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Green Analytical Chemistry in Determination of Volatile Fatty Acids in Wastewater

Bogdan Zygmunt [1], Anna Banel [1], Marta Wasielewska [1]
[1] Gdansk University of Technology
Chemical Faculty
11/12 Narutowicza Str., 80-233 Gdansk, Poland
e-mail: bogdan.zygmunt@pg.gda.pl

***Abstract*—The need for environmentally benign methodologies to determine volatile fatty acids (VFAs) in wastewater was emphasized. The reasons to apply gas chromatography (GC) as a separation technique were given. The advantages and the range of application of direct injection of aqueous samples into GC were discussed. Environmentally benign extraction techniques which are thought to be applicable to prepare wastewater for determination of VFAs were listed. The GC based analytical procedures employing direct injection of aqueous samples to GC and those preceded by sample preparation using such techniques as distillation, static headspace (HS), and solid phase microexctraction from sample headspace (HS-SPME) were discussed.**

Keywords- volatile fatty acids; gas chromatography; wastewater; green analytical procedures

I. INTRODUCTION

Great improvement in standard and comfort of living of wide fractions of populations, especially in developed countries, and the drastic increase in the total population of our globe have been observed since the last century. However, they were accompanied by environmental pollution, which has had large negative impact on the environment as a whole and human health in particular. Fortunately, people are thinking creatures and are able not only to predict the effects of their activities but also to take measures to reduce the damaging pollution to an acceptable level. A lot should and has been done to counteract environment damage by reducing production and use of chemicals. The consciousness, interest and activities in the field had reached such level that a new term "green chemistry" was introduced. It was first used by Anastas in a special program launched by the US EPA [1] and has become now increasingly popular. Green chemistry is an approach to synthesis, processing and use of chemicals in environmentally friendly way [2]. It is the 12 Principles of Green Chemistry which must be satisfied to make chemical products, processes and their application green [3]. The great role in environmental protection and management is played by monitoring of chemical pollutants, which, in general, is not an easy task. This is due to the fact that many environmental pollutants must be reliably determined even if present at ultra low concentrations often in very complex samples. When ultra-trace components are of interest majority of environmental samples appear to be very complex. It is why even modern analytical techniques are often not sufficiently sensitive and selective to analytes to assure reliable and meaningful data. Therefore, the application of standard instruments and procedures must often be preceded by extraction of analytes of interest from the large original sample and transfer them to a much smaller volume of a medium compatible with the applied technique, which is poorly sensitive to this medium. The process frequently results in generation of a large amount of waste, most often hazardous to people and the environment as a whole. The production of reagents and solvents which are used for the purpose could also be a source of pollution. To combat the problems new sample preparation techniques have been developed and research has been conducted on miniaturization of sample preparation and analytical measuring instruments. Analytical chemistry dealing with analytical methods, techniques, procedures and lab routines which are increasingly environmentally friendly is termed Green Analytical Chemistry (GAC) [4-6]. The analytical procedure can be made greener at any of the steps of chemical analysis. Up to now most effort has bees made to eliminate from or at least drastically reduce the use of hazardous solvents in analytical protocols.

Each human community produces some wastewater even if not engaged in manufacturing any goods. Organic matter present in wastewater is, at least partially converted into short chain alkanemonocarboxylic acids, often termed volatile fatty acids (VFAs) if they contain from 2 to 6 or even 7 carbon atoms in a molecule. They are unwanted in the environment since they have unpleasant smell, can acidify the environment and increase the mobility of harmful heavy metals. If wastewater is subjected to biological treatment, which is often the case VFAs play a helpful role in removal of unwanted phosphorous and nitrogen compounds. VFAs are also important intermediates in conversion of organic waste into biogas.

So monitoring of these acids in treated wastewater discharged into the environment, in raw wastewater and at particular steps of its treatment, in solid waste leachate and in many other aqueous and solid samples, e.g. sewage sludge is required. To study different processes the content of individual acids should be determined. So efficient separation techniques such as gas or liquid chromatography or electrophoresis must be applied. Gas chromatography is a method of choice due to high separation power, simplicity, easiness of use and that it can be regarded as a "green" one. However, very often the samples must be subjected to a

special treatment before GC analysis. The oldest approach is extraction of acids into organic solvent and analysis of the extract obtained by GC. This is regarded as environmentally unfriendly and should be avoided. The corresponding procedure can not be included in green analytical chemistry and all the recent papers on VFAs GC determination are based on solvent-free sample preparation.

The aim of this paper is to discuss the problems of wastewater sample preparation for chromatographic determination of volatile fatty acids in an environmentally friendly way as compared with solvent extraction.

II. GAS CHROMATOGRAPHY

Of separation techniques applicable to the separation of VFAs gas chromatography is a method of choice also due to environmental protection reasons. In GC environmentally friendly inert gas is a mobile phase. Capillary gas chromatography uses over two orders of magnitude less carrier gas than GC with packed columns, which makes it greener. It is very important since carrier gas must be of high purity, especially in trace analysis and hence requiring more sophisticated and expensive technology.

III. SAMPLE PREPARATION

Typical techniques of sample preparation used for GC determination of volatile organic compounds can also be attempted to apply in the case of VFAs in aqueous samples. Obviously, the simplest approach could be direct injection of an original sample into GC for analysis. However in majority of cases the analytes must be isolated and transferred to another medium. The sample preparation techniques which could be used and which seem to satisfy the principles of GAC, to a smaller or larger degree, are: gas extraction, mainly static headspace (HS) and purge and trap (PT); solid phase microextraction (SPME); stir bar sorptive extraction (SBSE); solid phase extraction (SPE); microextraction in a packed syringe (MEPS); liquid phase microextraction (LPME); different modes of membrane extraction (ME); supercritical fluid extraction (SFE); subcritical water extraction (SWE); dispersive liquid microextraction (DLLME); pressurized liquid extraction (PLE); and combination of the techniques, as for example HS-SPME. In all these techniques hazardous organic solvent use is either reduced or totally eliminated or at least exchanged for the solvent whose application can be harmless to the environment. Water, for example is totally environmentally friendly solvent and it should be used whenever possible and its application increases due to possibility of modifying its properties, to large degree, by changing its temperature and pressure. However one should not forget that water preparation for extraction can be a burden to the environment, as well.

Ionic liquids (ILs) have emerged as a new type of green solvent quite recently. They have been used not only in DLLME and supported liquid membrane extraction (SLME) but also as stationary phases for GC making it even greener. Up to now we have worked on developing procedures of VFAs determination employing only the most typical isolation and enrichment techniques but the research should be continued to apply the newest extraction techniques. The analytical procedures we developed are presented in Fig. 1 and their application in Fig.2.

A. Direct injection of aqueous samples into GC

In many analytical tasks the concentration of VFAs is sufficiently high to be detected without analyte enrichment. Such aqueous samples, if free of matter deteriorating the gas chromatographic system, should be directly injected into GC for analysis provided that the chromatographic column is resistant to water and enables satisfactory separation. Connecting two columns in series, one polar and the other non-polar satisfied the requirement and the corresponding procedure have been developed.

This approach could also have been used for the “dirty” samples cleaned up of suspended particular matter, some inorganic compounds and high molecular organics. This was shown to be done by sample refluxing in a special apparatus containing the small volume chamber collecting the rectificate. In the process acetic acid concentration drops. However, by matrix modification all the acids, including acetic acid can be enriched and obviously separated from column deteriorating matrix components. Some aspects of such an approach are given in [7].

B. Static headspace (HS)

In HS technique a vial closed with a flexible membrane is partially filled with the aqueous sample. It is kept at constant temperature for some time and the gas above the sample (headspace) is injected into GC. By selecting temperature and matrix modification the concentration in HS is determined by GC and recalculated to the initial concentration of an analyte of interest in the original sample. Using an automatic sampler connected with capillary GC the detection limits on sub mg/L level for VFAs with 2 to 6 carbon atoms in a molecule were achieved. At the present state-of-the art the procedure can be termed green. The problem has been partially dealt with in [8].

C. Solid phase microextraction from headspace (HS-SPME)

In the coupled technique a fused silica fiber coated with liquid polymer or solid sorbent dispersed in liquid polymer mounted in a syringe based device is exposed to headspace.

Green techniques of sample preparation for GC determination of VFAs in polluted aqueous samples

HEADSPACE

HEADSPACE SOLID PHASE MICROEXTRACTION

DIRECT INJECTION

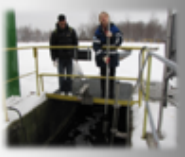
DISTILLATION DIRECT INJECTION

EXAMPLES OF APPLICATION

LANDFILL LEACHATE


WASTEWATER TREATMENT PLANT



WASTEWATER FROM ANIMAL FARM


WASTEWATER FROM ZOO LANDFILL


SURFACE AND UNDERGROUND WATER


The volatile sample components present in headspace partition between the fiber and the headspace.

Then fiber is withdrawn into the needle and inserted into a GC injection port heated to high temperature at which volatiles are desorbed and transferred into a GC column for separation and quantification. This step is green but obviously preparing the fiber requires some chemicals though in rather small amounts since the stationary phase volume on the fiber is from a few to ca. 100 μL and the fiber can generally be used more than hundred times depending on the coating, sample, desorption temperature, etc. Using this approach LODs which were analyte dependent ranged from ca. 0.1 mg/L to a few hundred mg/L. In the approach an additional dimension of selectivity was introduced; one is analytes interaction with water and their volatility and the second is the affinity of analytes to the fiber coating. The important advantage of this approach over HS is that sampling and analyte isolation can be performed on site so transportation of large wastewater samples is avoided and more reliable results could be expected since analytes are generally more stable in sorbed form on the fiber than in an original wastewater sample which was stressed in [9].

IV. CONCLUSION

Green analytical chemistry is a very important approach in determination of volatile fatty acids in "dirty" aqueous samples as wastewater of different origin since the samples are characterized by complex matrices. Gas chromatography is a method of choice since it is greener than other separation techniques which can be applied and is simple and easy to apply. Relatively clean aqueous samples can be directly injected into GC but in most cases they must be subjected to isolation and enrichment process before GC analysis. Nowadays solvent free techniques of sample preparation are proposed for the purpose, mainly HS and HS-SPME. Research should be continued to develop methods based on newer techniques of organic analytes isolation and enrichment before GC analysis.

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