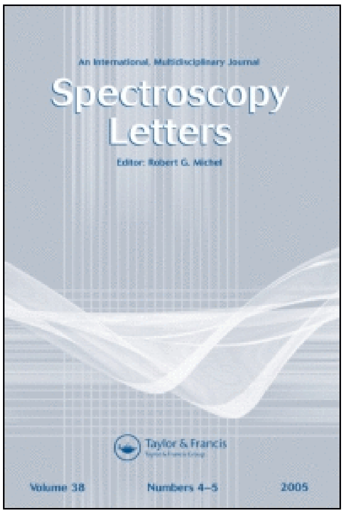

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Study of Pollutant gas Adsorption on Activated Charcoal Using FTIR Spectroscopy

C. Allegrini[a]; M. Guiliano[a]; M. Bourdin[b]; G. Mille[a]
[a] Faculté des Sciences et Techniques de Saint-Jéróme Centre de Spectroscopie Moléculaire, MARSEILLE, Cedex 20 [b] Délégation Générale pour l'Armement. DCN TOULON Centre d'Etudes et de Recherches Techniques Sous-Marines Laboratoire d'Hygiène Industrielle, TOULON NAVAL

To cite this Article Allegrini, C. , Guiliano, M. , Bourdin, M. and Mille, G.(1994) 'Study of Pollutant gas Adsorption on Activated Charcoal Using FTIR Spectroscopy', Spectroscopy Letters, 27: 3, 367 — 377
To link to this Article: DOI: 10.1080/00387019408000851
URL: http://dx.doi.org/10.1080/00387019408000851

SPECTROSCOPY LETTERS, 27(3), 367-377 (1994)

STUDY OF POLLUTANT GAS ADSORPTION ON ACTIVATED CHARCOAL USING FTIR SPECTROSCOPY

Key words : FTIR, Activated Charcoal, Pollutant Gas Adsorption.

C. ALLEGRINI, M. GUILIANO, M. BOURDIN* AND G. MILLE

Faculté des Sciences et Techniques de Saint-Jérôme
Centre de Spectroscopie Moléculaire. CNRS URA 1409
13397 MARSEILLE Cedex 20

*Délégation Générale pour l'Armement. DCN TOULON
Centre d'Etudes et de Recherches Techniques Sous-Marines
Laboratoire d'Hygiène Industrielle
83800 TOULON NAVAL

ABSTRACT

In this study, the efficiency of an air cleaning system, using activated charcoal cartridges, which must operate in a confined atmosphere with particularly high air flow rate, is tested.

A device which generates dynamic polluted atmospheres is described. A continuous quantitative analysis is made by means of the Fourier Transform Infrared Spectroscopy (FTIR). The pollutants studied are : carbon monoxyde (1500 ppm), sulfur dioxyde (100 ppm), nitrogen dioxyde (50 ppm) and hydrogen chloride (500 ppm). Gas adsorption kinetics on activated carbon are given and discussed by using breakthrough curves.

INTRODUCTION

The purpose of this study is to test the efficiency of an air cleaning system, using activated carbon cartridges, in a confined atmosphere polluted by gas given off from a fire in domestic premises. This air cleaning system recycles a high level of air, in a relatively short amount of time, which is the reason why the linear velocity of air passage through the activated carbon cartriges is very high (52 $cm.s^{-1}$).

Activated carbon is used widely in the fluid purifying process. Its high adsorbent power allows it to trap a lot of organic and inorganic compounds (1-5).

Various gaseous pollutants (thermolysis products) have been selected in relation to their probability of appearing and their toxicological importance. These pollutants are carbon monoxyde (1500 ppm), sulfur dioxyde (100 ppm), nitrogen dioxyde (50 ppm) and hydrogen chloride (500 ppm). These concentrations are called IDLH (Immediately Dangerous to Life or Health). According to the National Institute for Occupational Safety and Health, more than 30 minutes exposure to an IDLH concentration would cause irreversible toxic effets. In the cases of fires, l'IDLH is a particulary important criteria of toxicity.

The experimental part of the study covers the design and conception of a device that generates dynamic polluted atmospheres. This device controls the gas mixtures, followed up by continuous gas adsorption kinetics using activated carbon. Furthermore, this laboratory air cleaning device, must reproduce as precisely as possible the gas/solide exchange conditions according to the real air cleaning system. FTIR spectroscopy is used for this study because it's so well adapted to analysing a large number of gaseous compounds (characteristic spectra, high intensity bands and good sensibility).

In the second part of the study, the analytic system was tested and the CO, SO_2, NO_2 and HCl breakthrough curves obtained are discussed.

EXPERIMENTAL CONDITIONS

The experimental device consists of two separate parts. One part is relevant to gas manipulation technology (compressed gas cylinders, pressure regulators, stop valves, calibrated valves outlet compressed gas cylinders, massic flow meters, electronic pilot power supply and regulation of massic flow meters, stainless steel pipes). This device provides a means of reconstituting and regulating a polluted atmosphere by controlling parameters such as : linear gas velocity, pressure and concentration of one or several pollutants. Using a shunt system, the gas mixture can pass trough a filter when testing and optimising the efficiency of an adsorbent, or for finding out the adsorption kinetics. The gas flow rate adjustments (and consequently the concentrations ones) are made by using massic flow meters Brooks 5850 TR and 5850 E. The Brooks 5878 electronic pilot power supply and regulation, allows to control the massic flow meters. Each massic flow meter is calibrated for a given gas.

The other part of the device, is for analysing the polluted atmospheres, and consists of a gas cell and a FTIR spectrophotometer.The gas whether having passed through an adsorbent or not, are directed into a Spectra Tech gas cell, with a volume of 2.5 litres. The cell has an optical pathlength which can be adjusted between 1 and 10 meters. An optical transfer accessory is used to make this cell completely adaptable to the Nicolet 20 SXB spectrophotometer, equipped with a DTGS detector. The optical efficiency of the cell with a 2 meters optic pathlenght, is 20%. Tests are carried out at room temperature and 1 Bar pressure. The FTIR spectra are recorded between 4000 and 400 cm^{-1}. The background is obtained by using clean dry air (passage through three successive filters: particle filter, oil strainer and dryer). The spectral resolution is 4 cm^{-1} and the number of scans is 32 for each spectra. The quantitative approach is achieved by integrating IR characteristic absorption bands of each pollutant. One or all of the pollutants are thus detected continuouslly and specifically, by FTIR spectroscopy, by using a Nicolet macro language routine which sets the time interval between data collection. This procedure provides a possibility of adapting a selection of samples relating to the velocity of the development of the adsorption phenomenon studied. The FTIR spectroscopic measurements determine the vapour concentration [Cs], relating to the outflow pollutant concentration from the cartridge (exit concentration), versus time. The relation [Cs] = f(t), represents the breakthrough curve. The breakthrough time (tp), can be determined when the exit concentration detected is equal to a definite percentage of inlet concentration (which is equal to polluted atmospheric concentration, in this case: 1500, 100, 50 or 500 ppm) (6,7). In this study, the breakthrough time indicates when the outflow pollutant is detected for the first time.

Activated carbon is from vegetable origine (coconut shell), ground and sieved to 2 to 5 mm. The activated carbon filters used, are made up from glass cylindrical tubes (inside diameter 1,84 cm, section 2,66 cm^2). The adsorbent's bed depth varies according to the nature of the test. The linear velocity of air passage through activated carbon is 52,3 $cm.s^{-1}$. A flow rate of 500 litres per hour is required to achieve the linear velocity in the traps. The filters are placed vertically and granules of activated carbon are added, whithout being forced, by gravity only.

RESULTS AND DISCUSSION

Realisation of blanks

Beforehand, the activated carbon filters are cleaned with an constant air flow rate (500 $l.h^{-1}$) for a 13 hours period. The reason for this, is to detect any chemical compounds that may have been adsorbed by the adsorbent, and which would falsify the spectral results by desorption.

Measuring System Test

A calibration curve is established for each pollutant linking together the integrated areas of the IR bands, with the given concentration. Table 1 shows the integrated spectral ranges and calibration curves for quantitative analysis for each pollutant.

Results

1°) Carbon monoxyde

The exit concentration evolution of CO from a bed of 24 g of activated carbon, with an inlet concentration around 1500 ppm was followed. Three experiments are carried out which prove the good reproductibility of the results. The breakthroughs are almost instantaneous and the saturation phase is reached within 8 minutes.

It can be noted that an identical result is found without activated carbon and therefore, we can conclude that there is bad affinity between CO and this type of adsorbent.

In the case where the adsorption phenomenon exists (pollutant retention), the label "saturation phase" is incorrect because it doesn't correspond to the saturation of all the activated carbon adsorption sites. In

Table 1: Integrated infrared spectral ranges and calibration curves for quantitative analysis of various pollutants by FTIR spectroscopy.

Gas	Spectral windows (cm^{-1})	Equations
CO	2011-2245	Area = $0{,}217.[CO]^{0{,}599}$
SO_2	1308-1399	Area = $0{,}119.[SO_2]$
NO_2	1558-1657	Area = $0{,}210.[NO_2]$
HCl	2616-3089	Area = $0{,}0079.[HCl]$

fact, it corresponds to the chemical equilibrium between the pollutant molecules in the gas phase and the pollutant ones adsorbed on the adsorption sites.

2°) Sulfur dioxyde

The FTIR spectrum of SO_2 shows three bands at 1360, 1150 and 520 cm-1. The 1360 cm^{-1} band has been chosen to detect and quantify the presence of SO_2.

SO_2 can react with atmospheric water vapour to give H_2SO_3 and H_2SO_4 : these two compounds have not been detected in this study.

Figure 1 shows the three-dimensional kinetic of the SO_2 breakthrough. We observe first, the presence of H_2O vapour which then totally disappear and secondly the apparition of SO_2. H_2O vapour is probably due to H_2O molecules adsorbed on activated charcoal. The SO_2 detection threshold in this study (2m pathlenght) is 2,4 ppm.

Figure 2 shows the passage of atmospheres polluted by 100 ppm of SO_2 on different masses of activated charcoal and breakthrough times are given in table 2.

SO_2 is a gas which has a relatively significant affinity with activated charcoal, thus to achieve a reasonable breakthrough time, it is important not to use large masses of activated carbon. When the breakthrough time is zero, the adsorbent mass is referred to as critical mass (8). The results show that it is from 6g of adsorbent that the retention phenomenon becomes apparent for SO_2.

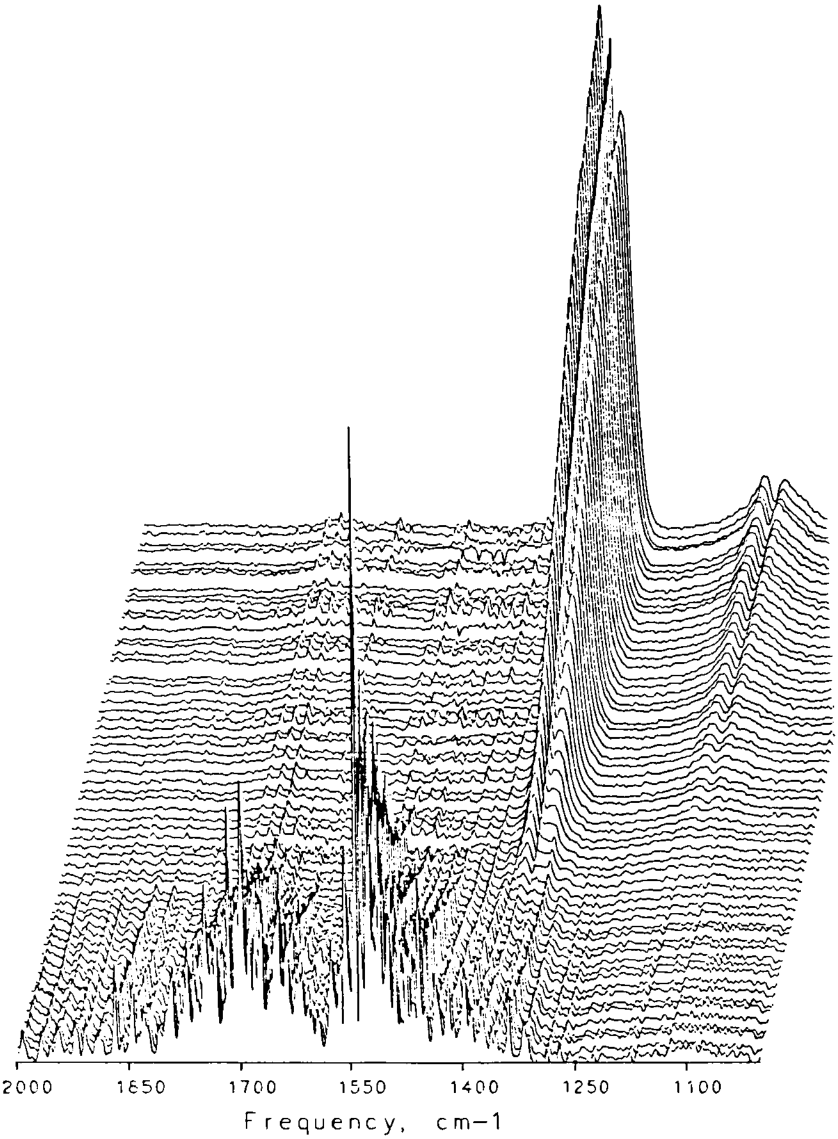

Figure 1 : Three-dimensional FTIR kinetic of SO_2 breakthrough on activated charcoal filter.

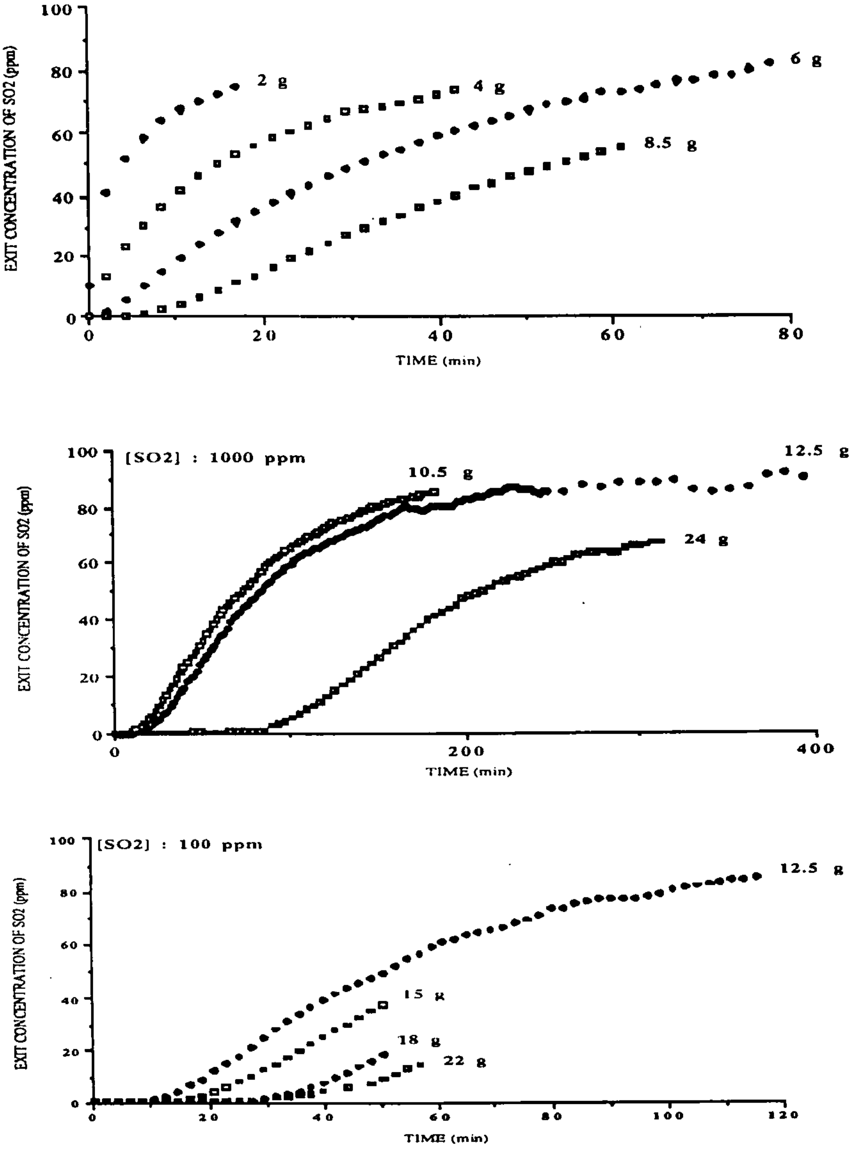

Figure 2 : Experimental breakthrough curves of sulfur dioxyde (100 ppm) on activated charcoal.

Table 2: Breakthrough times of CO, SO_2, NO_2 and HCl versus activated charcoal mass.

Gas	Concentration (ppm)	activated charcoal mass (g)	Breakthrough times (min)
CO	1500	24	immediate
SO_2	100	24	90
		22	31,5
		18	25
		15	17
		12,5	12,5
		10,5	10,5
		8,5	6
		6	1
		4	immediate
		2	immediate
NO_2	50	12,5	6
HCl	500	24	276,5
		12,5	70
		10	37,5
		8	25
		6	12,5
		4	7,5
		2	immediate

3°) nitrogen dioxyde

In the case of nitrogen oxydes, two species coexist at ambiant temperature and atmospheric pressure : NO_2 and N_2O_4. According to our experimental conditions (concentration, 50 ppm), only NO_2 spectrum is observed. The FTIR calibration curve has been elaborated using the 1605 cm^{-1} NO_2 band.

The breakthrough times for different masses of activated charcoal are given in table 2.

FTIR analysis of NO_2 is particularly difficult because its corrosiveness and also the presence of H_2O vapour at the beginning of the experiment (activated charcoal desorption) which absorbs in the same spectral range that NO_2. Consequently spectral substractions must be used for quantifying NO_2 as shown in figure 3. With this technique, the detection threshold is about 1,2 ppm.

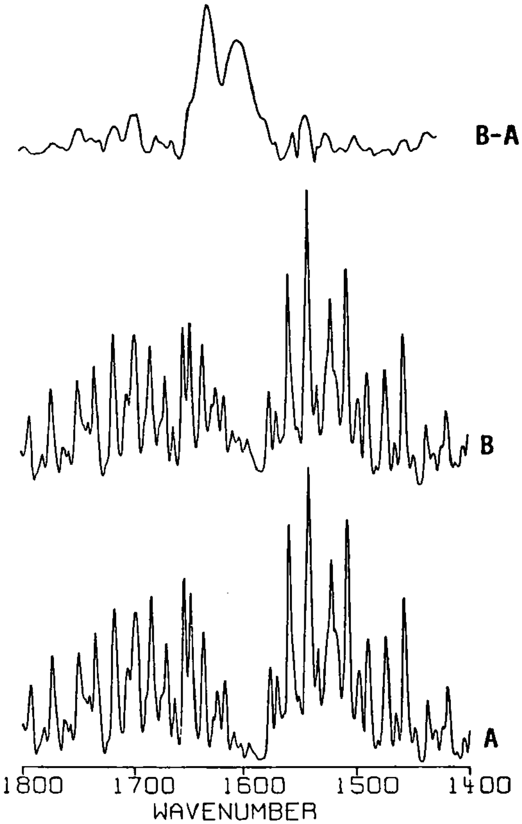

Figure 3 : Detection of NO_2 gas by FTIR spectral substraction of H_2O vapour (A : air, B : air polluted by 9 ppm of NO_2.)

The results obtained (table 2) may be questionable because KNO_3 has been detected at 1380 cm^{-1} (reaction of NO_2 with KBr windows of the FTIR cell) and a contaminant product has been also observed (N_2O, 2200 cm^{-1}).

4°) hydrogen chloride

For HCl measurements, any other species has been detected and the detection threshold is 11 ppm. Results are given in table 2.

5°) discussion

In the experimental conditions of this study (well fixed concentrations and linear velocity passages of gas), the obtained results prove that : (i) CO is not adsorbed by activated carbon, (ii) the three other pollutants are easily adsorbed, (iii) the gas affinities for the adsorbent increase as follows : CO « NO_2 < SO_2 < HCl.

This affinity scale is valid in ours experimental conditions, which correspond to the use of filters in a confined atmosphere. For a same mass of activated charcoal (12,5g for example) the breakthrough times increase as follow: CO (immediate), NO2 (6 min), SO2 (12,5 min) and HCl (70 min).

The breakthrough curves obtained do not present the classical sigmoid form (9,10). Three reasons can be found: (i) linear velocity of the gases passage through filters too high (11) (ii) pollutant concentrations too high (12,13) (iii) insufficient activated carbon mass.Taking into account the breakthrough curves obtained, the principal factor is the linear velocity of the gases passage through the activated carbon filters.

CONCLUSION

The study of the adsorption of CO and, in particular, SO_2, NO_2 and HCl using activated carbon is a delicate operation, because their very high toxcicity and/or corrosiveness. One of the main aims, was to fully master the handling of these gases, using an elabored device.

The device used for this study enables to synthetize in dynamic, the polluted atmospheres. Simulation is precise, with concentrations in the order of ppm. The value of an air pollution study, depends above all, on obtaining a polluted atmosphere that is completely homogenous and stable in course of time. The device developed satisfies such conditions.

It can work either in a dynamic or static way. It can be easily manipulable due to its small size. The device also enables a working routine. Consequently, associed with spectroscopy FTIR, it enables a regular on-going research on adsorption kinetics. It can also be used, for all the gases which absorb in infrared.

None of the breakthrough curves presents the classical sigmoid shape. This indicates that the air cleaning system doesn't work at its optimum (9).

In a future experiment, we will try to modelise the breaktrough of pollutants (and therefore, the adsorption) by determining a general kinetic equation. The importance of this type of modelling resides in the fact of certain parameters can be reached (saturation time, adsorption capacity to saturation) without having to carry through each experiment to the end. The gain of time, therefore, represents one of the essential advantages of this type of modeling.

Some of the breakthrough curve fluctuations found can probably be attributed to the variation in the granular size of activated carbon. Experiments will be carried out with a homogenous and reproductible granular size, with the aim to determine the thermodynamic and kinetic parameters of the pollutant/adsorbent interaction (rate constant, equilibrium constant, free energy variation and entropy variation).

REFERENCES

1. Hassler J.L., *Activated Carbon*, Leonard Hill.ed., London, 1967, p.1.
2. Hassler J.L., *Activated Carbon*, Leonard Hill.ed., London, 1967, p.15.
3. Cheremisinoff P.N. and Morresi A.C., *Carbon Adsorption Handbook*, P.N Cheremisinoff and F Ellerbush.ed., Ann Arbor Science, Ann Arbor (Mich.), 1978, p.1.
4. Leatherdale J.W , *Carbon Adsorption Handbook*, P.N Cheremisinoff and F Ellerbush.ed., Ann Arbor Science, Ann Arbor (Mich.), 1978, p.371.
5. Young D.M.and Crowell A.D., *Adsorption Physique des Gaz*, Presses Universitaires de France.éd., Paris,1967.
6. Guenier J.P.and Muller J. , Cahiers de Notes Documentaires n° 103, 2° Trimestre, INRS, 1981;197.
7. Tourres D.and Matyjasik Y., Analusis, 1987; 15: 540.
8. Balieu E., Ann.occup.Hyg., 1976; 19: 203.
9. Balieu E., Ann.occup.Hyg., 1977; 20: 375,1989;33:181,1990;34:1.
10. Wheeler A.et Robell A.J. , J. of Catalysis, 1969; 13: 299.
11. Nelson G.O.et Harder C.A., Am. Ind. Hyg. Assoc. J., 1972; IV: 797.
12. Nelson G.O.et Harder C.A., Am. Ind. Hyg. Assoc. J., 1974; V: 391
13. Nelson G.O.et Harder C.A., Am. Ind. Hyg. Assoc. J., 1976; VI: 205.

Date Received: November 8, 1993
Date Accepted: December 20, 1993