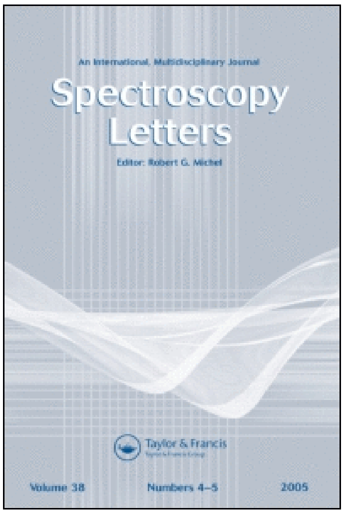

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Green Spectroscopy: A Scientometric Picture

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Green Spectroscopy: A Scientometric Picture

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ABSTRACT The state of the art of green spectroscopy, as a sustainable and friendly alternative to the classical spectrometric methods of analysis, has been established from the evaluation of the scientific literature published about this topic in the frame of the so-called Green Chemistry paradigm. Special attention has been paid to the fact that keywords like Green Analytical Chemistry, environmentally friendly, or clean analytical method or sustainable analytical chemistry are far from being commonly used in analytical studies. In spite of this fact there are numerous studies that provide direct analytical methodologies, or a reduction of reagents consumption or waste generation, the recycling of used solvents, or the replacement of toxic compounds by non-toxic or, at least, less toxic ones. So, additional efforts must be made to engage the scientific community in the practice of making the work safer and more sustainable in the analytical laboratories.

KEYWORDS clean analytical chemistry, environmentally friendly methods, green analytical chemistry, spectroscopy

INTRODUCTION

From the appearance of the Green Chemistry concept,[1] also called sustainable chemistry[2] or environmentally friendly chemistry,[3] scientists have been encouraged to design products and processes that could reduce or eliminate the use or generation of feedstock, products, by-products, solvents, reagents, and so on that are hazardous to human health or the environment. P. Anastas and J. C. Warner[1] developed twelve principles to explain what the definition means in practice.

This general concept can be, of course, also applied to Analytical Chemistry deriving in Green Analytical Chemistry (GAC). Thus, in 2001, Namiesnik[4] defined this concept by identifying four top priorities:

1. Elimination (or, at least, significant reduction) of consumption of reagents and organic solvents from analytical procedures;
2. Reduction of emission of vapors and gases, as well as liquid and solid waste, generated in analytical laboratories;
3. Elimination of reagents displaying high toxicity and/or ecotoxicity from analytical procedures (e.g., substituting benzene by other solvents);

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4. Reduction of labor and energy consumption of analytical procedures (per single analyte).

Taking into consideration the aforementioned four aspects, an ideal analytical methodology should be a reagentless procedure, nondestructive, fast and capable to determine several analytes (parameters) in the same run. It seems clear that many spectroscopic techniques fit perfectly with those four purposes. Moreover, when it is not possible to apply those procedures, the spectroscopists have developed different flow- based strategies with the aim to reduce sample pretreatment and also reduce or replace hazardous reagents.[5]

In short, the scope of this review is to provide a scientometric picture of GAC and, in particular, green spectroscopy–based techniques from the references found in the Chemical Abstracts Service (CAS), the US National Library of Medicine, and the Science Citation Index (SCI) database of the Institute for Scientific Information (ISI) in Philadelphia, PA, USA.

However, it must be taken into account that few papers contain the terms green, clean, environmentally friendly, or sustainable method and, because of that, a high amount of relevant literature concerning this topic cannot be obtained from the scientific databases and thus, the present study must be considered as a first approach to the literature in this field. It must be subjected to additional efforts and compromises of the analytical chemists for greening the proposed methods and also to include the aforementioned terms in their descriptions and methodologies.

EVOLUTION OF THE LITERATURE ON GREEN ANALYTICAL CHEMISTRY

The efforts to reduce the negative impact of the analytical methodologies on the environment have been focused through three different main ways: (i) development of direct analytical methodologies that do not require solvents or reagents; (ii) reduction of the amount of solvents and reagents required in both sample pretreatment and measurement, specially by means of automation and miniaturization; and (iii) the recovery of reagents and decontamination of toxic wastes.

The scientific references found in the CAS and SCI database, related to GAC (also called clean analytical chemistry or environmentally friendly analytical methods) have been growing significantly in recent years. Figure 1 depicts the evolution of the cumulated number of papers published on GAC, also including the evolution of the literature of the six main methodologies, such as atomic, vibrational and molecular spectroscopies, electrochemistry, and liquid and gas chromatography from the references compiled for the period 1990–2007.

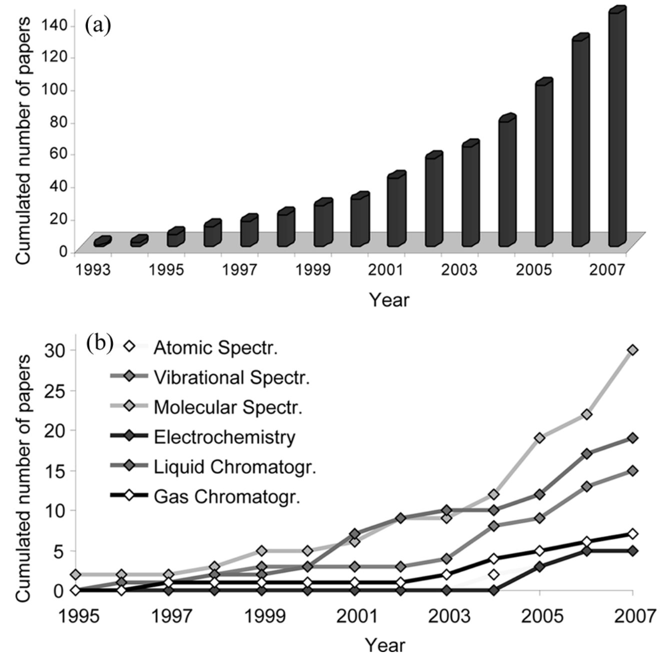

FIGURE 1 **Evolution of the scientific literature on Green Analytical Chemistry both, in general (Figure 1A) and distributed as a function of the methodologies used for analyte determination (Figure 1B).**

As it can be seen in this figure, the literature on this topic has been growth exponentially from the nineties. This gradual modification of the productivity on green analytical methods is probably related to the progressive concern of the scientific community about the environmental impact of their activity.

As it can be seen from Figure 1B, the methodology that used most commonly GAC, environmentally friendly method, or clean analytical chemistry terms is molecular-based spectroscopy. Analyzing in depth those papers, it can be seen that all of them are based on flow methodologies (FIA, SIA, or multicommutation), which drastically reduce the amount of reagents and also the amount of wastes generated, allowing the introduction in an easy and mechanized way of several sample treatment procedures. It is well known that greener analytical procedures are inherent to automated flow-based methodologies, due to their capability to reduce the reagent and solvent consumption and also to the possibility of incorporating on-line the decontamination of wastes.[6] However, not only flow-based methodologies should be considered as green ones and nowadays, only a few applications use the keyword green analytical chemistry in other context different to flow-based procedures.

Chromatographic techniques are good examples of procedures that also have contributed to greener analytical techniques, by improving the sample treatment methods, reducing the use of organic solvents in the mobile phase, and also developing new stationary phases that allow one to perform the separation of different analytes by using aqueous mobile phases. One of the advantages of chromatographic procedures, such as liquid chromatography (LC) or gas chromatography (GC) coupled on-line with mass spectrometry (MS) LC–MS or GC–MS, is that they facilitate the analysis of hundreds of pollutants in a single run. However, it is remarkable that from a long time ago, many researchers have pursued exactly the same objectives as in GAC (sample simplification, reduction in solvent and reagent consumption, less analysis time, less wastes generated...). However, in most of the papers in the literature, the concept and keywords of GAC have not been employed, so their contribution is not being recognized in GAC reviews.

The evolution of mathematical data treatments (Chemometrics) has allowed the development of solvent-free methodologies based on direct spectroscopic measurements on solid or liquid samples without any sample pretreatment to provide quantitative as well as qualitative information, molecular structure determination, and surface and trace analyses. Typical examples of those methodologies are the applications of vibrational spectrometric-based techniques (near infrared, mid infrared, or Raman spectrometry). However, it has not produced an increase of the use of green analytical chemistry as a keyword in the aforementioned studies.

On comparing the evolution of the literature concerning GAC in the different fields of spectroscopy, electrochemistry, and chromatography, it can be concluded that probably spectroscopy has been the most sensitive field to the concepts of Green Chemistry. Or at least, in this field, the scientific community has considered it relevant to add the aforementioned keywords as a novelty in their papers. In fact, the title of a recent review is "Spectroscopy: The best way toward Green Analytical Chemistry?"[7] thus evidencing the link between spectroscopy and sustainability of the analytical methods.

A specific aspect to be taken into consideration is the publication of books concerning Green Chemistry. In this sense, Table 1 indicates the available books in the field and from this table it can be concluded that from the pionering book of Anastas and William published by the American Chemical Society in 1996, it has been a constant effort to integrate the main contributions in the field in new books regarding both general and specific fields of Green

TABLE 1 **Green Chemistry Books**

Title	Authors	Editor	Year
Green Chemistry: Designing Chemistry for the Environment	P. T. Anastas and T. C. Williamson	American Chemical Society	1996
Organic Reactions in Aqueous Media	C. J. Li and T. H. Chan	John Wiley & Sons Inc.	1997
Green Chemistry: Theory and Practice	P. T. Anastas and J. C. Warner	Oxford University Press	1998
Green Chemistry: Frontiers in Benign Chemical Synthesis and Processes	P. T. Anastas and T. C. Williamson	Oxford University Press	1998
Real-World Cases in Green Chemistry	M. C. Cann and M. E. Connelly	American Chemical Society	2000
Green Chemistry: An Introductory Text	M. Lancaster	Royal Society of Chemistry	2002
Introduction to Green Chemistry: Instructional Activities for Introductory Chemistry	American Chemical Society	American Chemical Society	2002
Green Chemistry: Environment Friendly Alternatives	R. Sanghi, M. M. Srivastava	Alpha Science International	2003
New Trends in Green Chemistry	V. K. Ahluwalia, M. Kidwai,	Kluwer Academic	2004
Green Chemistry and Catalysis	R. A. Sheldon, I. Arends, U. Hanefeld	Wiley-VCH	2007

TABLE 2 Journals Devoted to Green Chemistry

Journal	Editor	Website	Year
Green Chemistry	Royal Society of Chemistry	http://www.rsc.org/greenchem	1999
Journal of Chemical Technology & Biotechnology	John Wiley and Sons, Inc.	http://www.wiley.com/journals/jctb/	2001
Clean Technologies and Environmental Policy	Springer	http://www.springerlink.com/content/103074/	2008
Green Chemistry Letters and Reviews	Taylor and Francis	http://www.tandf.co.uk/journals/titles/17518253.asp	2007
Journal of Cleaner Production	Elsevier	http://www.elsevier.com/wps/find/journaldescription.cws_home/30440/description#description	1993

Chemistry, as catalysis or synthesis. However, until now there is no specific book focused on GAC or on Green Spectroscopy. However, it is clear that the interest in this field is increasing year after year and, because of that from the publication in 1993 of the *Journal of Cleaner Production* by Elsevier, new editors have started new projects on Green Chemistry and Clean Technologies (see Table 2) in spite of the fact that, once again, until today there is no specific journal concerning GAC.

IDENTIFICATION OF THE MOST PRODUCTIVE RESEARCH GROUPS IN GREEN ANALYTICAL CHEMISTRY

Figure 2 summarizes (black color) the list of the main authors identified in the literature from their productivity on GAC. These authors have been ranged as a function of the number of published papers in which the aforementioned terms were used and the first conclusion that can be extracted is that Green Analytical Chemistry, clean analytical chemistry, or environmentally friendly procedures are not commonly used keywords in analytical chemistry papers. From the 18 most productive authors, 9 correspond to the same research group (M. de la Guardia, S. Garrigues, S. Armenta, A. Morales-Rubio, E. Rodenas-Torralba, J. Moros, M. L. Cervera, A. Pastor, and G. Quintás), and several of the other authors have done scientific collaborations with this research group (Analytical Chemistry Department of the University of Valencia) such as F. R. P. Rocha and B. F. Reis or have collaborated in the past with us, like A. Salvador. Thus, it can be concluded that although the scientific community is made aware of Green Analytical Chemistry the use of this concept as a keyword is not considered relevant. Thus, any

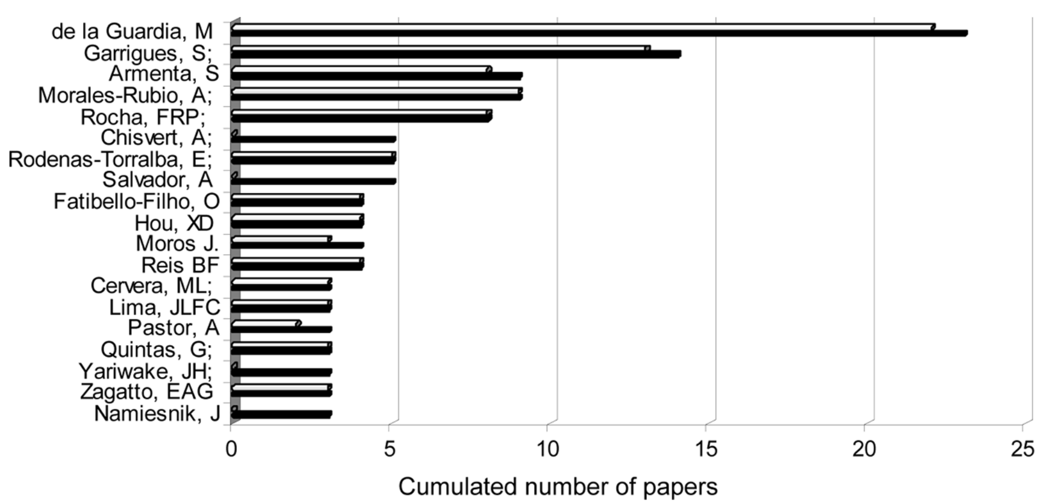

FIGURE 2 The most productive authors who use the term Green Analytical Chemistry or related ones in their publications concerning spectroscopy.

scientometric overview of this concept would be partial.

Taking into consideration only those papers based on spectroscopy methods the list regarding productivity of the different authors can be reduced to that depicted in Figure 2 (white color). Again, the most productive authors, who used those keywords in their papers, belong to the Analytical Chemistry Department of the University of Valencia. It can be explained, once again, because the use of green analytical chemistry, environmentally friendly, or clean analytical chemistry is not employed widely nor oftenly as keywords in analytical chemistry applications or developments.

On considering the scientific productivity in GAC special attention should be paid to research teams and centers who identify Green Chemistry or clean technology as the basis of their research and, as it can be seen in Table 3, at least 12 groups from the United Kingdom, 6 from the United States, and single groups from Italy, the Netherlands, Denmark, and Australia can be identified through their websites

TABLE 3 **Research Sites Regarding Green Chemistry**

Country	Institution	Website
UK	Centre for Clean Technology, York	http://www.york.ac.uk/depts/chem/staff/Clark-home.html
	Green Chemistry Network	http://www.chemsoc.org/gcn
	Institute for Applied Catalysis	http://www.iac.org.uk
	Centre for Alternative Technology (CAT)	http://www.cat.org.uk
	Questor	http://questor.qub.ac.uk/
	Queens University Ionic Liquids Laboratory	http://quill.qub.ac.uk/
	University of Nottingham—Clean Technology Research Group	http://www.nottingham.ac.uk/~pczsp/clnthome.html
	University of Reading—The Reading Centre for Surface Science and Catalysis	http://www.chem.rdg.ac.uk/dept/catrg/catrg.html
	Cardiff School of Biosciences—Clean Technology Group	http://www.cf.ac.uk/uwc/biosi/associates/ctgroup/
	University of Leeds— Leeds Cleaner Synthesis Group	http://www.chm.leeds.ac.uk/people/CMR
	University of Leicester— Leicester Green Chemistry Group	http://www.le.ac.uk/chemistry/greenchem
	University of York—Green Chemistry Group	http://www.york.ac.uk/res/gcg/GCG
Denmark	Technical University of Denmark—Center for Sustainable and Green Chemistry	http://www.csg.dtn.dk
Italy	Interuniversity Consortium of Chemistry for the Environment	http://www.unive.it/inca.html
	Italian Group of Catalysis	http://www.fci.unibo.it/gic/
Netherlands	Netherland Institute of Catalysis Research	http://www.chem.tue.nl/niok/
Australia	Murdoch University, Perth	http://wwwscience.murdoch.edu.au/teaching/m234/recycle32.htm
	Monash University, Clayton	http://www.monash.edu.au/
USA	Center for Clean Technology (University of California)	http://cct.seas.ucla.edu
	National Center for Environmental Research and Quality Assurance (NCERQA)	http://es.epa.gov/ncerqa/
	National Center for Clean Industrial and Treatment Technologies (CenCITT)	http://es.epa.gov/ncerqa/cencitt/cencitt.html
	Center for Green Manufacturing, University of Alabama	http://bama.ua.edu/~cgm/
	University of North Carolina—The NSF Science and Technology Center for Environment	http://www.nsfstc.unc.edu
	Carnegie Mellon University—Institute for Green Science	http://www.chem.cmu.edu/groups/Collins

and it could be an excellent link to follow the developments in this area. However, it seems that the main part of the research teams are involved in the general concept of Green Chemistry or in specific areas of synthesis, manufacturing, or catalysis, with a good representation of research groups working with supercritical fluids and ionic liquids and there is no specific group involved in GAC.

THE MAIN SOURCES FOR THE LITERATURE

Figure 3 shows the journals that have published papers related to GAC that use green analytical chemistry and related terms. It can be seen that 55% of the papers were published in only three journals (*Analytica Chimica Acta, Talanta*, and *Journal of Chromatography A*), while the contribution of the other journals is in all cases lower than 5 papers. Regarding papers based on Green Spectroscopy methodologies it can be seen that 52% of them were published in *Analytical Chimica Acta* (29.1%) and *Talanta* (23.6%), being that these journals are general journals on Analytical Chemistry. However, it is clear that the publication of this special issue of *Spectroscopy Letters* devoted to Green Spectroscopy will put this journal in the main group of journals that have considered the side-effect of spectroscopy methods as an important aspect to be considered.

CONCLUSIONS

Studies made in this scientometric evaluation of the research in Green Spectroscopy have identified the main weaknesses of the field. In fact, Analytical Chemistry is an area in which efforts have been conducted from early times to make sustainable, safe, and environmentally friendly the new developed methods. However, the amount of papers in which

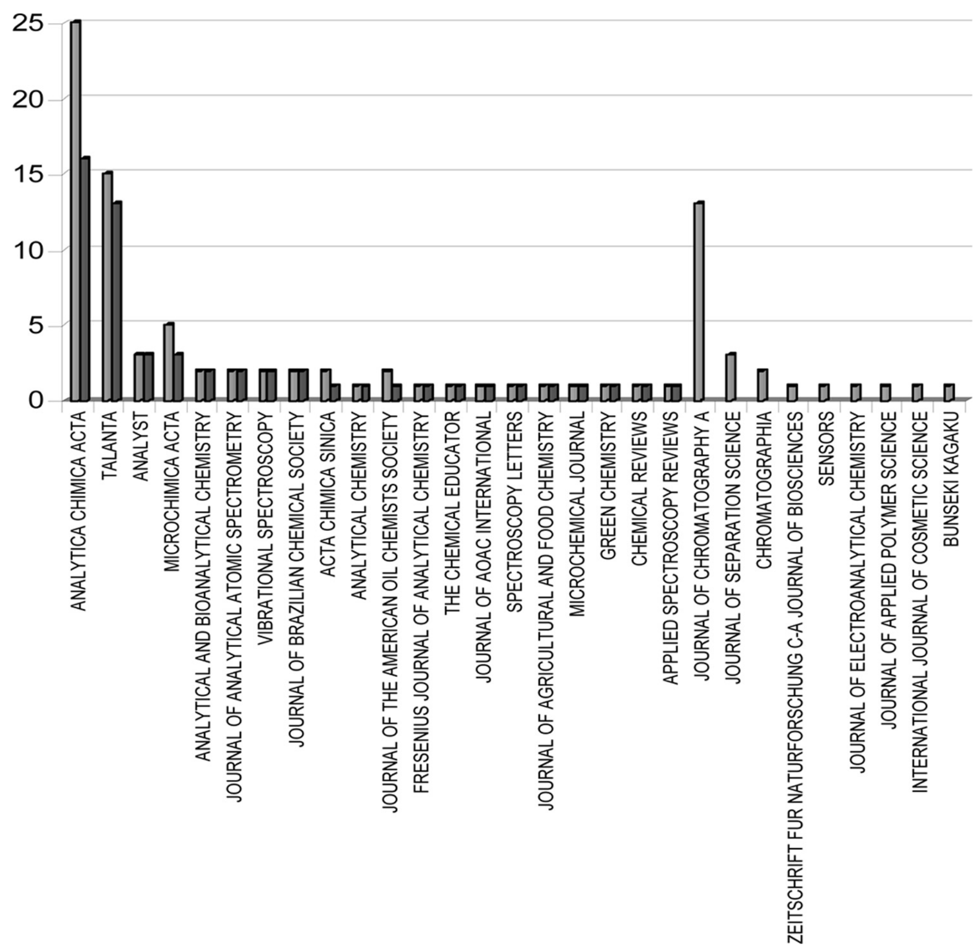

FIGURE 3 **Main journals publishing papers that contain the Green Analytical Chemistry term and related ones.**

the Green Chemistry keywords were employed is rare and thus probably means that although the scientific communities are made aware of improving the methods by replacing toxic reagents, reducing the amount of used reagents and wastes generated, and to recycle, as possible, solvents and reagents, they do not use Green Chemistry keywords to highlight the novelty of the work.

A special field in which Green Chemistry principles have improved the available methodologies is spectroscopy. In fact, spectroscopy methods require, in general, low amounts of reagents, a reduced treatment of samples, and are suitable to be easily mechanized, thus reducing the operator and environment risks and scaling down the consuming of hazardous products.

In the frame of the aforementioned comments, the changes made in sample preparation from hard treatments in open reactors to soft procedures in closed systems, together with the advances in chemometrics to establish screening and quantitative procedures applicable to untreated samples offer exciting possibilities for the new future.

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