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SURVEY, EMISSION AND EVALUATION OF VOLATILE ORGANIC CHEMICALS

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Abstract. Environmental and Health and Safety legislation requires certain processes to be monitored and is the main reason VOC emissions need to be determined. Analysis for VOCs should be of concern to all companies that use solvents or materials containing residual solvents. The VOCs concentrations into the atmosphere are determined according with the SR EN 12619/2002, SR EN 13526/2002 and SR EN 13649/2002 standard requirements.

Keywords: survey, emission, volatile organic compounds (VOCs).

AIMS AND BACKGROUND

Air quality in Europe has been improving for several years, and will continue to improve as a result of existing measures. A number of industries are engaged actively in helping to meet air quality targets. The solvents industry is playing its part in looking at man-made contributions to ground level ozone and has already made significant progress in reducing emissions.

Taking into account the noxious consequences of VOCs emissions upon human health and environment, the main priority is the reduction of these emissions resulted from the activities and the installations using organic solvents.

The objective of Council Directive 1999/13/EC (Ref. 1) on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations is to prevent or reduce the direct or indirect effects of volatile organic compounds (VOCs) emissions into the environment, mainly into air, and their potential risks to human health, by providing measures and procedures to be implemented for the activities defined in Annex I of the Directive.

The Directive was transposed into Romanian legislation through GD No 699/2003 on setting certain measures for reducing the volatile organic compounds emissions due to the use of organic solvents in certain activities and installations[2].

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As regard the necessary tools to put into force the requirements of those regulations mentioned before there are 3 standards for VOCs concentration determination into the air:

– SR EN 12619:2002 Stationary source emissions. Determination of the mass concentration of total gaseous organic carbon at low concentrations in flue gases. Continuous flame ionisation detector method[3];

– SR EN 13526:2002 Stationary source emissions. Determination of the mass concentration of total gaseous organic carbon in flue gases from solvent using processes. Continuous flame ionisation detector method[4];

– SR EN 13649/2002 Stationary source emissions. Determination of the mass concentration of individual gaseous organic compounds. Activated carbon and solvent desorption method[5]. This Standard specifies procedures for the sampling, preparation and analysis of samples of gaseous or vapour phase organic components such as those arising from solvent using processes. The results obtained using this Standard are expressed as the mass concentration (mg/m^3) of the individual gaseous organic components. The Standard is suitable for use in the range of about 0.5 to 2000 mg/m^3. The method utilises adsorption and is suitable when the desorption efficiency is greater than 80%.

The present needs to develop appropriate analyses methods in the field of VOC emissions in compliance with the EU norms and standards and comparable to those of the similar systems applied in the EU Member States became more acute in the context of a general unsatisfactory status of the environmental protection business that requires an increased Government commitment to protect the environment.

EXPERIMENTAL

In this context we tested the methods for sampling and analyses of VOCs according with the EU norms and regulation.

Concerning the SR EN 13649/2002 (Ref. 5) standard requirements we have tested and establish the performance parameters for BTX, esters and chlorinated hydrocarbons determination method.

The sampling device used was a Dynamic Dilution Sampler designed and realised to meet the requirements of the UNI EN 13649 'Determination of the mass concentration of single volatile organic compounds, using charcoal tubes and solvent desorption method'.

The analyses were carried out using a Varian CP 3800 gas chromatograph with FID detector. For separation was used a VF – 1MS 15 m × 0.25 mm ID DF=0.25 type capillary column with solid phase 100% dimethylpolysiloxane. As a mobile phase 5.0 hydrogen was used.

The working conditions were established through repeated injections with solution containing 20 ppm organic compound following a proper separation of

the compounds in the repeatability conditions of the retention time and peaks area (standard deviation for time retention less than 2% and for peaks area less than 10%).

The following performance parameters were calculated: detection limit (LOD), quantification limit (LOQ), sensitivity, working range, calibration curve and its performance characteristics, repeatability and recovery using synthetic samples and real samples from an international proficiency testing scheme.

The detection limit for chromatographic methods represents the concentration corresponding to a detector signal equal to three times stronger noise signal.

The quantification limit for chromatographic methods represents the concentration corresponding to a detector signal equal to ten times stronger noise signal.

The method sensitivity for a detector depending on mass flow as is the case of FID detector is determined with the next formula:

$$S = \frac{A}{m},$$

where S is sensitivity, V s g^{-1} or A s g^{-1}; A – peak area, V s or A s; m – aliquot mass, g, and represents the calibration curve slope.

The working range represents the concentrations range for which the method can be applied.

RESULTS

The data obtained for BTX determination are presented in Table 1.

Table 1. Performance parameters for BTX chromatographic determination

Parameter	Benzene	Toluene	*o*-Xylene	*m*-Xylene
Retention time (min)	1.799	3.052	4.392	4.170
Working linear range	0-100 ppm	0-100 ppm	0-100 ppm	0-100 ppm
Detection limit (ppm)	0.122	0.099	0.076	0.075
Quantification limit (ppm)	0.406	0.331	0.253	0.249
Sensibility (V s g^{-1})	12.92×10^6	13.91×10^6	13.88×10^6	14.41×10^6
Relative repeatability (%)	4.08-6.99	6.96-7.84	6.40-8.99	3.07-9.49
Trueness error (ppm)	0.22-2.8	–2.79-(–0.90)	0.21-0.95	0.17-1.94
Bias (%)	0.89-3.74	–1.20-(–2.79)	0.83-1.27	0.70-2.59
Recovery (%)	100.89-103.74	97.21-98.80	100.83-101.27	100.7-102.59

Table 2. Calibration values for BTX determination

Compound		Concentration (ppm)				
		20	40	60	80	100
Benzene	Area (mV s)	23.4	46.9	69.5	93.2	110
Toluene	Area (mV s)	25.2	50.5	80.1	104	123
m-Xylene	Area (mV s)	26.7	52.3	86.2	105	136
o-Xylene	Area (mV s)	24.6	50.4	77.3	101	124

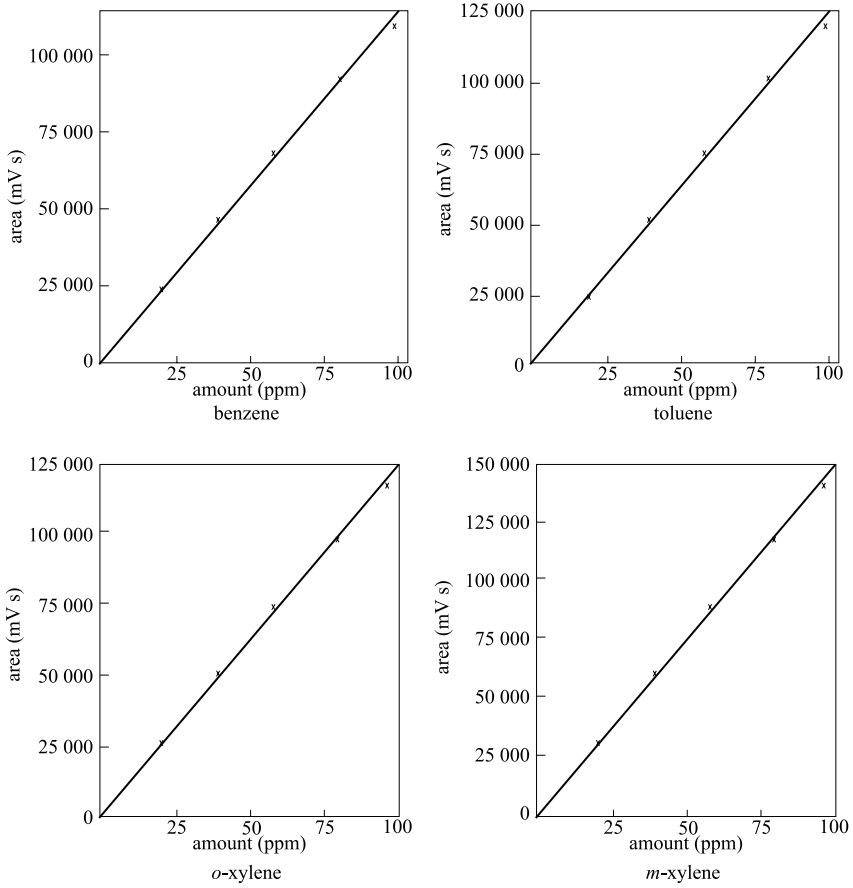

Fig. 1. Calibration curve for BTX determination

Table 3. Sensitivity for BTX determination

Compound	Area (V s)	Mass (g/injection)	Sensitivity (V s g^{-1})
Benzene	46.9×10^{-3}	3.63×10^{-9}	12.92×10^{6}
Toluene	50.5×10^{-3}	3.63×10^{-9}	13.91×10^{6}
m-Xylene	52.3×10^{-3}	3.63×10^{-9}	14.41×10^{6}
o-Xylene	50.4×10^{-3}	3.63×10^{-9}	13.88×10^{6}

The data obtained for esters are presented in Table 4.

Table 4. Performance parameters for esters chromatographic determination

Parameter	Ethyl acetate	*t*-butyl acetate	Butyl acetate
Retention time (min)	1.45	2.27	3.61
Working linear range	0-30	0-30	0-30
Detection limit (ppm)	0.47	0.27	0.23
Quantification limit (ppm)	1.56	0.91	0.75
Sensibility (V s g^{-1})	2.34×10^6	4.39×10^6	4.01×10^6
Relative repeatability (%)	4.23-8.83	4.55-7.86	5.57-8.63
Trueness error (ppm)	–0.22-0.15	0.37-0.48	0.36-0.47
Bias (%)	–0.87-0.60	1.93-2.49	1.40-1.90
Recovery (%)	98.55-100.6	101.93-102.49	101.42-103.16
Method recovery (%)	93	97	97

Table 5. Calibration values for esters determination

Compound		Concentration (ppm)		
		10	20	30
Ethyl acetate	area, counts	2392	4684	6842
t-Butyl acetate	area, counts	5562	8795	13004
Butyl acetate	area, counts	4554	8016	11980

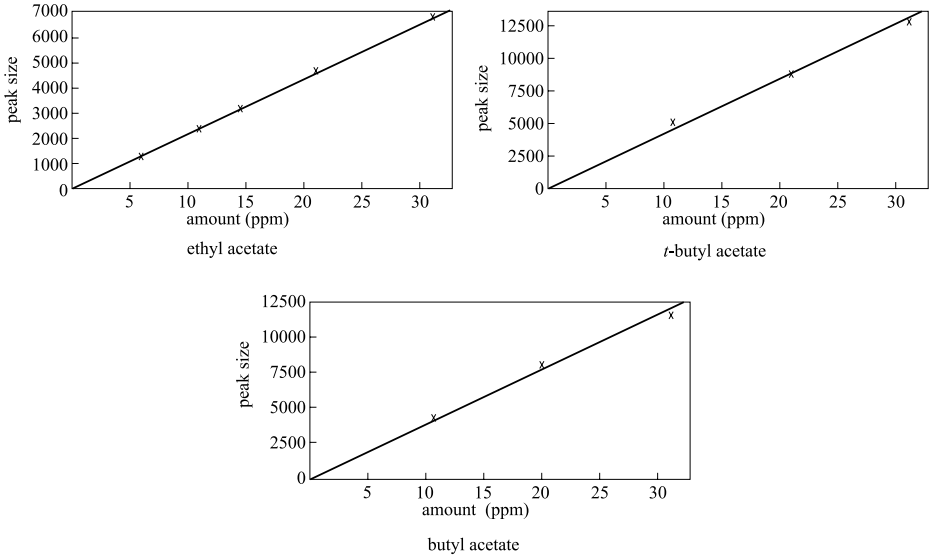

Fig. 2. Calibration curve for esters determination

Table 6. Sensitivity for esters determination

Compound	Area (V s)	Mass (g/injection)	Sensitivity (V s g^{-1})
Ethyl acetate	4.68×10^{-3}	2×10^{-9}	2.34×10^{6}
t-Butyl acetate	8.79×10^{-3}	2×10^{-9}	4.39×10^{6}
Butyl acetate	8.01×10^{-3}	2×10^{-9}	4.01×10^{6}

The data obtained for chlorinated compounds are presented in Table 7.

Table 7. Performance parameters for chlorinated compounds by chromatographic determination

Parameter	Carbon tetrachloride	Trichloroethylene	Tetrachloroethylene
Retention time (min)	1.88	2.16	3.57
Working linear range	0 – 50	0 – 50	0 – 50
Detection limit (ppm)	0.87	0.27	0.26
Quantification limit (ppm)	2.89	0.90	0.86
Sensibility (V s g^{-1})	0.78×10^{6}	3.47×10^{6}	2.90×10^{6}
Relative repeatability (%)	5.75-10.2	5.99-8.25	5.50-7.88
Trueness error (ppm)	–0.27-0.95	0.57-0.74	0.44-0.91
Bias (%)	–1.09-3.81	2.27-4.93	1.77-3.65
Recovery (%)	98.19-103.81	102.27-104.93	101.77-106.09
Method recovery (%)	90	93	100

Table 8. Calibration values for chlorinated compounds determination

Compound		Concentration (ppm)				
		10	20	30	40	50
Carbon tetrachloride	area, counts	918	1555	2515	–	–
Trichloroethylene	area, counts	3107	6948	9830	13557	16760
Tetrachloroethylene	area, counts	2540	5797	8543	10841	13803

Table 9. Sensitivity for chlorinated compounds determination

Compound	Area (V s)	Mass (g/injection)	Sensitivity (V s g^{-1})
Carbon tetrachloride	1.55×10^{-3}	2×10^{-9}	0.78×10^{6}
Trichloroethylene	6.95×10^{-3}	2×10^{-9}	3.47×10^{6}
Tetrachloroethylene	5.80×10^{-3}	2×10^{-9}	2.90×10^{6}

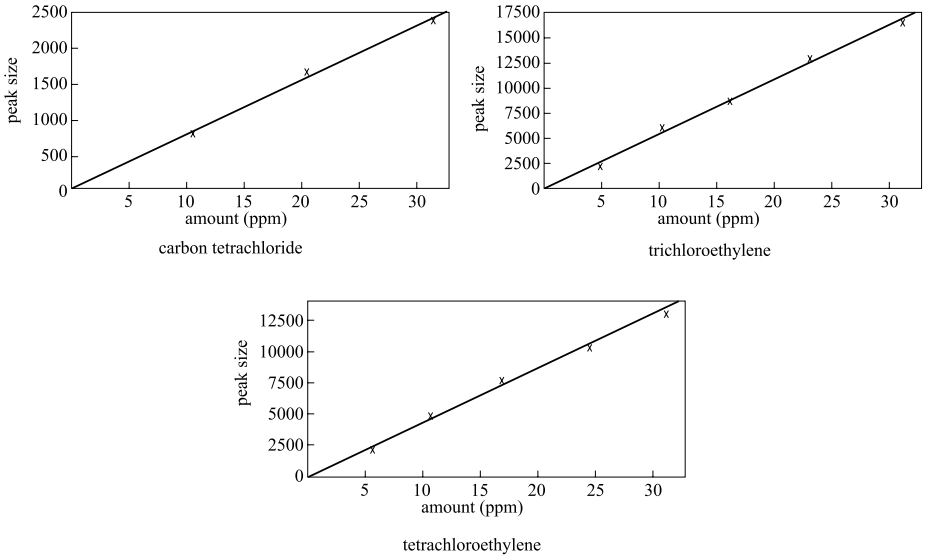

Fig. 3. Calibration curve for chlorinated compounds determination

VOCs as total organic carbon determination. As regard determination of the VOC as total organic carbon we respect the requirements of SR EN 12619:2002 and SR EN 13526:2002 which imply the usage of a portable flame ionisation detector – thermo-FID equipment.

The Thermo-FID is used in a variety of industrial applications and environmental measurement systems. Typical use of the Thermo-FID are flue/exhaust gases at waste incinerators or the petro- and chemical industry, ambient air analysis.

Principle of operation Thermo-FID. Burning organic components in a hydrogen flame creates negative ions which are measured by having a negative driven voltage (potential) across the burner nozzle and an electrode. The current measured value is directly proportional to the content of organic C in the sample/burning flame. A flame is created by burning pure hydrogen plus cleaned air (burner air) in a temperature controlled burning chamber. An additional constant feed of measuring sample is added to the burning chamber. Flow and pressure conditions of the burning process are 'constant' and allow long-term stability/low drift behaviour.

CONCLUSIONS

The objective of Council Directive 1999/13/EC (Ref. 1) on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations is to prevent or reduce the direct or indirect effects of volatile organic compounds (VOCs) emissions into the environment, mainly into

air, and their potential risks to human health, by providing measures and procedures to be implemented for the activities defined in Annex I of the Directive.

The Directive was transposed into Romanian legislation trough GD No 699/2003 (Off. J. No 489/8.07.2003) on setting certain measures for reducing the volatile organic compounds emissions due to the use of organic solvents in certain activities and installations[2].

The project scope was to assure the necessary environment to apply adequate methods, sensitive and accurate, for COV determination based on laboratory experiments, on site sapling and statistical calculus.

All the performance parameters as well as the results obtained from the international proficiency scheme we participate in, indicate that the established/ tested methods are proper to be used for determination of COVs from industrial sources.

REFERENCES

1. Directive 1999/13/EC. On the Limitation of Emissions of Volatile Organic Compounds Due to the Use of Organic Solvents in Certain Activities and Installations.
2. GD No 699/2003 (Off. J. No 489/8.07.2003). On Setting Certain Measures for Reducing the Volatile Organic Compounds Emissions Due to the Use of Organic Solvents in Certain Activities and Installations.
3. EN 12619 (1999). Stationary Source Emissions. Determination of the Mass Concentration of Total Organic Carbon at Low Concentrations in Flue Gases – Continuous Flame Ionisation Detector Method.
4. EN 13526 (2001). Stationary Source Emissions. Determination of the Mass Concentration of Total Gaseous Organic Carbon at High Concentrations in Flue Gases – Continuous Flame Ionisation Detector Method.
5. EN 13649 (2002). Stationary Source Emissions. Determination of the Mass Concentration of Individual Gaseous Organic Compounds – Activated Carbon and Solvent Desorption Method.

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