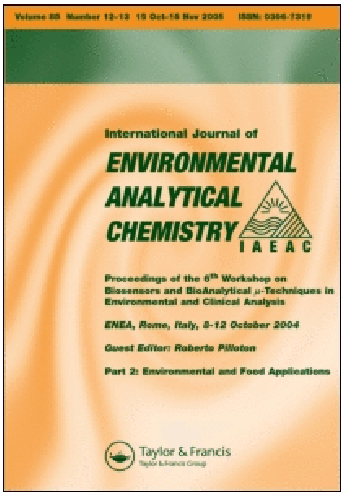

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DETERMINATION OF NITRATE AND NITRITE BY ION-SELECTIVE ELECTRODES IN RELATION TO GYPSUM FORMATION ON SOME TRAVERTINE BUILDINGS IN POLLUTED ATMOSPHERE OF ANKARA

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Gypsum formation on calcareous building stones in the polluted atmosphere of cities is thought to be accelerated by the presence of nitrogen-containing compounds. A reliable method for nitrate and nitrite determinations is proposed and the presence of nitrogen compounds is discussed in relation to their possible influence on gypsum formation. Investigations on nitrate and nitrite determinations with ion-selective electrodes have been carried out along with gypsum determinations on the samples taken from altered surfaces of some travertine buildings in Ankara. Interfering effects of the ions which may be present in the matrix studied have been examined and the proper masking solutions for their removal have been introduced. Investigations show that nitrate and nitrite determinations with ion-selective electrodes are reliable, rapid and inexpensive in stone extracts. The sulphate to nitrate ratios in this study vary between 32 and 393. These data are compared with earlier results and the possible effects of nitrogen-containing compounds in gypsum formation are discussed.

KEY WORDS: Stone, gypsum formation, nitrate, nitrite, ion selective electrode.

INTRODUCTION

The purpose of this study is to provide additional data on the presence of nitrogen-containing compounds with gypsum, by means of a reliable method like the use of ion-selective electrodes, in order to investigate their possible contribution to gypsum formation on calcareous building stones in polluted atmospheres. One of the many harms of air pollution to man and his environment are its effects on building materials. It is well known that several types of air pollutants, together with the help of climatic conditions and airborne particles accelerate the deterioration of stone through mechanisms such as gypsum formation.

In recent studies[1,2] it has been found that the Ankara atmosphere with its coinciding high relative humidity and high sulphur dioxide concentration favours gypsum formation on calcareous stones. According to the measurements of the Institute of Health Protection (Ankara), the sulphur dioxide concentration (the major pollutant in the atmosphere) exceeds $400\,\mu g/m^3$ of air in winter time.[1,2] As published in the Bulletins of the Directorate of State Meteorological Studies, the average relative humidity reaches its maximum of about 80% in the same period. The average total rainfall is highest in spring time when the temperature gradually increases and the relative humidity decreases.

Pollutants in the Ankara atmosphere other than sulphur dioxide have also been studied. The Institute of Health Protection (Ankara) indicates considerable amounts of nitrogen oxides in the atmosphere. Although the analyses were carried out for a limited period of time, it is clear that the concentration may be as high as 30–40 $\mu g/m^3$ (Figure 1).

Nitrogen gases in the atmosphere are mainly introduced by industrial sources and traffic, but their sources may be biological as well.[3] Unlike sulphur dioxide, oxides of nitrogen exist in several forms such as nitrous oxide (N_2O), nitric oxide (NO) and nitrogen dioxide (NO_2). In an urban atmosphere they are usually in the forms of nitric oxide and nitrogen dioxide, in amounts varying under the influence of ozone and sunlight.[4] Nitrogen species reaching calcareous stone surfaces like travertine, may be in various forms, the primary species being nitrogen oxides in gaseous form. Another important compound is nitric acid. It is found in rain water and in the atmosphere both in the dissolved state and as nitric acid vapour.[5–7] Particulate ammonium nitrate as aqueous droplets has also been detected in the atmosphere.[4]

In addition to the nitrogen species in the atmosphere, nitrogen may be introduced from biological sources to the stone surface by the activities of certain bacteria in which nitrites produced by bacterial decomposition of ammonia or nitrates in the soil reach the walls by rising damp. Bird droppings are another source of nitrogen species of organic origin on the stone surfaces.

Gypsum is the main mineral formed on the surface of calcareous building stones such as travertines in a polluted atmosphere. The presence of sulphur dioxide leads to its formation through not well defined mechanisms. Possible ways of gypsum formation have been summarized in a previous study,[1] and gypsum formation in relation to the deterioration of different types of calcareous stones, and the factors which may affect its formation have been studied by several workers.[8–11] Among these, the role of nitrogen species which coexist with sulphur dioxide in the polluted atmosphere is not well defined.

Nitrogen oxides react relatively slowly with calcium carbonate in comparison with sulphur dioxide. This is supported by data on the free energies and kinetics of the reactions:[4,12,13]

$$CaCO_3 + SO_2 + \tfrac{1}{2}O_2 \rightleftharpoons CaSO_4 + CO_2 \quad \Delta G = -68\,\text{kcal/mole} \tag{1}$$

$$CaCO_3 + 2NO_2 + \tfrac{1}{2}O_2 \rightleftharpoons Ca(NO_3)_2 + CO_2 \quad \Delta G = -26\,\text{kcal/mole} \tag{2}$$

Reaction (1) occurs in two steps, an intermediate calcium sulphite being formed first:

$$CaCO_3 + SO_2 \rightleftharpoons CaSO_3 + CO_2 \tag{3}$$

$$CaSO_3 + \tfrac{1}{2}O_2 \rightleftharpoons CaSO_4. \tag{4}$$

Oxidation of calcium sulphite to sulphate takes place rapidly in the presence of nitrogen oxides. On the other hand, nitrogen oxides do not form stable inter-

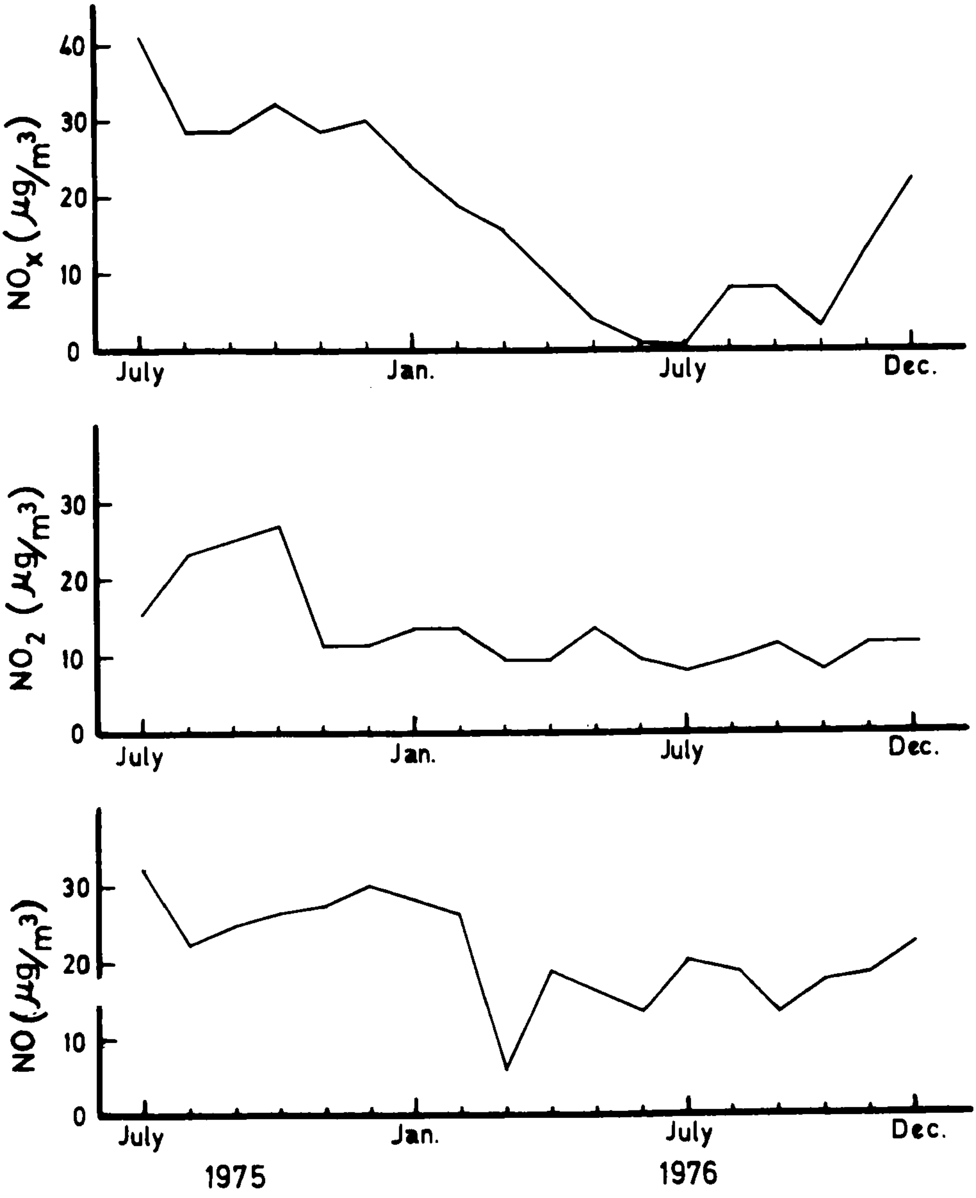

Figure 1 Average concentration of nitric oxide, nitrogen dioxide and nitrogen oxides in Ankara atmosphere.

mediate compounds with calcium carbonate; consequently their adsorption and calcium nitrate formation are not favoured.

In laboratory simulation experiments carried out by Johansson *et al.*[12] calcium sulphite ($CaSO_3 \cdot \frac{1}{2}H_2O$) was formed on a marble surface with no gypsum, in an atmosphere of $4.2 \times 10^3\ \mu g/m^3$ of sulphur dioxide and at 90% relative humidity. If this sample is exposed to air containing $5.8 \times 10^3\ \mu g/m^3$ of nitrogen dioxide and at 90% relative humidity, gypsum starts to be formed in 24 hours, although in small quantities. This shows that nitrogen dioxide is capable of promoting the oxidation of $CaSO_3 \cdot \frac{1}{2}H_2O$ to gypsum, $CaSO_4 \cdot 2H_2O$.

In the same study it was found that under high-humidity conditions, and in the presence of nitrogen dioxide, the rate of sulphur dioxide deposition increases on calcareous stone surfaces, desorption of sulphur dioxide being suppressed because of rapid oxidation of adsorbed sulphur dioxide to sulphate.[12] The authors have proposed the following reaction and underlined the catalytic contribution of nitrogen dioxide in gypsum formation at high relative humidity conditions:

$$SO_2(g) \overset{\text{fast}}{\rightleftharpoons} SO_2(\text{ads}) \overset{\text{slow}}{\rightleftharpoons} CaSO_3 \cdot \tfrac{1}{2}H_2O(s) \overset{\text{slow}}{\rightleftharpoons} CaSO_4 \cdot 2H_2O(s).$$

EXPERIMENTAL

An Orion Research Digital Ionalyzer Model 801 A was used for the potentiometric determinations. An Orion Research Model 93-07 Nitrate Electrode[14] which is coupled to an Orion Research Model 92-02 double-junction reference electrode[15] was used for nitrate determination. For nitrite determinations, the Orion Research Model 95-46 nitrogen oxide electrode was used. All potentiometric measurements were performed by using calibration curves prepared in the concentration ranges of interest.

Gypsum determinations were done gravimetrically by barium sulphate precipitation.

All reagents were of analytical-reagent grade quality. Stock solutions were prepared from these chemicals with triple-distilled water. Stone samples were taken from sheltered places of travertine buildings of different age and at various locations in Ankara, by scrubbing deteriorated parts of the stone surfaces.

Samples collected from the Mausoleum of Atatürk (Anıtkabir), Maltepe Mosque and 100.Yıl Shopping Center were dried at 35 °C for 24 h prior to analysis. The samples which were used for nitrate and nitrite determinations were extracted in 10 mL of water for about 28 h.

RESULTS AND DISCUSSION

The determination of low concentrations of nitrate and nitrite in small samples presents a problem. Among the various techniques, the use of an ion-selective electrode (ISE) is a practical and convenient method. The experimental parameters were verified[14,15] and optimized by us as follows.

- *Response time.* Both the nitrate and nitrite electrode exhibit good response within 5 min, in the concentration range of 10^{-6}–10^{-2} M.
- *Limit of detection.* The lower limits of detection are 1.7×10^{-6} M for nitrate, and 1.3×10^{-6} M for the nitrogen oxide electrode used in this study.
- *Reproducibility.* With calibration every 2 h, the electrode measurements were found to be reproducible within $\pm 2\%$.
- *Ionic strength adjuster for nitrate electrode.* The best calibration curve is obtained when 2 M $(NH_4)_2SO_4$ is used as ionic strength adjuster.
- *Osmotic strength adjuster for nitrogen oxide electrode.* A 1 M osmotic strength adjuster (sodium sulphate, sulphuric acid buffer)[15] is found to be most convenient for the system being investigated.
- *Effect of interferences and the use of masking agents.* Carbonate, chloride, sulphate and nitrate/nitrite anions are the main interferences expected in the travertine matrix studied. The results obtained in the determination and elimination of their effects are discussed below.

Nitrate Determinations

The presence of sulphate, carbonate, chloride and nitrite affects the response of the nitrite electrode in the 10^{-6}–10^{-2} M nitrite concentration range. Their effects were eliminated as follows. For the removal of the sulphate interference, instead of adding barium hydroxide or barium chloride, which would change the pH of the solution or would introduce more interfering ions to the medium, matrix modification was performed by the addition of a known amount of sulphate to the medium through sulphuric acid and silver sulphate. The sulphate level is then considered to remain constant through the measurements, since the sulphate contribution from the stone extracts is expected to be relatively low. Besides, the addition of sulphuric acid eliminates the carbonate and the addition of silver sulphate masks the interfering chloride ion present. Nitrite interference was prevented by sulphamic acid.[14] As a result, for nitrate ISE measurements, the masking solution is 10^{-4} M in sulphuric acid, 2.5×10^{-5} M in silver sulphate and 2.5×10^{-4} M in sulphamic acid. The masking solution was tested with several solutions containing varying amounts of nitrate, nitrite and chloride. The carbonate concentration was taken to be 1.4×10^{-4} M in each case, which is the expected amount in travertine extracts (Figure 2). As seen, the masking solution eliminates the effects of chloride, nitrite and carbonate ions, and the potentiometric readings were brought back to their original values. For further measurements masking solutions were added to both standard and sample solutions prior to potentiometer readings.

Nitrite Determinations

It was found that the presence of sulphate, nitrate and chloride has no effect in nitrite determinations, as expected.[15] The carbonate effect can be eliminated by the

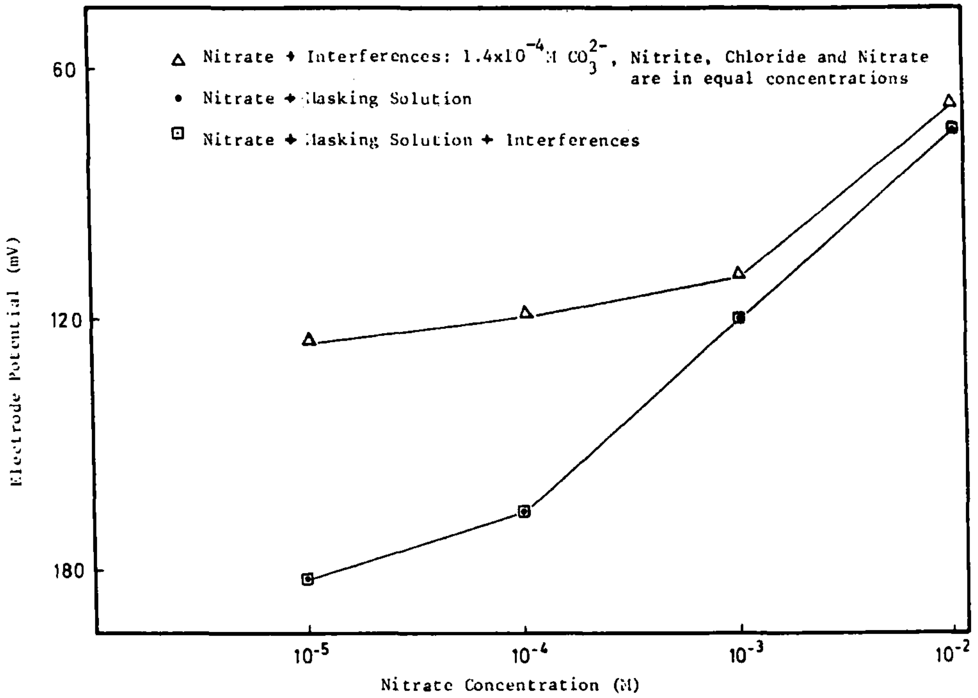

Figure 2 Effect of masking solution in nitrite electrode.

addition of potassium hydrogen phthalate and perchloric acid to the solution which would produce a buffer of pH 4.0 and convert carbonate into carbon dioxide. The produced gas is removed from the medium by bubbling nitrogen through the solution for 5 min. Figure 3 shows the result of this treatment.

A summary of the optimum working conditions is given in Table 1. In order to test the validity of the ISE measurements performed under these conditions, a set of test solutions and solids were prepared and analyzed accordingly. The results obtained are given in Tables 2 and 3. There is good agreement between the theoretical and experimental results, which demonstrates the reliability of ISE measurements performed under the conditions of Table 1. The flowchart proposed for nitrate, nitrite and gypsum analysis of the stone samples is given in Figure 4.

Stone Samples

The results of analyses of stone samples are given in Table 4. As seen, the nitrate concentration of each sample is higher than that of nitrite. Total nitrogen concentrations were calculated from the sum of the nitrate and nitrite contents. Since the nitrogen content of the unpolluted travertine is below the detection limit, the values found are attributed to the effects of air pollution. The total nitrogen contents of the stone samples are rather low, but because of the high solubility of nitrate and nitrite salts, these salts can easily be washed from stone surfaces by

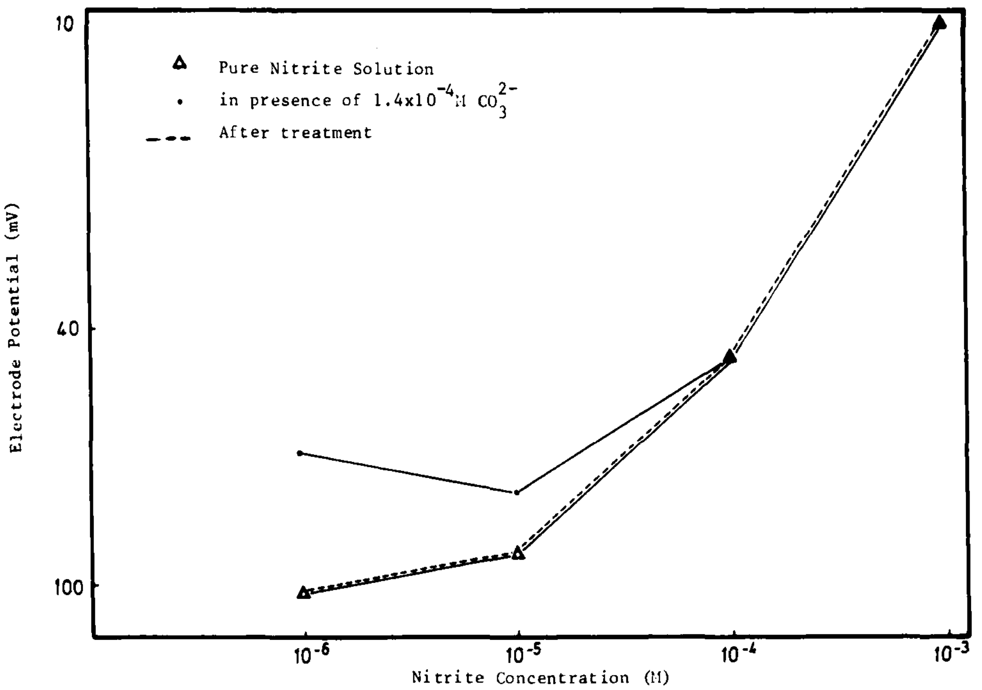

Figure 3 Carbonate interference and effect of masking solution in nitrogen oxide electrode.

Table 1 Optimum working conditions

Parameter	*Nitrate ISE*	*Nitrogen oxide ISE*
pH	4.0–4.5	1.1–1.7
ISA/OSA	2 M	1 M
Response time	5 min	5 min
Matrix of the final solution	2.5×10^{-4} M sulphamic acid 2.5×10^{-5} M silver sulphate 10^{-4} M sulphuric acid	0.25 M perchloric acid 0.25 M potassium hydrogen phthalate

Table 2 Analysis of trial solutions

Trial solution no.	*M NO_3^-*		*M NO_2^-*	
	Present	*Measured*	*Present*	*Measured*
1	1.0×10^{-5}	1.1×10^{-5}	5.0×10^{-6}	4×10^{-6}
2	5.0×10^{-5}	4.0×10^{-5}	2.5×10^{-5}	2×10^{-5}
3	1.0×10^{-4}	0.9×10^{-4}	5.0×10^{-5}	5×10^{-5}
4	5.0×10^{-4}	4.5×10^{-4}	2.5×10^{-4}	2×10^{-4}
5	1.0×10^{-3}	9.5×10^{-4}	5.0×10^{-4}	5×10^{-4}

Table 3 Analysis of trial solid samples

Solid sample[a]	*$NaNO_3$(g)*		*KNO_3(g)*	
	Present	*Measured*	*Present*	*Measured*
1	1.2×10^{-3}	2×10^{-3}	6×10^{-4}	6×10^{-4}
2	1.2×10^{-4}	1.2×10^{-4}	6×10^{-5}	6×10^{-5}

[a]Each sample is brought to a mass of 5 g by addition of powdered unpolluted (original) travertine.

rain. That is, the values found can be considered as the lower limit of nitrogen contents present in stone samples.

CONCLUSION

For the purpose of this study, which was to determine rather low concentrations of nitrate and nitrite on calcareous stones, it is convenient to use ion-selective electrodes. When the interferences due to the calcareous stone matrix and possible impurities are eliminated as suggested, the ion-selective electrode technique is a simple, fast and reliable method for nitrate and nitrite determinations. Under the proposed conditions nitrate and nitrite concentrations ranging from 10^{-6} M–10^{-2} M can be successfully measured.

Neither nitrates, nitrites nor gypsum were present in the unpolluted travertines, but the surfaces exposed to atmospheric conditions do contain them. As found previously,[12] the relative humidity is an important variable which affects the adsorption of sulphur dioxide and nitrogen oxides on calcareous stones. The climatic conditions of the Ankara atmosphere,[1] with a high average relative humidity in the winter months and during the night throughout the year, even in summer times, favour the adsorption of both nitrogen oxides and sulphur dioxide on calcareous stones. These gases are expected to be adsorbed on travertine surfaces. However, we do not know the contribution of nitric acid vapour formed in the atmosphere, which may also be reaching the surface. In any case, the present study provides novel quantitative data about the nitrate and nitrite presence on travertines in Ankara, where these species quite likely are main causes of this pollution effect. Therefore, gypsum formation on these surfaces has been advancing most likely under the influence of nitrogen species.

Although simulation experiments showed the presence of calcium nitrate on marble with larger concentrations of nitrogen oxides in the atmosphere (100–1000 $\mu g/m^3$), nitrogen oxides in the Ankara atmosphere at much lower concentrations seem to reach the surface of travertines, contributing to gypsum formation and the formation of nitrates and nitrites on the surface.

Sulphate to nitrate ratios found in this study are in the range of 32–393 for travertines, whereas in the literature a large range of ratios has been reported (Tables 5 and 6). However, the values from the other studies are for a wide variety of different stones and they were determined with different analytical techniques. Still, it turns out that the nitrate and nitrite amounts found on the travertines are

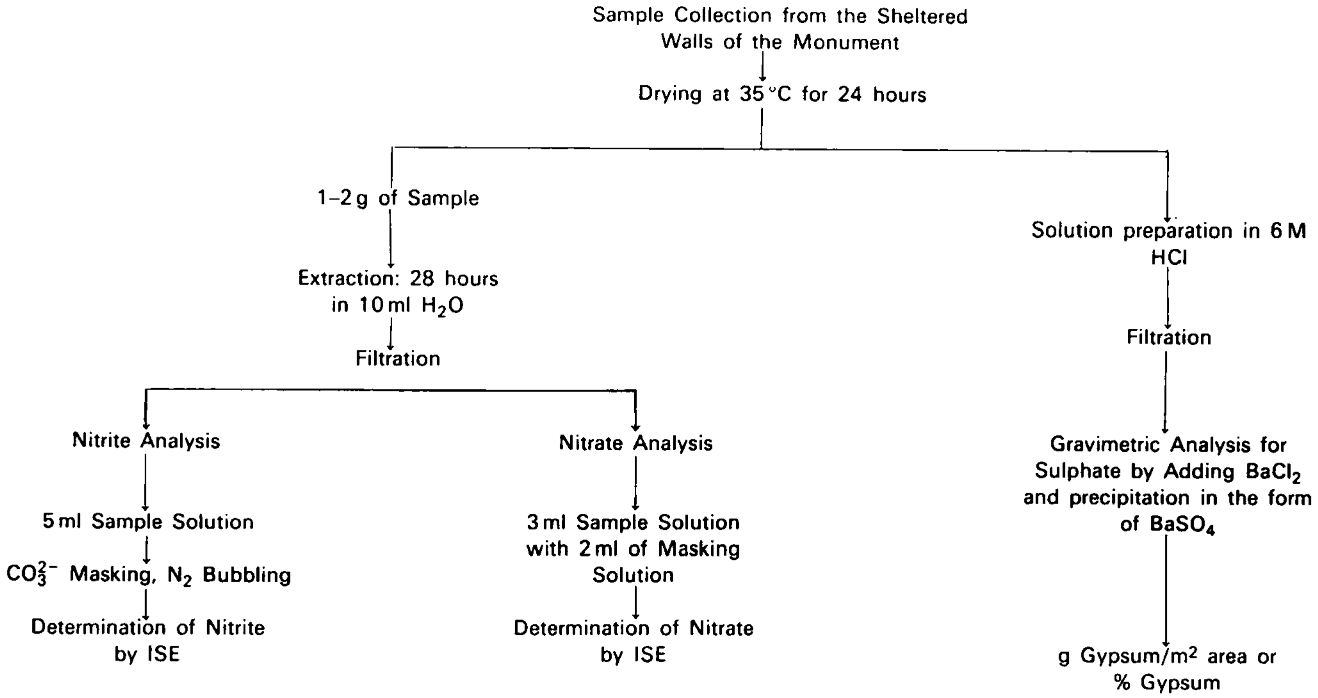

Figure 4 A flowchart for the analysis of stone sample.

Table 4 Analysis of stone samples

Sample code	*% nitrate*	*% nitrite*	*% nitrogen*	*% gypsum*	*g gypsum/m*^{2}
Anıtkabir 1	35.6×10^{-3}	3.1×10^{-3}	8.7×10^{-3}	25.1	94.0
Anıtkabir 2	91.0×10^{-3}	4.3×10^{-3}	24×10^{-3}	29.7	117.7
Maltepe 1	355×10^{-3}	8.7×10^{-3}	83×10^{-3}	27.2	90.5
Maltepe 2	224×10^{-3}	3.0×10^{-3}	51×10^{-3}	13.2	59.6
Maltepe 3	200×10^{-3}	4.8×10^{-3}	47×10^{-3}	11.9	56.0
Maltepe 4	67.3×10^{-3}	3.1×10^{-3}	15×10^{-3}	17.1	62.7
100.Yil	89.4×10^{-3}	4.3×10^{-3}	21×10^{-3}	9.0	7.6
Anıtkabir unpolluted yellow travertine	N.D.	N.D.	N.D.	N.D.	N.D.

N.D. = Not detected.

Table 5 SO_4^{2-}/NO_3^- ratio in this work

Location	*Stone type*	SO_4^{2-}/NO_3^-
Anıtkabir 1	Yellow travertine	393
Anıtkabir 2	Yellow travertine	182
Maltepe 1	White travertine	43
Maltepe 2	White travertine	32
Maltepe 3	White travertine	33
Maltepe 4	White travertine	141
100.Yil Shopping Center	White travertine	56

Table 6 Summary of SO_4^{2-}/NO_3^- ratios in other field studies[4]

Location	*Stone type*	SO_4^{2-}/NO_3^-
Milan	Marble	Trace
Padua	Mortar	125–360
Rome	Tuft	Trace
Poitiers	Limestone	0.6–60
Schenectady, NY	Marble	2–10
Venice	Marble	10–30
Bordeaux	Limestone	10
Chicago	Marble	10–100
Taj Mahal	Marble	Trace
Venice	Marble	1600

not quantitatively related as was found in other studies. Nevertheless, it may be concluded that pollution in Ankara leads to the formation of nitrates and nitrites—along with gypsum—on travertines. Their role in gypsum formation is expected. However, since the data obtained in this study are not complete enough to propose any correlation, further results are needed to clarify this relationship, ion-selective electrodes being considered as convenient tools for such analyses. In addition, measurements of nitric acid vapour levels around the buildings, kinetic studies and studies on the role of biogenic nitrate should also be made.

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