can be seen in Fig. 4, from the first paper on classical FIA-infrared analysis, published in 1985,[18] the number of applications of automated or mechanized procedures in this field has grown exponentially to reach maturity in this century.

APPLICATION FIELDS OF THE QUANTITATIVE VIBRATIONAL STUDIES

Regarding the fields of application of quantitative vibrational studies (Fig. 5), it is clear that industrial and pharmaceutical samples are those to which the main part of studies have been devoted, and it is not at all astonishing because the lack of sensitivity of vibrational techniques makes them highly appropriate for quality control of active principles.

On the other hand, the tremendous possibilities offered by the use of chemometric-based methodologies has been applied especially in the fields of food and beverages and environmental or agricultural products (25% and 21.5%, respectively).

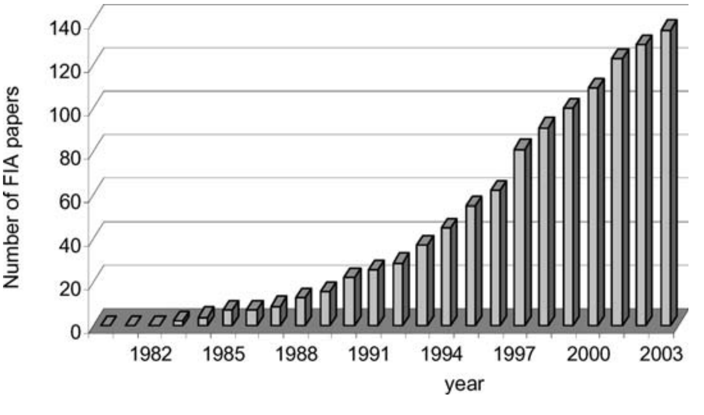

Figure 4. Evolution of the literature on automatized or mechanized methods in quantitative vibrational spectrometry (source: *Anal. Abstr.*, 1980–2004).

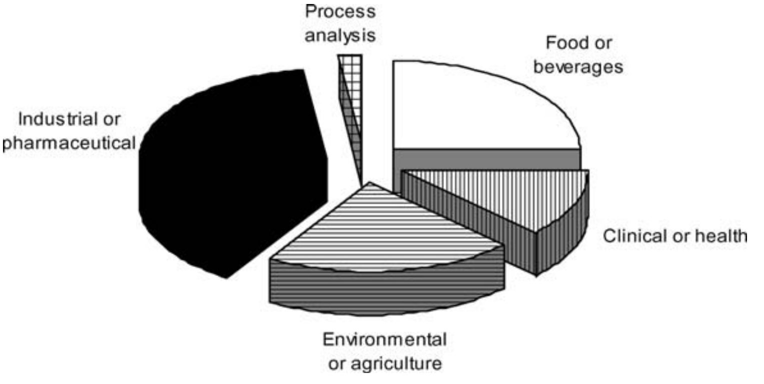

Figure 5. Distribution of the literature published on quantitative vibrational spectrometry as a function of the different application fields.

However, in our opinion, the future development in the use of vibrational techniques will improve diagnostics and characterization of small changes in clinical samples and their relationships with diseases and will prove to be a valuable tool for process analysis, based on the information contained in the NIR, MIR, or Raman spectra. Also important will be the application to reaction tanks involving the formation or destruction of products and reagents, as these techniques are able to be applied to the analysis of untreated samples or reaction mixtures, thus providing serious possibilities for the continuous monitoring of industrial processes.

REFERENCES

1. Price, D. J. S. *Little Science, Big Science*; Columbia University Press: New York, 1963.
2. Bran, T.; Bujdoso, E.; Schubert, A. *Literature of Analytical Chemistry: A Scientometric Evaluation*; CRC Boca Raton: Florida, USA, 1987.
3. López-Calafi, J.; Salvador, A.; de la Guardia, M. Estudio bibliométrico de la literatura científica sobre la determinación de elementos metálicos en aceites lubricantes por Espectroscopía de A.A. *Rev. Esp. Doc. Cient.* **1985**, *8* (3), 201–213.
4. Georgiou, C. A.; Thomaidis, N. S. Analytical chemistry in the European Union during 1993–1999: an appraisal on the basis of papers abstracted in Analytical Abstracts. *Trends Anal. Chem.* **2001**, *20* (9), 462–466.
5. Diospatonyi, I.; Horvai, G.; Braun, T. The publication speed of information in bibliographic chemical databases. *J. Chem. Inf. Comput. Sci.* **2001**, *41* (6), 1446–1451.
6. Kostoff, R. N.; Bedford, C. D.; del Rio, J. A.; Cortés, H. D.; Karypus, G. Macromolecule mass spectrometry: Citation mining of user documents. *J. Am. Soc. Mass Spectrom.* **2004**, *15* (3), 281–287.
7. Christy, A. A.; Ozaki, Y.; Gregoriou, V. G. *Modern Fourier Transform Infrared Spectroscopy*; Elsevier: Amsterdam, 2001.

8. Schraler, B. *Infrared and Raman Spectroscopy: Methods and Applications*; VCH: Weinheim, 1995.
9. Cadet, F.; de la Guardia, M. Quantitative analysis. Infrared. In *Encyclopedia of Analytical Chemistry*; Meyers, R. A., Ed.; J. Wiley: Chichester, 2000.
10. Sharaf, M. A.; Illman, D. L.; Kowalski, B. R. *Chemometrics*; J. Wiley: New York, 1986.
11. Hurst, W. J. *Automation in the Laboratory*; VCH Pub. Inc.: New York, 1995.
12. Ruzicka, J.; Hansen, E. H. *Flow Injection Analysis*; J. Wiley: New York, 1988.
13. Iñon, F. A.; Garrigues, S.; de la Guardia, M. Nutritional parameters of commercially available milk samples by FTIR and chemometric techniques. *Anal. Chim. Acta.* **2004**, *513* (2), 401–412.
14. Garrigues, S.; Andrade, J. M.; de la Guardia, M.; Prada, D. Multivariate calibrations in Fourier transform infrared spectrometry for prediction of kerosene properties. *Anal. Chim. Acta.* **1995**, *317* (1–3), 95–105.
15. Hua, R.; Sun, S. Q.; Zhou, Q.; Noda, J.; Wang, B. Q. Discrimination of Fritillary according to geographical origin with Fourier transform infrared spectroscopy and two-dimensional correlation IR spectroscopy. *J. Pharm. Biomed. Anal.* **2003**, *33* (2), 199–209.
16. Sato, H.; Shimoyama, M.; Kamiya, T.; Amari, T.; Sasic, S.; Ninomiya, T.; Siesler, H. W.; Ozaki, Y. Near infrared spectra of pellets and thin films of high-density, low-density and linear low-density polyethylenes and prediction of their physical properties by multivariate data analysis. *J. Near Infrared Spectrosc.* **2003**, *11* (4), 309–321.
17. Garrigues, S.; de la Guardia, M. Flow injection analysis-Fourier transform infrared spectrometry (FIA/FTIR). In *Handbook of Vibrational Spectroscopy*; Chalmes, J. M., Griffiths, P. R., Eds.; J. Wiley & Sons: Chichester, 2002; pp. 1661–1675.
18. Curran, D. J.; Collier, W. G. Determination of phenyl isocyanate in a flow-injection system with infrared spectrometric detection. *Anal. Chim. Acta.* **1985**, *117*, 259–262.
19. Garrigues, S.; Gallignani, M.; de la Guardia, M. Flow-injection determination of water in organic-solvents by near-infrared spectrometry. *Anal. Chim. Acta.* **1993**, *281* (2), 259–264.
20. Leopold, N.; Haberkorn, M.; Nilsson, J.; Baene, J. R.; Frank, J.; Lendl, B. On-line monitoring of airborne chemistry in levitated nanodroplets: In situ synthesis and application of SERS-active Ag-sols for trace analysis by FT-Raman spectroscopy. *Anal. Chem.* **2003**, *75* (9), 2166–2171.
21. Shindler, R.; Watkins, M.; Vonach, R.; Lendl, B.; Kellner, R.; Sara, R. Automated multivariate calibration in sequential injection Fourier transform infrared spectroscopy for sugar analysis. *Anal. Chem.* **1998**, *70* (2), 226–231.
22. Ródenas-Torralba, E.; Ventura-Gayete, J.; Morales-Rubio, A.; Garrigues, S.; de la Guardia, M. Multicommutation Fourier transform infrared determination of benzene in gasoline. *Anal. Chim. Acta.* **2004**, *512* (2), 215–221.