Short communication

Determination of atmospheric sulfur dioxide by ion chromatography in the city of Cabimas, Venezuela

Harvi Velásquez*, Hervín Ramírez, José Díaz, Marlene González de Nava,
Beatrice Sosa de Borrego, José Morales

Laboratorio de Química Ambiental, Departamento de Química, Facultad Experimental de Ciencias, Universidad del Zulia,
Maracaibo 4011, Venezuela

Abstract

Sulfur dioxide (SO_2) is an atmospheric pollutant that at certain concentrations may produce harm to human health and contribute to acid rain formation. Measurements of SO_2 concentrations were made at two sampling sites in the city of Cabimas, Venezuela, during several months of the dry season (March and April) and of the rainy season (May to July) of 1994. SO_2 samples were collected in a dilute solution of hydrogen peroxide (H_2O_2) with a Graseby/Andersen sampler, Model 209068 and analyzed as sulfate by ion chromatography (IC) using Dionex equipment, Model 2000i/sp. The detection limit for sulfate was 0.044 $\mu g/ml$, based on three times the standard deviation of the blank ($n = 23$). For a sulfate sample with a mean of 0.198 $\mu g/ml$ ($n = 7$), a relative standard deviation of 5.56% was obtained. The recovery of a sulfate standard (0.2 $\mu g/ml$) was 99%. The pararosaniline method was also used during the dry season in order to compare the results. Most of the SO_2 concentrations were detected during the dry season by the H_2O_2 IC method. The average concentrations at the sampling sites were 15.4 $\mu g/m^3$ ($n = 14$) and 16.6 $\mu g/m^3$ ($n = 15$). The total average (16.0 $\mu g/m^3$) represents 20% of the lowest Venezuelan air quality standard (80 $\mu g/m^3$).

Keywords: Environmental analysis; Air analysis; Sulfur dioxide

1. Introduction

Sulfur dioxide (SO_2) is an atmospheric pollutant that at certain concentration may produce harm to human health. The sulfate-aerosol product of SO_2 oxidation is thought to be the major anthropogenic contributor to acid rain and haze. Air pollution is not only confined to cities, it extends beyond those boundaries to cover rural sites, countries or a global scale where pollution could cross international boundaries. One example of this is the transport of SO_2 from highly populated and industrial sites to rural areas of Zulia State (Venezuela) where a high contribution of sulfuric acid (H_2SO_4) to the acidity of rain was found [1].

Information regarding prior levels of atmospheric SO_2 in the city of Cabimas is not available. This city is well known for petroleum industry activities. The city covers an extension of approximately 862 km^2 and has a population of 230 000 inhabitants. The main local sources of atmospheric pollution are the automotive traffic, the petroleum production (832 wells are located inland) and a small thermoelectric plant. Other pollution sources located up-wind of Cabimas are a hydrated alcohol chemical industry (18 km), the El Tablazo petrochemical complex (45 km) and the Cardon and Amuay petroleum refineries (200 km).

*Corresponding author.

This paper describes a method for the determination of atmospheric SO_2 concentrations using the ion chromatography (IC) technique. SO_2 is absorbed in a dilute hydrogen peroxide (H_2O_2) solution and analyzed as sulfate by IC. The pararosaniline reference method (US Environmental Protection Agency) was also used in order to compare the results with those found by the H_2O_2 IC method [2]. In practice, the pararosaniline method was too insensitive and hence the data generated could not be used for comparison. SO_2 levels measured in Cabimas were compared with Venezuelan air quality standards.

2. Experimental

2.1. Sampling sites

The city of Cabimas is located on the north-oriental coast of Lake Maracaibo in Zulia State,

Venezuela, between the following geographical coordinates: $10°20'15''-10°27'5''$ N and $71°28'37''-71°24'5''$ W. Two sampling sites were selected: site A, at the Engineering Faculty building of the University of Zulia State and site B, at the Social Assistance building of the Ministry of Education (Fig. 1). The selected sites were 1.5 km away from each other and were located in a residential area influenced by high-density automotive traffic. Furthermore, site B is near the La Salina oil-embarking terminal.

2.2. H_2O_2 IC method

2.2.1. Reagents

The absorbent solution was prepared by mixing 20 ml of 30% H_2O_2 (Baker, Phillipsburg, NJ, USA) with 0.1 ml of 0.6 M HCl (Fisher, Fair Lawn, NJ, USA) and diluted to 1 l with sulfate-free deionized water. Sulfate stock solution (1000 $\mu g/ml$) was
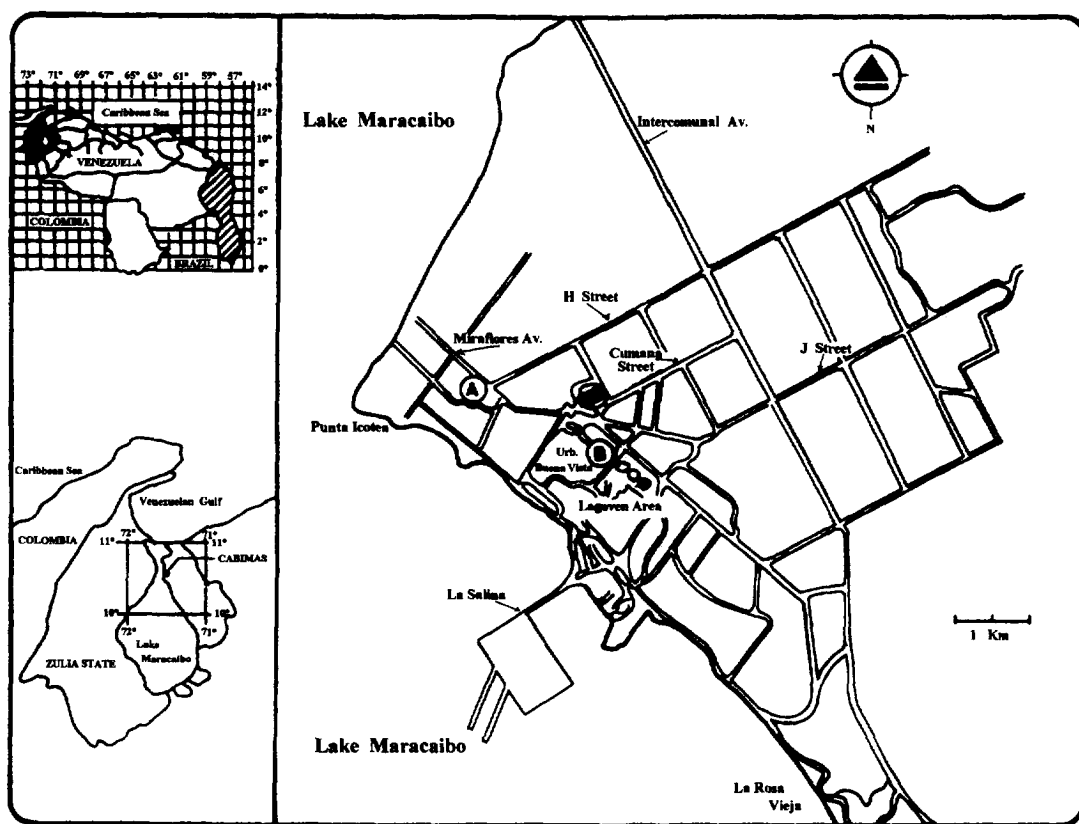

Fig. 1. Map of Cabimas showing the location of the sampling sites (A and B).

prepared from Na_2SO_4 (Merck, Darmstadt, Germany). The calibration standards for SO_4^{2-} were prepared from the stock solution by serial dilutions with the absorbent solution.

2.2.2. Procedure

SO_2 samples were simultaneously collected at both sampling sites at an altitude of approximately 15 m during the months of March and April of the dry season and the months of May, June and July of the rainy season of 1994. The number of samples collected was 31 ($n=14$ during the dry season and $n=17$ during the rainy season) and 32 ($n=15$ during the dry season and $n=17$ during the rainy season) in sites A and B respectively, for a total of 63 samples.

Samples were collected with a Graseby/Andersen (Atlanta, GA, USA) sampler, Model 209068, in 50 ml of a 0.6% H_2O_2 absorbent solution, at an air flow-rate of 185 ml/min during 24 h. In order to remove sulfate particulates from the air stream, a filter holder and a 5 μm pore PTFE membrane filter (Millipore LSWP 047-00) was used.

After the collection of SO_2, samples were transferred to 50 ml volumetric flasks and diluted to the mark with water to replace losses by evaporation during sampling. Samples were stored in polyethylene bottles and cooled at 5°C until analysis. Samples of the SO_2 oxidized to sulfate by the H_2O_2 were analyzed by the IC method using Dionex (Sunnyvale, CA, USA) 2000i/sp equipment. Operation conditions are presented in Table 1.

Blank (absorbent solution), standards and samples were introduced in the equipment's injection valve using a 0.45 μm pore disposable nylon filter. The

Table 1
Experimental conditions for ion chromatography

Columns	Dionex IonPac AG4A/AS4A
Supressor	Dionex AMMS-II
Eluent	1.8 mM Na_2CO_3
	1.7 mM $NaHCO_3$
Regenerant	12.5 mM H_2SO_4
Eluent flow-rate	1.3 ml/min
Regenerant flow-rate	3.3 ml/min
Injection volume	100 μl
Conductivity sensitivity	10 μS
Chart speed	0.5 cm/s
Background conductivity	18 μS
Detector	Dionex CDM-2 conductivity
Integrator	Dionex 4400

analysis time was 10 min which permitted the elution of the sulfate peak. External standardization was used with recalibration before every sample group was analyzed. A calibration graph was plotted of peak height (PH) against sulfate concentration, $[SO_4^{2-}]$ and used to interpolate unknown concentrations.

3. Results and discussion

3.1. Ion chromatography

After injection, sulfate ions were eluted from the column and detected with a conductivity detector, then recorded and quantified with an integrator. The resolution of the sulfate and the analysis time for a blank, a standard solution and sample are shown in Fig. 2. As can be seen, there is a well defined resolution, giving results in less than 10 min.
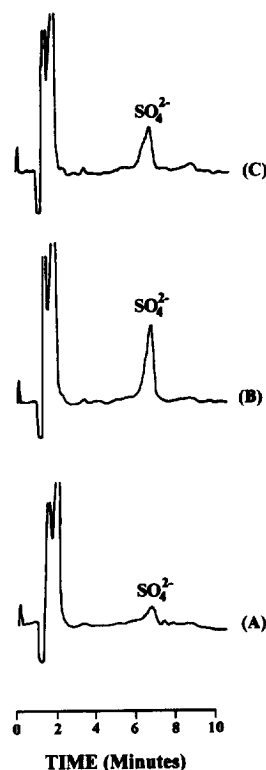
The response for SO_2 was linear in the working

Fig. 2. Chromatograms: A = Blank; B = Sulfate standard solution (0.5 g/ml); C = Sample.

range 0 (blank)–1 μg/ml. Linearity of the response is guaranteed by the dependence of the conductivity on concentration, provided that other effects or matrix effects do not intervene. The correlation coefficient (r) for the linear equation PH = 15 302 + 64 547 [SO_4^{2-}] was 0.9997. The relative standard deviation for the slope and the intercept were 1.17% and 1.25%, respectively, and the 95% confidence limits for the slope and the intercept were ±2,096 and ±531, respectively. The intercept is related with the blank which contains sulfate. The detection limit for sulfate was 0.044 μg/ml, based on three times the standard deviation of the blank (n = 23), that corresponds to a SO_2 concentration of 5.5 μg/m^3. For a sulfate sample with a mean of 0.198 μg/ml (n = 7), a relative standard deviation of 5.56% was obtained. The recovery of a sulfate standard (0.2 μg/ml) was 99%.

3.2. SO$_2$ concentrations

Most of the SO_2 concentrations were detected during the dry season by the H_2O_2 IC method (Table 2). The concentration levels obtained at the sampling

Table 2
Sulfur dioxide concentrations measured during dry season by H_2O_2 IC method

Days (1994)	Site A (μg/m^3)	Site B (μg/m^3)
1–2 March	23.1	26.0
3–4 March	21.3	26.4
7–8 March	17.3	18.8
10–11 March	20.3	21.1
14–15 March	22.6	29.6
17–18 March	20.0	27.8
21–22 March	6.6	8.7
24–25 March	—	10.4
4–5 April	7.6	10.8
7–8 April	11.3	10.6
11–12 April	10.6	10.3
14–15 April	20.4	13.0
21–22 April	15.0	16.5
25–26 April	16.9	16.7
28–29 April	<5.5[a]	<5.5[a]
Average[b]	15.4	16.6
S.D.	6.6	8.1

[a] For average calculations the value 5.5/2 = 2.8 was used.
[b] Total average: 16.0 (S.D. = 7.3; n = 29). Range: <5.5–29.6.

Table 3
Air quality standards for SO_2 in Venezuela

Limits (μg/m^3)	% of exceedence in sampling lapse[a]	Measurement period (h)
80	50	24
200	5	24
250	2	24
365	0.5	24

[a] Maximum % of samples that can exceed the SO_2 concentration limits.

sites did not exceed the Venezuelan air quality standards (Table 3). All samples had values smaller than 30 μg/m^3. The maximum daily value registered was 29.6 μg/m^3 at site B. Average concentrations obtained in sites A and B were 15.4 and 16.6 μg/m^3, respectively. Global SO_2 average for the city of Cabimas during the dry season (including both sites, n = 29) was 16.0μg/m^3. This value represents 20% of the lowest Venezuelan air quality standard concentration (80 μg/m^3).

The average of the concentration relation [SO_2]$_B$/[SO_2]$_A$ is 1.11 (S.D. = 0.21; n = 14). However, statistical analysis revealed no significant difference among the SO_2 concentrations of both sites at a level of 5% (P = 0.05).

On the other hand, a good [SO_2]$_A$–[SO_2]$_B$ correlation was found (r = 0.90; P < 0.01). This indicates that both sampling sites are influenced by the same sources of SO_2: heavy traffic, incineration of natural gas emitted by petroleum wells and hydrogen sulfide (H_2S) emitted to the atmosphere during the crude oil production and well reactivation by steam injection. Hydrogen sulfide in the atmosphere is converted to SO_2 in the presence of O_2 and O_3.

During the rainy season only three samples revealed a detectable concentration of SO_2 by H_2O_2 IC. This fact can be associated with the remotion processes of rain on atmospheric aerosols and gases. SO_2 can also be removed by conversion to sulfuric acid (H_2SO_4) and sulfate salts, which precipitate with rainfall.
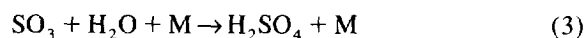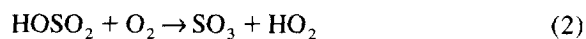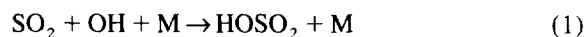
It is generally recognized that the two most important oxidation processes are homogeneous gas-phase reactions involving free radicals such as hydroxyl (OH) and heterogeneous reactions in droplet phase and on aerosol particle surfaces.
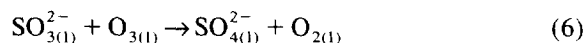
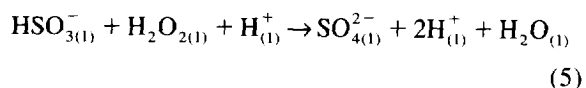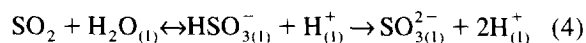The year-round tropical climate in Cabimas may

facilitate both processes. During the months of May, June and July of the rainy season, the average relative humidity increased to 78% (from 75% during the dry season) while solar radiation remained high (423 cal/cm^2/day^1; 1 cal=4.184 J). During a study in Nagoya [3], a good correlation was found between the conversion of the SO_2 to sulfate and the relative humidity when the oxidant concentrations were more than 20 ppb. These results indicate that droplet phase reactions are important for the SO_2 oxidation to sulfate. On the other hand, due to a larger flux of solar ultraviolet radiation, the highest OH concentration occurs in the tropics [4]. This fact favors the homogeneous gas-phase reactions for the SO_2 oxidation.

SO_2 is oxidized in the atmosphere to produce H_2SO_4 through the following reactions [5]:

(a) Homogeneous reactions

$$SO_2 + OH + M \rightarrow HOSO_2 + M \qquad (1)$$

$$HOSO_2 + O_2 \rightarrow SO_3 + HO_2 \qquad (2)$$

$$SO_3 + H_2O + M \rightarrow H_2SO_4 + M \qquad (3)$$

(b) Heterogeneous reactions

$$SO_2 + H_2O_{(l)} \leftrightarrow HSO_{3(l)}^- + H_{(l)}^+ \rightarrow SO_{3(l)}^{2-} + 2H_{(l)}^+ \quad (4)$$

$$HSO_{3(l)}^- + H_2O_{2(l)} + H_{(l)}^+ \rightarrow SO_{4(l)}^{2-} + 2H_{(l)}^+ + H_2O_{(l)} \qquad (5)$$

$$SO_{3(l)}^{2-} + O_{3(l)} \rightarrow SO_{4(l)}^{2-} + O_{2(l)} \qquad (6)$$

Concentrations of SO_2 could not be detected with the pararosaniline method (detection limit=25 $\mu g/m^3$). The low SO_2 concentrations and elevated temperatures (average $T=28°C$) observed during the sampling period (March and April) could have influenced the collection efficiency. This method presents certain temperature stability problems and its collection efficiency falls off rapidly at low concentrations.

4. Conclusions

The results of this study provide valuable background information that can be applied in dispersion modelling as well as in the evaluation of the possible impacts that a future industrial development in the area could generate upon atmosphere.

The H_2O_2 IC method allowed atmospheric SO_2 measurements at low concentrations (<30 $\mu g/m^3$) and high ambient temperatures (28°C) which makes it an adequate method to be used in hot weather.

The high reactivity of the atmosphere in Cabimas, due to elevated solar radiation and relative humidity, may have influenced the transformation of SO_2 to sulfate and determined the low concentration values observed for SO_2.

Acknowledgments

References

[1] J.A. Morales, H.L. de Medina, M.G. de Nava, H. Velásquez and M. Santana, J. Chromatogr. A, 671 (1994) 193.
[2] Intersociety Committee: APCA, ACS, AIChE, APWA, ASME, AOAC, HPS, ISA, in J.P. Lodge (Editor), Methods of Air Sampling and Analysis, Lewis Publishers, MI, 1989, Part II, pp. 493, 503.
[3] S. Kadowaki, Environ. Sci. Technol., 20 (1986) 1249.
[4] E. Sanhueza, Interciencia, 17 (1992) 208.
[5] S. Schwartz, Science, 243 (1989) 753.