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Article

Development of a Coulometric Method for the Determination of Gaseous Sulfur Compounds in Urban Atmospheres

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Uma nova metodologia para a determinação de compostos gasosos de enxofre presentes em atmosferas urbanas foi desenvolvida e aplicada durante três meses na região central da cidade de Porto Alegre- RS e em uma refinaria de petróleo, localizada próxima à essa cidade. O método se baseia na determinação coulométrica da taxa de sulfetação da prata pura. Os resultados foram comparados com o método da pararosanilina, que está sendo atualmente utilizado para a determinação de SO_2 em alguns dos locais aqui estudados. Os resultados obtidos mostraram que uma boa correlação entre o método coulométrico e o método da pararosanilina é observada quando somente SO_2 está presente, como normalmente é esperado para atmosferas urbanas. Quando H_2S está também presente, como no caso das áreas industriais, a nova metodologia tende fortemente a super estimar derivados gasosos de enxofre.

A new procedure for the determination of atmospheric sulfur compounds was developed and applied during three months in the central area of the City of Porto Alegre- RS, and one month near an oil refinery located close to this city. The method is based on the coulometric determination of the tarnishing rate of pure silver. The results were compared with the method of pararosaniline, which is being currently used in some of the studied sites for the determination of SO_2. The results obtained showed a good correlation between the coulometric method and the pararosaniline method, when only SO_2 is present, as usually is the case of urban atmospheres. When H_2S is also present, as in the case of industrial areas, the methodology tends to strongly overestimate SO_2 concentration.

Keywords: coulometric method, tarnishing of Ag, urban pollution, SO_2, H_2S

Introduction

Besides suspended particles, gaseous compounds, such as carbon monoxide (CO), carbon dioxide (CO_2) and sulfur dioxide (SO_2), are normally the main atmospheric pollutants in urban areas[1, 2]. Previous studies showed that in Porto Alegre- RS, approximatly 3.7 tons of SO_x are daily emitted. Further 3.4 tons of SO_x per day are produced in the industrial metropolitan area around the city[3].

The main SO_2 source in urban areas is commonly accepted as resulting from the use of fossil fuels. In warm regions like Southern Brazil, the main source should be attributed to the transport activity and to the use of Diesel oil. Due to local variations in the traffic density and in the wind velocity in a city, a local monitoring of SO_2 is more adequate to identify critical areas, which are harmful to the human health and are also very corrosive to metals, stones and concrete structures.

The aim of the present study was to develop a method for the determination of atmospheric SO_2 content. The method should be inexpensive and simple, making possible the local determination of the mean concentration in several points in an urban area. As showed below, the tarnishing rate of silver shows the desired characteristics for an indicator of the SO_2 concentration.

Pure silver, when exposed to H_2S or SO_2, forms a tarnishing layer consisting only of achantite (alpha Ag_2S). This sulfide has an extremely low solubility product in water, K_{ps}=1 10^{-50} mol L^{-1} [3,4] and is very conductive and adherent to the silver surface, enabling its coulometric determination after the atmospheric exposure of silver[3, 5].

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Moreover, due to the high mobility of Ag^+ ions in the Ag_2S salt, the tarnishing rate is time independent for tarnishing layers up to several microns thick, being directly proportional to the H_2S and SO_2 concentrations[5]. As an example, the tarnishing rate of Ag in 1ppm H_2S, which is higher than the one in SO_2, remains controlled by surface reaction for several days[6, 7].

The results presented here were measured during the southern hemisphere summer of 1999 in three urban points of Porto Alegre- RS, showing heavy traffic, where only SO_2 is expected, and also in two sites near an oil refinery, with different distances from a H_2S source. An increasing SO_2/H_2S concentration ratio is expected here for greater distances from the H_2S source, resulting from the oxidation of H_2S to SO_2 during its transport from the source to the measuring site. A long-term study is now under way to determine the influence of traffic intensity and climate parameters in the correlation between the coulometric and pararosaniline methods.

Experimental

For the coulometric determination of tarnishing rates, coupons of pure silver (Sigma-Aldrich, 99.99% Ag) with geometric areas between 5 and 6 cm^2 were cut and provided with a 0.5 mm diameter hole. After vacuum annealing (650 °C $h^{-1}10^{-2}$ atm) the coupons were polished on both sides with emery paper up to 2400 mesh and degreased in ethanol. For the atmospheric exposure, the coupons were hanged by a PTFE thread in the vertical position at five “monitoring stations”, where a good ventilation and rain protection were provided, and also other atmospheric data were being collected. Three monitoring stations were located in downtown sites, with dense traffic, *Rodoviária*, *Borges* and *Azenha*. Among these sites, *Rodoviária*, where the Central Bus Station is located, shows usually the highest SO_2 emissions. The other two monitoring stations were located at 19 km far from downtown of Porto Alegre- RS, at the oil refinery “Refinaria Alberto Pasqualine-Petrobras”, namely *REFAP1* and *REFAP2*. The station *REFAP1* lied 750 m far from an H_2S-SO_2-source, and *REFAP2*, respectively 1,500 m. At three of these stations, *Rodoviária*, *REFAP1* and *REFAP2*, SO_2 was also collected and the concentration determined by the pararosaniline method as described in the appropriate norm[8]. The exposures were proceeded from January to March 1999. The mean relative humidity and temperature during this period were 79.4% and 24.9 ºC respectively, as determined for Porto Alegre- RS by the local state climate station.

After exposure for different times, the Ag coupons were rinsed with water and acetone and reduced potentiodynamically in a standard three electrodes cell. The electrolyte was a borate buffer of pH 10 (3.092 g L^{-1} H_3BO_3, 3.728 g L^{-1} KCl, 1.756 g L^{-1} NaOH), with addition of small quantities of Na_2S and purged previously for 8 h with N_2. Good results were obtained for sweep velocities in the negative direction of 0.1 mV s^{-1}, starting from the Ag_2S/Ag equilibrium potential. This low sweeping rate was necessary to avoid the superposition of the Ag_2S reduction peak and the current related to the hydrogen evolution reaction. The equilibrium potential (Ag_2S/Ag) was determined by a previous potentiodynamic sulfidation and reduction of a blank Ag probe in the same solution. The potentials were measured against an AgCl/Ag reference electrode in 3.5 mol L^{-1} KCl, but are referred in the text to the normal hydrogen electrode (NHE). After data acquisition by computer, the mass of Ag_2S per area was calculated from the charge density under the observed cathodic peak, assuming Ag_2S as the only tarnishing product and subtracting the charge related to the background current density.

Results and Discussion

The voltammograms of the reduction of the exposed Ag coupons are shown in Figures from 1 to 5. A sharp reduction peak in the range between E(Ag_2S/Ag) and –200 mV more negative than this, *i.e* (from –350 to 550 mV) is always observed. The peak current density grows with the exposure time, and it can be attributed undoubtedly to the reduction of the environmentally formed Ag_2S. No reduction peaks could be observed for unexposed Ag samples. The background current density, measured on unexposed samples, or estimated on exposed samples as the current minimum between the Ag_2S peak and the hydrogen evolution region, ranged between 0.2 and 1μA cm^{-2}, indicating the reduction of residual O_2 dissolved in the electrolyte. The coupons exposed at urban sites, *i.e*. R*odoviária*, *Borges* and *Azenha*, (Figures 1-3, respectively) showed less pronounced reduction peaks, comparing to the ones exposed at the oil refinery sites, *REFAP1* and *REFAP2* (Figures 4 and 5). For exposures at the less aggressive sites *Borges* and *Azenha*, a clear identification of the reduction peaks, at a potencial sweep rate of 0.1 mV s^{-1} was only possible for exposure times of *ca*. 10 days or longer. For the more aggressive sites at the refinery, clear peaks were already identified after seven days of exposure.

Samples exposed for more then 20 days at the most aggressive sites showed a second reduction peak (Figure 1, 4, 5). Its current density, subtracting the background current, grows with time of exposure and with the aggressivity of the atmosphere, and its current was allways less than 3% of the main Ag_2S peak. A second reduction peak was also observed by the reduction of Ag samples tarnished strongly in aqueous sulfide solutions of 0.01mol L^{-1}

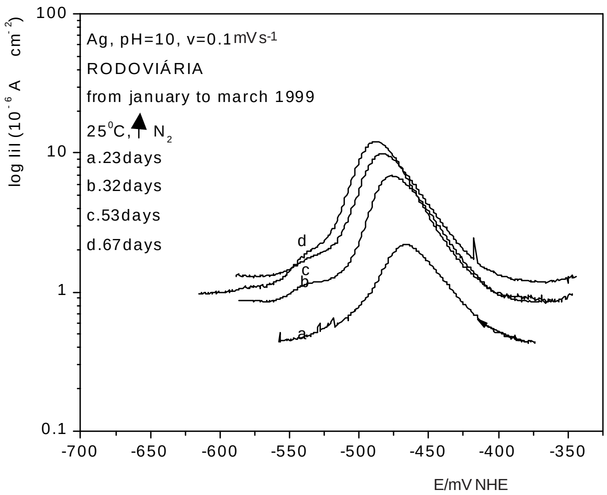

Figure 1. Voltammograms for the reduction of Ag_2S on Ag coupons in borate buffer, v = 0.1mV s^{-1}, after atmospheric exposure during January-March 1999 at the *Rodoviária* site in Porto Alegre.

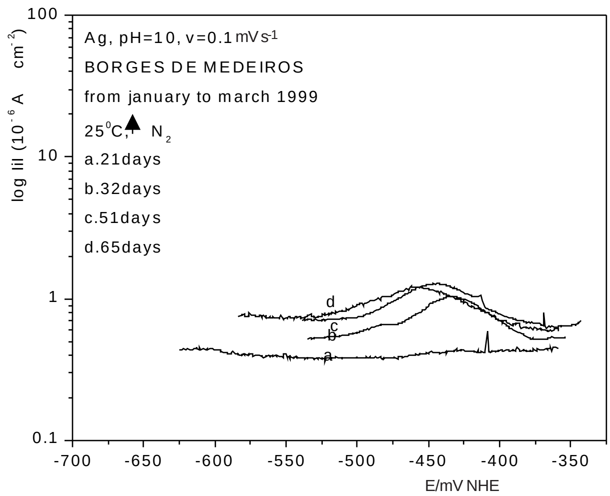

Figure 3. Voltammograms for the reduction of Ag_2S on Ag coupons in borate buffer, v = 0.1mV s^{-1}, after atmospheric exposure during January-March 1999 at the *Borges de Medeiros* site in Porto Alegre.

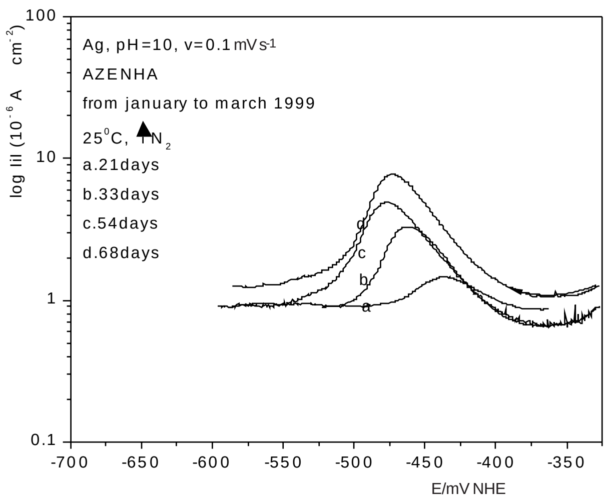

Figure 2. Voltammograms for the reduction of Ag_2S on Ag coupons in borate buffer, v = 0.1mV s^{-1}, after atmospheric exposure during January-March 1999 at the *Azenha* site in Porto Alegre.

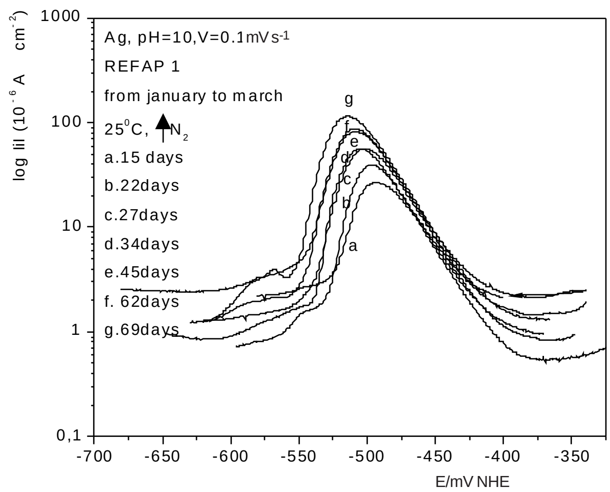

Figure 4. Voltammograms for the reduction of Ag_2S on Ag coupons in borate buffer, v = 0.1mV s^{-1}, after atmospheric exposure during January-March 1999 at the *REFAP1* site in Refinaria Alberto Pasqualine.

Na_2S[6,7]. Only Ag_2S could be detected in that case by X-ray diffraction and thus, it is here assumed that only Ag_2S is formed atmospherically.

The mass of Ag_2S formed *vs.* the exposure time is shown for all sites in Figure 6. For the determination of the respective tarnishing rates, a linear correlation was found for the mass *vs.* time curves. The correlation coefficients were normally higher then 0.93, with exception of the *Borges* site, where R = 0.70 was measured. The aggressivity of the sites and the respective Ag tarnishing rates, lie in the following decrescent order: $\partial m/\partial t_{REFAP1} = 1.00$, $\partial m/\partial t_{REFAP2} = 0.34$, $\partial m/\partial t_{Rodoviária} = 0.08$, $\partial m/\partial t_{Azenha} = 0.06$ and $\partial m/\partial t_{Borges} = 0.007 \mu g\ Ag_2S\ cm^2\ day^{-1}$. These results indicate that there are differences of more than one order of magnitude in the tarnishing rates and SO_2 concentrations of sites lying only 1.1km apart in downtown Porto Alegre (*Borges* and *Rodoviária*). Moreover, for a distance of 2.5 km from the H_2S-SO_2 source at the refinery, the atmosphere is still 4.25 times more aggressive than the most polluted site identified in downtown Porto Alegre, *i.e. Rodoviária.*

The comparison between the Ag tarnishing rate and the mean SO_2 concentration as determined by daily measurements during the same period with the pararosaniline method is presented in Figure 7. Using the data from the two sites where only SO_2 is expected (*Rodoviária* and *REFAP2*) a ratio between the SO_2 concentration and the Ag tarnishing rate of 86±4g SO_2 m^{-3}/g Ag_2S cm^{-2} day^{-1}. For the site *REFAP1*, where H_2S is also present, a 4 times smaller ratio is found. This is certainly due to a much higher Ag tarnishing rate in H_2S than in SO_2. The coulometric

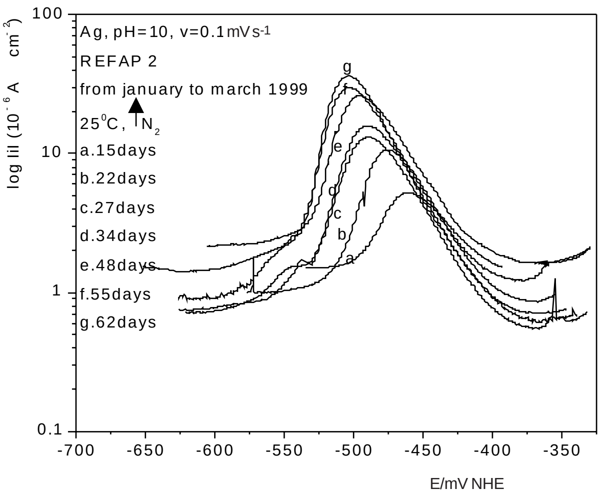

Figure 5. Voltammograms for the reduction of Ag_2S on Ag coupons in borate buffer, v = 0.1mV s^{-1}, after atmospheric exposure during January-March 1999 at the *REFAP2* site in Refinaria Alberto Pasqualine.

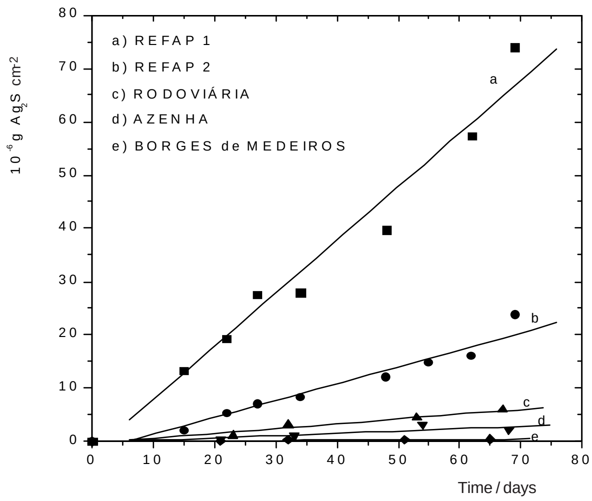

Figure 6. Tarnishing curves of Ag_2S growth for Ag samples exposed at different sites.

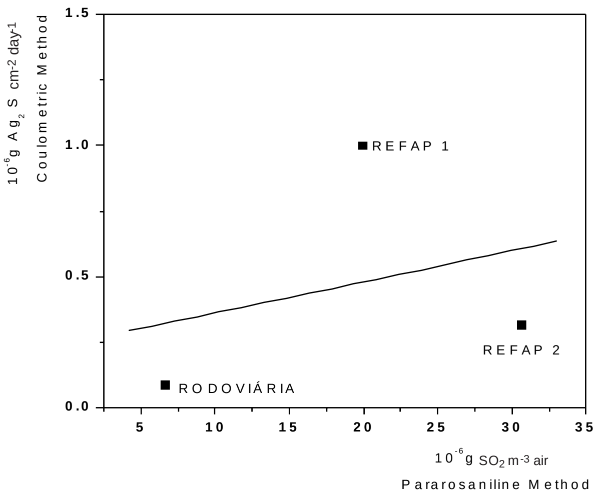

Figure 7. Comparison between the Ag tarnishing rates and the mean SO_2 concentration determined by the pararosaniline method.

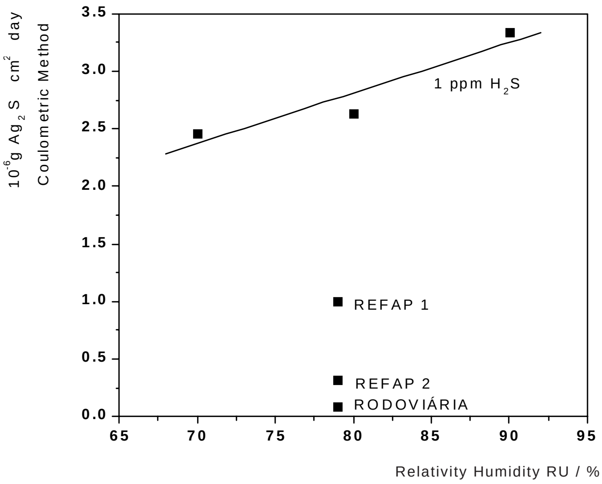

Figure 8. Comparison between the Ag tarnishing rate measured in an environmental chamber at 25 ºC, $1H_2S$, at 70, 80 and 90% relative humidity and the mean tarnishing rates determined at the monitoring stations.

method suffers from H_2S interference, and no quantitative results can be expected in this case. Even so, it points out that the site *REFAP1* has a much more aggressive atmosphere than *REFAP2*. The pararosaniline method, currently in use, indicated a SO_2 concentration 1.5 times higher at the most distant point from the source than at a closer one. This is probably due to the oxidation of H_2S to SO_2 in the way between the source and *REFAP2*.

A comparison between tarnishing rates measured in an environmental chamber[6, 7] containing 1 ppm H_2S at T= 25ºC and the ones determined in this work at a mean relative humidity of 79.4% and temperature of 24.9°C is presented in Figure 8. Assuming that the tarnishing rate is directly proportional to the H_2S concentration, an equivalent H_2S concentration can be calculated. The values obtained are 0.36 ppm for *REFAP1*, 0.12 ppm for *REFAP2* and 0.03 ppm for *Rodoviária.*

Conclusions

The coulometric method, based on the determination of the tarnishing rate of Ag, can be used for the determination of SO_2 concentrations in urban atmospheres. When H_2S is also present, as in industrial areas, an over estimation of the SO_2 concentration is expected, as the method can not separate the effect of these two species. At least one week is necessary till the presence of SO_2 can be detected in urban sites. Due to its low cost and simplicity, the method is more adequate for the local determination of long term average concentrations of SO_2.

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