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DEVELOPMENT OF AN ALTERNATIVE SAMPLER FOR
THE ATMOSPHERIC GASEOUS POLLUTANTS

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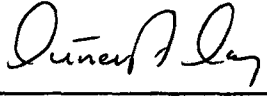
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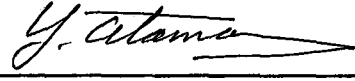
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ABSTRACT

DEVELOPMENT OF AN ALTERNATIVE SAMPLER FOR ATMOSPHERIC GASEOUS POLLUTANTS

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M.S. in Chemistry

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In this work an alternative sampler for the automated analyzers was developed to sample the gas phase pollutants in a simple, inexpensive, and efficient way. The developed sampler has a detection limit 10 times smaller than that of automated instruments have.

The developed sampler contains a pump, cellulose filters which were impregnated with special chemical adsorbents and/or absorbents, and a gas flowmeter. For the collection of SO₂ the filter papers were impregnated with sodium carbonate and for the sampling of nitric acid and ammonia the filter

papers were impregnated with sodium chloride and oxalic acid, respectively. For the collection of atmospheric nitrogen oxides (as NO₂) the cellulose filters were impregnated with triethanolamine.

The collection efficiencies for the sulfur dioxide, nitric acid, and ammonia were around 100% and for the nitrogen oxides it was around 87%.

The three pollutants, namely, sulfur dioxide, nitric acid, and ammonia can be sampled simultaneously but the nitrogen dioxide is sampled individually because of low flow rate of air sample around 1 L/min.

Key words: Filter Pack System, Nitrogen Oxides, Sulfur Dioxide, Gaseous Nitric Acid, Gaseous Ammonia, Atmospheric Sampling.

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ÖZ

ATMOSFERDE BULUNAN GAZ FAZI KİRLETİCİLERİ İÇİN ALTERNATİF BİR ÖRNEKLEYİCİ GELİŞTİRİLMESİ

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Bu çalışmada gaz fazı kirleticileri için otomatik örnekleyicilere alternatif olarak basit, ucuz ve etkili olan yeni bir örnekleyici geliştirildi. Geliştirilen örnekleyici otomatik analizörlerden 10 kat daha düşük gözlenebilme (tayin edilebilen en düşük konsantrasyon) sınırına sahiptir.

Geliştirilen örnekleyici, özel kimyasal adsorbent veya absorbent emdirilmiş selüloz filitrelerden, bir hava pompası ve bir gaz akı ölçerinden oluşmaktadır.

Selüloz filitrelerde; sodyum karbonatla kükürt dioksiti, sodyum klorür ile atmosferdeki gaz fazı nitrik asiti, trietanolamin ile azot oksitleri (NO_2 olarak), ve okzalik asit ile de atmosferdeki gaz fazı amonyağı yüksek birer toplama verimi ile tutmak gerçekleştirilmiştir.

Azot oksitler %87 lik bir verimle, diğer üç analit ise 100%' lük bir toplama verimi ile örneklenebilmektedir.

Azot oksitler hariç; SO_2 , HNO_3 , ve NH_3 aynı anda örneklenebilmektedirler. Fakat 1 L/dak. gibi düşük bir örnek hava akış hızı nedeniyle azot oksitler ayrı olarak örneklenmelidir.

Anahtar Kelimeler: Filtre Paket Sistemi, Azot Oksitler, Kükürt Dioksit, Gaz Fazı Nitrik Asit, Amonyak Gazı, Atmosferik Örnekleme.

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CHAPTER I

INTRODUCTION

1.1 Air Pollution

Air Pollution may be defined as any atmospheric condition in which substances are present at concentrations high enough above their normal ambient levels to produce a measurable effect on man, animals, vegetation, and materials. By "substances" we mean any natural or man-made chemical elements or compounds capable of being airborne. These substances may exit in the atmosphere as gases, liquid drops, or solid particles [1].

The air pollution problem involves a system consisting of three basic components; (1) Sources, responsible for emission of pollutants, (2) Atmosphere, is a medium, for mixing and chemical transformations of pollutants, (3) Receptors, are receivers of airborne pollutants [1].

Major emission sources are; (1) Transportation, (2) Electric power generation, (3) Refuse burning, (4) Industrial and domestic fuel burning, and (5) Industrial processes. Pollutants are emitted to the atmosphere which acts as a medium for transport, dilution, and physical and chemical transformation. Pollutants may subsequently be detected by instruments or by human beings, animals, plants or materials. Detection by these various "sensors" is manifested by some responses, such as irritation [1].

1.2 Air Pollutants

Air Pollutants are divided into two general categories:

1. Primary Pollutants, those emitted directly from sources
2. Secondary Pollutants, those formed in the atmosphere by chemical interactions with primary pollutants and/or natural atmospheric constituents [1].

Sulfur oxides, carbon monoxide, hydrocarbons, and nitrogen oxides are the examples of primary pollutants. They can undergo chemical reactions in the atmosphere and produce new substances which are called "secondary pollutants" (such as, sulfuric acid, nitric acid, and ozone). A general list of primary air pollutants is given in Table 1.1. There are large number of compounds in each group. Some of these compounds which are produced

as a result of various industrial operations have been shown to have acute toxicity [1]. Sources of primary pollutants and the emission values of these pollutants are given in Table 1.2 and Table 1.3, respectively. The most important of these pollutants in local and regional scale are nitrogen compounds, sulphur compounds, and aerosols. Classification of gaseous air pollutants is given in Table 1.4 and comparison of concentration levels between clean and polluted air is given in Table 1.5. In several cases global natural emissions (but not local emissions in an urban area) of a particular pollutant far exceed man-made (anthropogenic) emissions. This is the case for ammonia (NH_3), the nitrogen oxides (NO and NO_2), and methane (CH_4). CO and CO_2 are both products of the combustion of carbonaceous fuels, from incomplete and complete combustion, respectively. Certain halogen compounds such as HF and HCl are produced in metallurgical and other operations. Fluoride compounds are harmful and irritating to human beings, animals, and plants, even when they are present at very low concentrations. The primary pollutants are harmful to the living organisms and their environments by themselves or their secondary products that are called as secondary pollutants, such as acid rain, are more harmful to the organisms and the whole environment. The values of cation and anion concentrations of secondary pollutants in the acidic precipitation is given by Table 1.6.

Table 1.1. Major Classes of Air Pollutants*

Sulphur Compounds

Nitrogen Compounds

Carbon Compounds

Halogen Compounds

Radioactive Compounds

Particulate Matters (aerosols)

Organic Compounds

* Work et al., (1979) [2]

Table 1.2. Major Sources of Air Pollutants*

Natural	Man-made
Volcanoes	Combustion processes
Fires	Chemical processes
Breaking seas	Nuclear or atomic processes
Blowing dust	Roasting, heating and refining
Pollens, terpenes-	processes
bacteria, viruses	Mining, quarrying, farming

* Lutgens et al., (1989) [3]

Table 1.3. Global Man-made and Natural Emissions of Various Species (estimates for 1976)*

Species	Emission Estimate (10 ⁹ kg.yr ⁻¹)	
	Man-made	Natural
CO ₂	2*10 ⁴	1*10 ⁶
CH ₄ , HC's	188	1800
CO	600	2500
SO ₂	207	10
H ₂ S	2	50
NO _x (as NO)	90	1200
NH ₃	7	1200

* Wayne, (1991) [4]

Table 1.4. Classification of Gaseous Air Pollutants *

Class	Primary pollutants	Secondary pollutants
Sulphur containing- compounds	SO_2 , H_2S	SO_3 , H_2SO_4 , MSO_4^{**}
Nitrogen containing- compounds	NO , NH_3	NO_2 , MNO_3^{**}
Carbon containing- compounds	C_1 - C_5 compounds	Aldehydes, ketones, acids
Oxides of Carbon	CO , CO_2	None
Halogen compounds	HF , HCl	None

** MSO_4 and MNO_3 denote general sulfate and nitrate compounds.

*J. H. Seinfeld, (1975) [5].

Table 1.5. Comparison of Concentration Levels between Clean and Polluted Air*

Component	Clean air	Polluted air
SO ₂	0.001 - 0.01 ppm	0.02 - 2 ppm
CO ₂	310 -330 ppm	350 - 700 ppm
CO	< 1 ppm	5 - 200 ppm
NO _x	0.001 - 0.01 ppm	0.01 - 0.5 ppm
HC's	1 ppm	1 - 20 ppm
Particulate matter	10 - 20 µg/m ³	70 - 700 µg/m ³

* J. H. Seinfeld, (1975) [5]

Table 1.6. Typical values of cation and anion concentrations in acidic precipitation *

Cations		Anions	
Ion	Conc.(eq/l*10 ⁶)	Ion	Conc.(eq/l*10 ⁶)
H ⁺	56	SO ₄ ⁻²	51
NH ₄ ⁺	10	NO ₃ ⁻	20
Ca ⁺²	7	Cl ⁻	12
Na ⁺	5		
Mg ⁺²	3		
K ⁺	2		
Total:		Total:	
83		83	

* G. E. Likens, (1976) [9].

1.2.1 Sulfur Dioxide in the Atmosphere:

Sources and Effects

The sulfur cycle involves primarily H_2S , SO_2 , SO_3 , and sulfates; a summary is shown in Figure 1.1. There are many uncertainties regarding the sources, reactions, and fates of these atmospheric sulfur species. On the global basis, sulfur compounds (along with carbon monoxide, lead, and a few other trace elements) enter the atmosphere to a very large extent through human activities [7].

It is estimated that in the 1970s, anthropogenic sulfur constitutes approximately one - third of the total sulfur input to the atmosphere each year. This sulfur, a quantity of approximately 65 million tonnes per year, is produced primarily as SO_2 from the combustion of fossil fuels. The largest source of sulfur entering to the atmosphere, some 106 million tonnes annually, is H_2S , originating primarily from the decay of organic matter and from the biological reduction of sulfate, especially by anaerobic bacteria in intertidal flats.

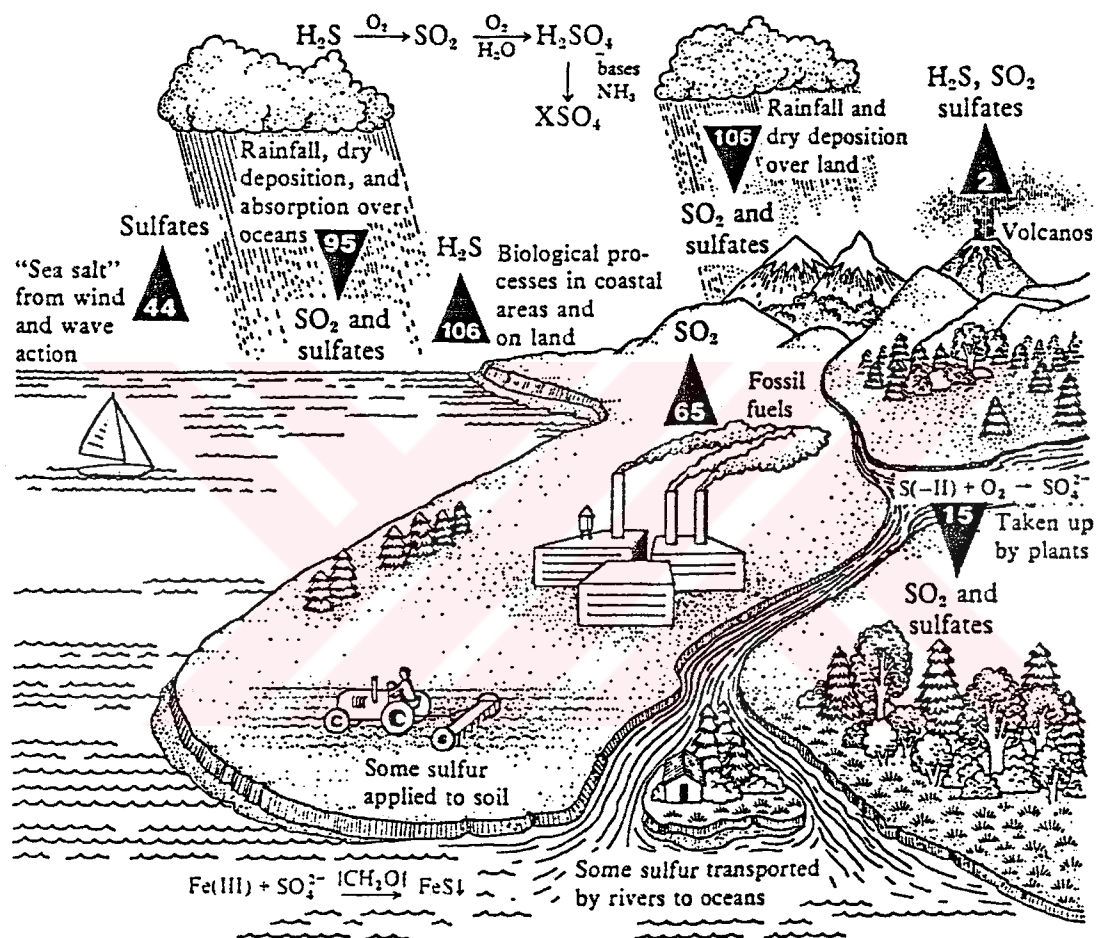
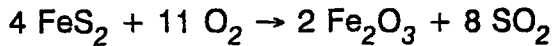


Figure 1.1 Atmospheric Sulfur Cycle. Values are in millions tonnes (teragrams) of S [7].

The primary source of anthropogenic sulfur dioxide is coal combustion. Approximately half of the sulfur in coal is in some form of pyrite, FeS_2 , and the other half is organic sulfur. The production of sulfur dioxide by the combustion of pyrite is given by the following reaction:



Essentially all of the sulfur is converted to SO_2 , with only 1 or 2% leaving the stack as SO_3 .

Sulfur dioxide in the atmosphere has its primary effect upon the respiratory system, producing irritation and increasing airway resistance. Therefore, exposure to sulfur dioxide may increase the effort required to breathe. Mucus secretion is also stimulated by exposure to air contaminated by sulfur dioxide. People who already have respiratory problems are particularly susceptible to high levels of sulfur dioxide in the atmosphere. Although SO_2 causes death in humans at 500 ppm, it has not been found to harm laboratory animals up to 5 ppm [7,8].

Atmospheric sulfur dioxide is harmful to plants. Acute exposure to high levels of the gas kills leaf tissue. The edges of the leaves and the areas

between the leaf veins are particularly damaged. Chronic exposures of plants to sulfur dioxide causes chlorosis, a bleaching or yellowing of the normally green portions of the leaf. Plant injury increases with increasing relative humidity.

Long-term exposure to sulfur dioxide has been shown to have a serious detrimental effect upon yields of wheat and barley (Raymond et al., 1978). In experiments conducted during the 1977 growing season, it was observed that reduction in yield of 15% were observed when exposure of the grain was raised from 5 parts per hundred million to 10 pphm for exposures of three days per week. These losses increased to 50% for exposures of 15 pphm [8].

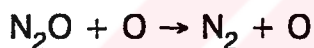
Other damage [8] was observed in addition to crop yield reductions. Foliage injury and loss occurred. In addition, chlorophyll levels were reduced.

Sulfur dioxide is converted to sulfuric acid in the atmosphere. In areas receiving high levels of sulphur dioxide pollution, plants may be damaged by sulfuric acid aerosols. Such damage appears as small spots where sulfuric acid droplets have impinged upon the leaves.

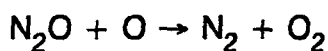
1.2.2 Nitrogen Oxides in the Atmosphere:

Sources and Effects

The three oxides of nitrogen normally encountered in the atmosphere are Nitrous Oxide (N₂O), Nitric Oxide (NO), and Nitrogen Dioxide (NO₂). Nitrous oxide, a commonly used anaesthetic known as "laughing gas", is produced by microbiological processes and is a component of the unpolluted atmosphere at a level of approximately 0.25 ppm. This gas is relatively unreactive and probably does not significantly influence important chemical reactions in the lower atmosphere. Its concentration decreases rapidly with altitude in the stratosphere due to the photochemical reaction



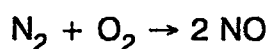
and some reaction with singlet atomic oxygen:



These reactions are significant in depletion of the ozone layer. Increased global fixation of nitrogen accompanied by increased microbial production of N_2O , could constitute a threat to the ozone layer [6].

Colorless, odourless nitric oxide (NO) and pungent red-brown nitrogen dioxide (NO_2) are very important in polluted air. Collectively designated NO_x , these gases enter the atmosphere from natural sources, such as lightning and biological processes, and from some pollution sources, such as automobiles. The latter are much more significant because of regionally high NO_x concentrations, which can cause severe air quality deterioration [6]. Practically all anthropogenic NO_x enters the atmosphere as a result of the combustion of fossil fuels in both stationary and mobile sources. Globally, around 86 million tonnes of nitrogen oxides are emitted to the atmosphere from these sources each year, compared to several times that much from widely dispersed natural sources.

Most NO_x entering the atmosphere is in the form of NO. At very high temperatures, the following reaction occurs:



The speed with which this reaction takes place increases steeply with temperature. A mixture of 3% O₂ and 75% N₂, typical of that which occurs in the combustion chamber of an internal combustion engine, produces 500 ppm of NO in 23 minutes at 1315°C and in only 0.117 seconds at 1980°C. The equilibrium concentration of NO in such a mixture is shown as a function of temperature in Figure 1.2 [6]. The equilibrium concentration of NO in this mixture at room temperature (27°C) is only 1.1×10^{-10} ppm.

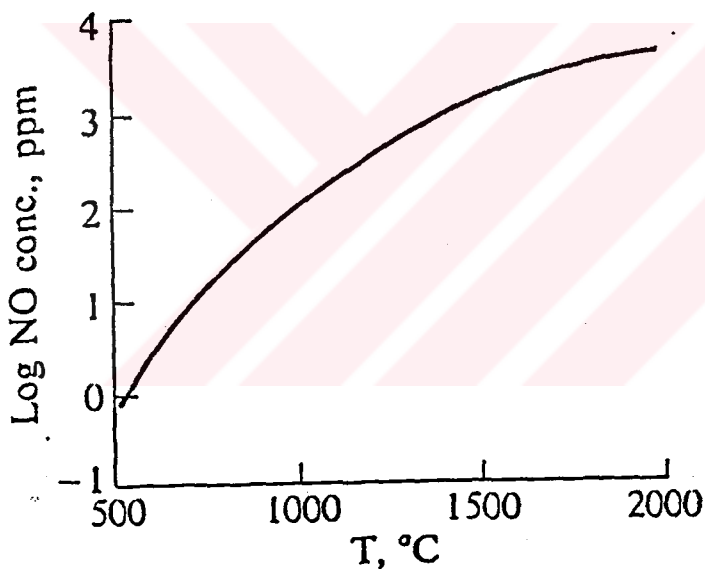


Figure 1.2 Log of equilibrium NO concentration as a function of temperature in a mixture containing 75% N₂ and 3% O₂ [6]

High temperatures favour both a high equilibrium concentration and a rapid rate of formation of NO. Rapid cooling of the exhaust gas from combustion "freezes" NO at a relatively high concentration because equilibrium is not maintained. Thus by its very nature, the combustion processes both in the internal combustion engine and in furnaces produces high levels of NO in the combustion products.

Nitric oxide, NO, is biochemically less active and less toxic than NO₂. Like CO and nitrite, it attaches to hemoglobin and reduces the oxygen transport efficiency. However, in a polluted atmosphere, the concentration of nitric oxide normally is much lower than that of carbon monoxide so that the effect on hemoglobin is much less.

Acute exposure to NO₂ can be quite harmful to human health, a fact which should be taken into consideration in performing laboratory operations involving this toxic gas. The health effects of nitrogen dioxide vary with the degree of exposure. For exposures ranging from several minutes to one hour, a level of 50 - 100 ppm of NO₂ causes inflammation of lung tissue for a period of 6 - 8 week, after which time the subject normally recovers. Death generally results from 2 - 10 days after exposure to 500 ppm or more NO₂. Although extensive damage to plants is observed in areas receiving heavy exposure to

NO_x , most of this damage probably comes from secondary products of nitrogen oxides, such as Peroxyacetyl Nitrate, (PAN), formed in smog. Exposure of plants to several parts per million of NO_2 in the laboratory causes leaf spotting and breakdown of plant tissue. Exposure to 10 ppm NO causes a reversible decrease in the rate of photosynthesis. Nitrogen oxides are known to cause fading of dyes used in some textiles [6].



1.3 Importance of Air Sampling

Efforts to control air pollution can be successful only if we are able to determine accurately the nature and levels of pollutants in the atmosphere and from emission sources. Therefore, good analytical methodology, particularly that applicable to automated analysis and continuous monitoring, is essential to the study and alleviation of air pollution. The atmosphere is a particularly difficult analytical system because of a number of factors, including the very low levels of substances to be analyzed; sharp variations in pollutant level with time and location; differences in temperature and humidity; and difficulties encountered in reaching desired sampling points, particularly those substantially above the earth's surface.

In the monitoring of atmospheric pollution, the sampling is the most important and the first part of the study. Especially gas phase pollutant sampling is the most difficult work. The automated instruments that have been used for this purpose are very expensive and need trained personels. The places where these types of instruments are not found or they may not be installed, there will be need for an alternative sampler which has little maintenance problems, light weight, low cost, and at least same efficiency as the others.

1.4 The Aim of This Study

The aim of this study is to design and to develop an alternative sampler to sample and monitor gaseous atmospheric pollutants namely SO_2 , NO_x , HNO_3 and NH_3 in the ambient atmosphere. For this purpose, Whatman-41 filter papers were impregnated with suitable impregnates (chemicals) to collect gaseous pollutants in the ambient air by absorption or adsorption processes on the surface. Several experiments were carried out to characterize the suitable impregnates for specified gaseous pollutants.

Determination of the collection efficiencies of impregnated filters were done using commercial collectors of above mentioned gases and by the comparison of first treated filter with the second one.

1.4.1 Works Done on Sampling of Gaseous Pollutants

As it mentioned before, gaseous pollutants can be collected on chemically treated filter papers by adsorption or absorption processes. J. Forrest, et al., 1979, [10], collected gaseous nitric acid on NaCl-impregnated paper filters. NaCl impregnated cellulose filters collect nitric acid vapors from ambient atmospheres at efficiencies of $\approx 95\%$ when placed downstream from

pretreated quartz particle filters in a high volume sampler, and almost no adsorption of NO_2 on the NaCl filters with retention as nitrate was observed. Conversion of NO_2 to nitrate on quartz (either retained as nitrate or released as artifact nitric acid) was negligibly low with the removal of the less than 1% of the incident NO_2 . But at high relative humidity adsorption of HNO_3 on the quartz prefilter can become significant [10].

Quinn P.K. et. al., 1989, [11], studied the collection efficiencies of a tandem sampling system for atmospheric aerosol particles and gaseous NH_3 and SO_2 . They coated 47 mm Whatman-41 paper filters with oxalic acid and either K_2CO_3 or LiOH. When known amounts of NH_3 and SO_2 were generated and collected on the coated filters, the collection efficiency of the system for the NH_3 was found to be $103 \pm 30\%$. The SO_2 collection efficiency on K_2CO_3 and LiOH - coated filters found to be $100 \pm 21\%$ and $88 \pm 9\%$ respectively, and was not affected by the presence of reduced sulphur gases or ozone in the sampled air stream.

Collection of NO_x or (NO_2 and NO) on Triethanolamine, (TEA), coated filters was studied by D. Krochmal et. al., 1991 [12]. They used a diffusive sampler. Several materials were used as carriers for TEA in the sampler. The mass of NO_2 absorbed in the sampler determined spectrophotometrically as

nitrite by using Saltzman Solution. The relative precision of the method characterized by RSD was 10%; the detection limit of NO_2 was $10 \mu\text{g}/\text{m}^3$ for a 24 - hours exposure.

An alternative method for collecting air samples and determining concentrations of SO_2 was investigated by Sumitra et.al., 1990 [20]. Air samples were done using low-cost air pumps and filters of 37-mm diameter. SO_2 was collected on filters impregnated with 5% Sodium Carbonate and 5% Glycerol. They used two types of filter papers, membrane (Millipore type AA) and cellulose (Whatman no. 42). Measurements were done in free air and K X-rays of 2.308keV S were counted and the minimum detectable quantity of S on the filter was found to be about $30\mu\text{g}$ on both types of filter papers.

The collection efficiencies of aerosol particles and gaseous NH_3 and SO_2 were tested for a tandem sampling system consisting of a cyclone separator followed by a $1.0\mu\text{m}$ pore size 47-mm Millipore Teflon particle filter and four 47-mm Whatman-41 filters coated with oxalic acid and either K_2CO_3 or LiOH by Patricia et.al., [11]. The collection efficiency of the cyclone was compared with an $8.0 \mu\text{m}$ pore size Nucleopore filters impregnated by NaCl . It was found that both the cyclone and filter had a 50% collection efficiency at $0.9\mu\text{m}$. The collection efficiency of the coated filter was found to be $103 \pm 30\%$. And the

SO₂ collection efficiency on Potassium Carbonate -and LiOH -coated filters was 100 ± 21 and $88 \pm 9\%$, respectively [11].

David Y.H. et. al., 1990, [13], worked on a different sampling technique for atmospheric SO₂. A compact coiled Denuder was designed and its performance was evaluated both theoretically and experimentally. The design was based on special features of laminar flow in a curved tube, which significantly enhance the mass transfer Sherwood number governing gas collection at the wall. At 10 standard L/min (slpm) the gas collection efficiency for SO₂, using a Na₂CO₃ / Glycerine wall coating, was measured to be $99.3 \pm 0.5\%$.

Recent improvements to the Carbonate impregnated filter technique for measuring low-level SO₂ concentrations have resulted in dramatically improved performance (Ronald J.F. et. al., 1991), [14]. The improvements are the followings: a better cleaning procedure for the filter paper substrates; resulting in approximately 60% reduction of their sulfate blank, the use of an ion-exchange resin to remove the carbonate matrix from the sample extract; resulting in a 100% increase in the signal to noise ratio, the use of high-purity glycerol in the filter impregnate; resulting in approximately 10% further reduction of blanks, and improved chromatographic and standardization

procedures for more accurate quantification of sample peaks. All of these improvements allow measurements to be made of SO₂ concentrations in marine background air with a 2 σ uncertainty of ± 6 parts per trillion by volume (pptv) and, based on this a 3 σ detection limit of 9 pptv for air volumes of 4 m³. Measurements in polluted air showed better than 95% collection efficiency, even at concentrations as high as 100 ppbv [14].

A new type of Personal Sampler was reported by Palmes E.D. et. al., in 1976, [15]. This sampler was adapted for the measurement of NO₂. The sampler was depending on the transfer of NO₂ by diffusion to a Triethanolamine coated collector at the sealed end of a tube; the open end of the tube was exposed to the test environment. The device was accurate, light, simple to use and had very good shelf life before and after sampling.

A precise, high-rate passive sampler for NO₂ was developed from a commercially available device by Barry C.C. et. al., 1983, [19]. They also, used TEA as a coating material to collect NO₂. The device was diffusion controlled and sampled at a rate of approximately 110 mL/min. The sampler was tested at NO₂ concentrations ranging from 61 to 335 ppb with sampling periods as short as 1-hour, and they proved that the presence of large excess of NO does not interfere the NO₂.

CHAPTER II

EXPERIMENTAL

2.1 Sampling of Gaseous Pollutants

The ideal analysis techniques are those which make sampling and analysis simultaneously, such as, long-path laser resonance absorption monitoring. For most analyses, however, various types of sampling are required. In some very sophisticated monitoring systems, samples are collected and analyzed automatically and the results are transmitted to a central receiving station. Generally, however, a batch sample is collected for later chemical analysis.

The analytical result from a sample can be only as good as the method employed to obtain that sample. A number of factors enter into obtaining a good sample [16]. The size of the sample required (total volume of air

sampled) decreases with increasing concentration of pollutant and increasing sensitivity of the analytical method. Often a sample of 10 or more cubic meters is required. The sampling rate is determined by the equipment used generally ranges from approximately $0.003 \text{ m}^3/\text{min}$ to $3.0 \text{ m}^3/\text{min}$. The duration of sampling time influences the result obtained, as shown in figure 2.1. The actual concentration of the pollutant is shown in the solid line. A sample collected over an eight-hour period has the concentration shown in the dashed line, whereas samples taken over one-hour intervals exhibit the concentration levels shown in the dotted line [16].

Sampling for gases may range from methods designed to collect only one specific pollutant to those designed to collect all pollutants.

Absorption in a solvent, such as by bubbling the gas through a liquid, is a very common method for the collection of gaseous pollutants. A number of very pure solvents can be used. Pure water is effective in collecting some gaseous pollutants, such as hydrogen fluoride. Generally alkaline gases are retained in acidic solutions and acidic gases are collected in basic solutions.

Two characteristics of the absorbing device that increase collection efficiency are small bubble size and increased residence time. Among the

types of absorbers used are impingers, countercurrent scrubbers, packed columns, and fritted glass scrubbers.

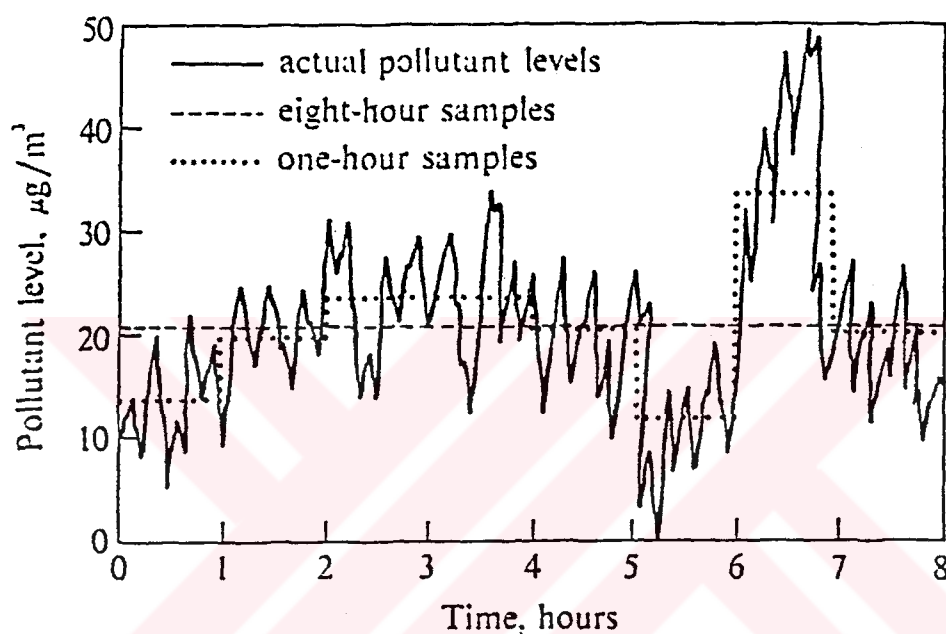


Figure 2.1. Effect of duration of sampling upon observed values of air pollutant levels [16].

Adsorption, in which a gas collects on the surface of a solid, is gaining popularity as a means of sample collection. Adsorption is particularly useful for the collection of samples to be analyzed by gas chromatography; in some

cases, the sample may be injected directly into the chromatography from the collecting device. A number of different adsorbent materials are used, including alumina, charcoal, silica gel, and a variety of synthetic substances, such as "molecular sieves". After adsorption, the sample must be removed for analysis by techniques, such as heating the column and flushing it with gas, or by applying a vacuum.

The most important advantage of the treated filters is the use of coating materials that are generally selective to the analyte resulting less chemical matrices in the analysis. It is easy to coat and use the filters in the sampling. By using a set of treated filters that coated with different materials, more than three or four gaseous pollutants can be sampled simultaneously. The impregnated filters are good collectors for the pollutants as much as the other sampling methods, such as trapping techniques or liquid absorbents.

2.2 Preparation of Treated Filter Papers

Whatman-41 paper filters (47mm in dia.) are used as collection medium in the filter package system. Filters are soaked with special impregnates for every gaseous pollutants to work selectively. The pollutants are absorbed or adsorbed by the impregnate on the filter papers.

2.2.1 Preparation of Paper Filters For SO₂ Sampling

Potassium carbonate or sodium carbonate are the suitable impregnate for the collection of atmospheric SO₂.

Whatman-41 cellulose filters first pretreated by soaking in 20 (w/v)% KOH solution to neutralize the acidic sides on the filter paper. The excess liquid is drained and are dried for 2.5 hours at 110°C. Then filters are rinsed free of KOH with distilled water and filters are dried in a vacuum desiccator overnight. Dryness is completed at 110°C for 10-15 minutes. For the final impregnation, a 0.10 M Na₂CO₃ solution (in 10 (v/v)% Glycerol; 30(v/v) H₂O; and 60(v/v)% Methanol solution) is used. Excess liquid is removed and then the filters are dried for 5 minutes at 110°C. Finally filters are stored in a desiccator until sampling time.

2.2.2 Preparation of NaCl Filters

For the collection of Gaseous Atmospheric Nitric Acid, NaCl was used as an impregnate. 47mm (dia.) Whatman-41 paper filters first prewashed with deionized distilled water and dried at 100°C. Then filters are immersed in 5 (w/v)% NaCl solution and again dried at 100°C.

2.2.3 Preparation of Paper Filters for NO_x Collection

Triethanolamine which is a solid at temperatures below 21°C and a viscous liquid above 21°C, is a selective absorbent and impregnate for atmospheric NO₂. Whatman-41 cellulose filters (47mm in dia.) are first rinsed with distilled deionized water and dried at 100°C. Then filters soaked with the solution prepared by mixing 10(v/v)% TEA - 10(v/v) H₂O - 80(v/v)% Acetone. The filters again dried at 50°C for 15-20 minutes and stored in a desiccator.

2.2.4 Preparation of Paper Filters for the Collection of Ammonia

Whatman-41 cellulose filters are pretreated with dilute NaOH or KOH solution to neutralize the acidic sides on the filter and then rinsed with distilled deionized water. Filters are dried at 100°C. For the final impregnation, they immersed in 0.10 M aqueous solution of oxalic acid and dried again at 100°C for 30 minutes.

2.3 Sampler Construction

The design goals in constructing the sampler were that the collecting medium be efficient, that the device be simple to use in the field, that it be light-weight and durable, and that it be cheap.

Sampler contains a pressure - vacuum air pump, a filter package system, a mass flow meter and treated paper filters. Schematic diagrams of the sampler are given in figures 2.2.a, 2.2.b, and 2.2.c.



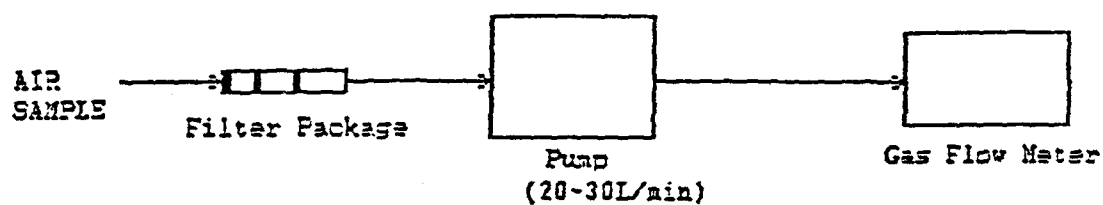


Figure 2.2.a. Sampler flow diagram for SO_2 , HNO_3 , and NH_3

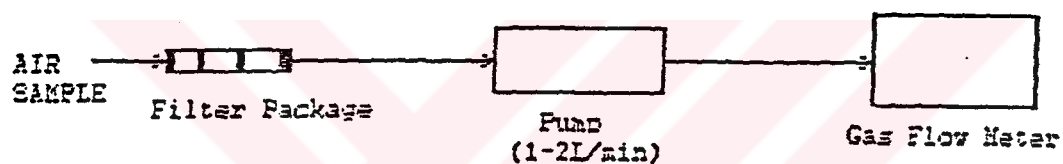


Figure 2.2.b. Sampler flow diagram for NO_2

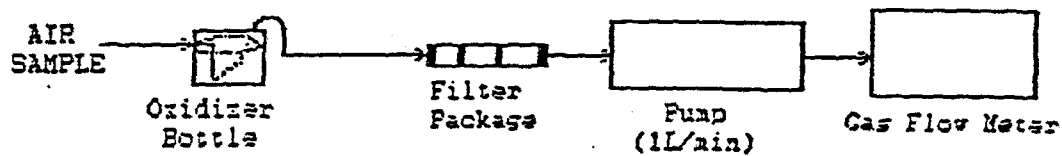


Figure 2.2.c. Sampler flow diagram for NO_x

Filters are exposed to stream of air sample at flow rates of 15 to 25 litres/min for the sampling of SO_2 , HNO_3 , NH_3 and flow rates of 1.0 to 2.0 liters/min for the collection of atmospheric nitrogen oxides. At polluted areas hourly measurements are possible with the sampler. Twenty four hour samplings can also be done for the pollutants mentioned above in field studies.

The connection tubes used in sampler are made from polyethylene and from other non-absorbing or non-adsorbing materials such as teflon to prevent the loss of analyte.

2.3.1. Sample Collection and Handling

For the simultaneous collection of SO_2 , $\text{HNO}_3(\text{g})$, and $\text{NH}_3(\text{g})$; one Na_2CO_3 filter, one NaCl filter or nylon filter and one Oxalic acid filter, are placed in filter package system in the order written. The first cell of filter pack system contains one untreated nucleopore (teflon) particulate filter.

Since the absorption of NO_2 by the TEA is slow, three TEA impregnated filter papers were placed in a filter package system after a teflon particulate filter.

After filters were exposed to air sample for a specific time interval; sodium carbonate filter was put in 50 ml 3(w/v)% H_2O_2 (pH = 3.0; prepared by adding 23.1 mL of 0.10 M NaOH to 26.9 mL of 0.10 M H_3PO_4 solution in 3(w/v)% H_2O_2), Sodium chloride or Nylon filter was treated with 50 ml distilled deionized water and reduced to nitrite, NO_2^- , with hydrazine, Oxalic acid filter was put in 50 ml distilled deionized water- Nessler solution which is prepared by dissolving 100 g of anhydrous mercuric iodide (HgI_2) and 70 g of anhydrous potassium iodide (KI) in a small volume of water. Then this solution is added by stirring to a cooled solution of 160 g of sodium hydroxide (NaOH) in 500 mL of water and diluted to 1.0 L.

The TEA treated filters were extracted in 50 mL solutions of Saltzman reagent which is prepared by dissolving 5.3 g of sulfanilic acid ($\text{H}_2\text{NC}_6\text{H}_4\text{SO}_3\text{H}$) in a small volume of water containing 53 mL of glacial acetic acid (CH_3COOH). Then 0.05 g of N-1-Naphthylethylenediamine dihydrochloride ($\text{C}_{10}\text{H}_7\text{NHCH}_2\text{CH}_2\text{NH}_2 \cdot 2\text{HCl}$) is dissolved in this solution and final solution is diluted to 1.0 L.

Before passing to the simultaneous sampling procedure, every pollutant sampling system must be optimized individually, as followings.

2.3.2 Sampling of Atmospheric SO₂

Sodium Carbonate treated filters were used to collect atmospheric SO₂. To the first cell of filter pack, a nucleopore filter was placed to retain atmospheric particulates. To the second and third cells; Na₂CO₃ filters were placed to collect SO₂ by means of absorption process. Then the filter pack with treated filters was joined to sampling pump. Air sample was passed at a flow rates between 15 to 25 litres per minute for several samplings. By this way 1.0 hour sampling to 24 hours samplings were done. When treated filters exposed to sample air they absorbed sulphur dioxide, selectively. One carbonate treated filter was kept in desiccator for the blank measurements. It was seen that the treated filters do not show any loss of SO₂ even after one month if they are stored below 4°C in a refrigerator.

2.3.3 Sampling of Gaseous Nitric Acid

For the collection of atmospheric gaseous nitric acid three cells of filter package system were used. To the first cell, a nucleopore particulate filter was placed, and to the second and third cells of filter pack system, two NaCl impregnated filters were placed. In laboratory atmospheres, hourly measurements was done and in the field 24 hours saplings were done. As in

other cases, a NaCl impregnated filter paper must be processed for the blank measurements. The sampling flow rate was 15 to 25 liters per minute.

Some times nylon filters were used for the collection of atmospheric nitric acid to analyze nitrate by ion chromatography. Because of high concentration of chloride ion coming from the treated filters, it is impossible to analyze nitrate by ion chromatography which is in Environmental Engineering Department, METU. The chloride peak with an high concentration of chloride ion overlaps with the nitrate peak.

2.3.4 Sampling of Atmospheric Ammonia Vapor

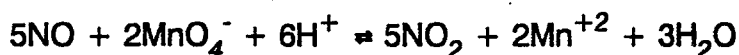
Cellulose filters impregnated with 0.10 M oxalic acid was used to collect atmospheric ammonia vapor. In this sampling procedure again a nucleopore filter and two oxalic acid treated filters were used. The sampling flow rates were 15 to 25 liters per minute. One oxalic acid filter paper was also used as a blank for every measurement.

2.3.5 Sampling of Atmospheric Nitrogen Oxides (NO_x)

Triethanolamine treated filter papers can absorb only NO₂ form of nitrogen oxides. To sample Nitrogen oxides that are NO and NO₂, an oxidizing unit is necessary. For the oxidation of NO to NO₂, an oxidizer bottle was filled with 25(w/v)% KMnO₄ and combined with the sampler (Figure.2.2.c) that containing TEA treated filters in filter pack system. In this sampling process, a nucleopore filter was used as a prefilter to prevent the passage of particulate matters to the treated filters. Nitrogen oxides were sampled hourly at polluted areas and they were sampled for 24 hours at the lower polluted areas. In this process it is also necessary to store a treated filter paper for the blank measurement purpose.

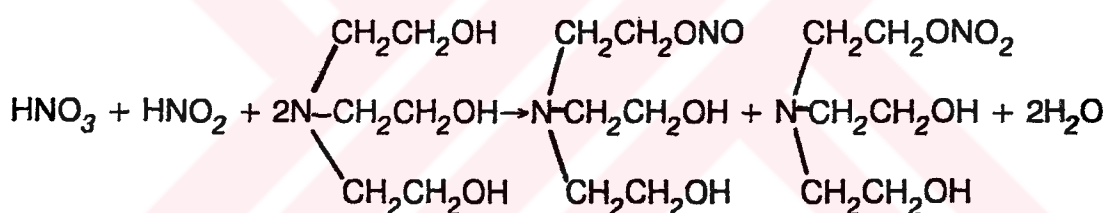
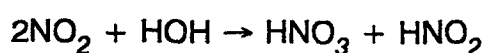
During the sampling of NO_x the following reactions take place;

a) Oxidation of NO to NO₂ in the oxidizer bottle:



b) Absorption reaction of NO₂ on triethanolamine:

The chemistry of absorption of NO₂ by the TEA absorbed as yet is undetermined. The experimental runs indicate that the absorption is not due to the alkaline surface of TEA but is possibly due to nitrite and nitrate ester formation which could proceed as follows [24].



2.3.6 Simultaneous Sampling of SO₂, NO₂, HNO₃, and NH₃

The individual optimization works done for the above pollutants showed that the NO_x sampling system is not compatible to the simultaneous sampling procedure because of low flow rate and slow absorption by the TEA. But the sampling procedures for SO₂, HNO₃, and NH₃ are compatible with the

developed system and these three pollutants' sampling works at flow rates of 15 to 25 Liters/min without any fluctuation.

The order of filters used in the filter pack system for the sampling is given in the Figure 2.3.

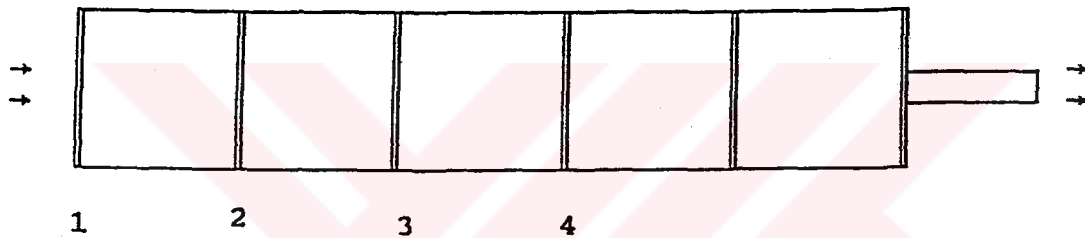


Figure 2.3. The placement order of Treated Filters in the Filter Pack System.

- 1) Teflon particulate filter,
- 2) NaCl impregnated or Nylon filter,
- 3) Oxalic acid impregnated filter,
- 4) Sodium carbonate filter.

2.4 Analytical Techniques Used

The collected nitrogen oxide samples were treated with Saltzman Reagent immediately and the amount of nitrogen oxide was determined by means of spectrophotometric method. The samples of atmospheric nitric acid and ammonia were also analyzed spectrophotometrically. The nitric acid samples collected by nylon filters were analyzed by an Ion Chromatography. The samples of atmospheric sulfur dioxide were first treated with 3.0% H_2O_2 solution and after one hour they were filtered and stored in a refrigerator until analysis. For the analysis ion chromatographic method was used .

2.4.1 Colorimetry

The NO_2 sampled is converted to nitrite ion by Triethanolamine and is extracted by 50 mL of Saltzman Reagent. The procedure bases on measurement of the absorption of pink-red colored complex which is measured at 545nm by using LKB Novaspec II Spectrophotometer and quartz cells.

The NO_3^- on the filter paper is first extracted and reduced to nitrite in 25 mL solution of hydrazine and is diluted to 50 mL by adding Saltzman Reagent.

It is measured spectrophotometrically at 545nm as it was done for NO_2 analysis. Atmospheric ammonia that collected on oxalic acid treated filter paper is converted to NH_4^+ by the impregnate. The ammonium ion was extracted in 25 mL of distilled-deionized water. When 80 mL of tetraiodomercurate (II) solution is added to above ammonium solution a red-brown colored complex is formed [17] and the absorption of the colored complex was measured at 425nm by the spectrophotometer used above.

2.4.2 Ion Chromatography

The collected SO_2 that is converted to SO_3^{2-} by the neutralization reaction with CO_3^{2-} on the filter paper was extracted by 50 mL of 3.0 (w/v)% solution (pH = 3; prepared by adding 23.1 mL of 0.10 M NaOH to 26.9 mL of 0.10 M H_3PO_4 solution in 3(w/v)% H_2O_2 , pH = 2.50 to pH = 4.0 can be used for this purpose) of H_2O_2 to oxidize SO_3^{2-} to SO_4^{2-} . The SO_4^{2-} sample was filtered with membrane filters and measured by injecting with a manual loop valve having 100 μL loop size to VYDAC 302 IC Anion Exchange Column. The mobile phase was the aqueous potassium hydrogen phthalate (KHP) buffer having pH = 4.9 and the detector used was JASCO 850 UV-VIS. Flow rate was 3 mL/min and the temperature was the ambient temperature.

CHAPTER III

RESULTS AND DISCUSSIONS

3.1 Estimate of the Collection Efficiencies of Treated Filters

For the determination of the collection efficiency of the filter pack system used, the concentration of any gaseous pollutant, under consideration, on the first treated filter paper was compared with the concentration of same pollutant on the second filter paper. For the blank corrections one treated but unexposed filter paper was used as blank for every parameters.

To determine the collection efficiency of the treated filter papers the following equation was used;

$$\%CollectionEfficiency = \frac{(C_1 - C_2)}{C_1} * 100 \quad (3.1)$$

C_1 and C_2 are the concentration of atmospheric gaseous pollutants on the first and the second filter papers, respectively, in $\mu\text{g}/\text{m}^3$.

3.1.1 Efficiency of Carbonate Filters For SO_2 Collection

As mentioned in the experimental part, for the collection of atmospheric sulfur dioxide, Na_2CO_3 impregnated 47 mm Whatman 41 filter papers were used. On the treated filter paper, SO_2 is collected by the following neutralization reaction;



The SO_2 collected by this way was observed to stay as it is for several weeks or a month if it is kept below 4°C in polyethylene bags.

The unsaturation property and the high collection capacity of carbonate filter papers for SO_2 are the most important advantage of our system. To find the collection capacity of carbonate filters, we performed experiments by using SO_2 permeation tube (DYNACAL SO_2 Permeation Device, 10 cm size, 410 ng/min per cm $\pm 10\%$ at 30°C) which was calibrated gravimetrically. The permeation tube was placed in the sampling tube and the sample air was

passed through the filters with the flow rates of 15 to 25 L/min (depending on the number of filters used in the experiments the flow rates were changed between the values given). Sampling times were starting from 1 hour to 24 hours. Stream of air sample containing $76.5 \mu\text{g}/\text{m}^3$ of SO_2 , saturated the first carbonate filter paper after approximately 25 m^3 , (Figure 3.1.a), of air sample was passed through the filter pack system. Approximately $765 \mu\text{g}$ of SO_2 was observed to be the saturation amount as shown by the Figure 3.1.b. The filters were impregnated in 0.1 M CO_3^{2-} but if the saturation concentration is wanted to be increased, the impregnate concentration can be increased to 25 (w/v)% CO_3^{2-} without disturbing the analysis by ion chromatography.

The observed, saturation amount of SO_2 corresponds to atmospheric concentration of $30.6 \mu\text{g}/\text{m}^3$ for 24-hours sampling and this will not cause any saturation problem during the field samplings, since the sampling sites where we have been working do not reach the atmospheric SO_2 concentration of more than $5\text{-}6 \mu\text{g}/\text{m}^3$. For a 24-h sampling period, the sampled air volume is 25 m^3 on the average and this much volume of air sample will contain around $150 \mu\text{g}$ of SO_2 that is much more lower than the SO_2 amount saturating the carbonate filter. However, this concentration may be higher in urban atmospheres (for example, in Ankara atmosphere, in winters it is approximately $100 \mu\text{g}/\text{m}^3$) and may cause the rapid saturation of carbonate filters.

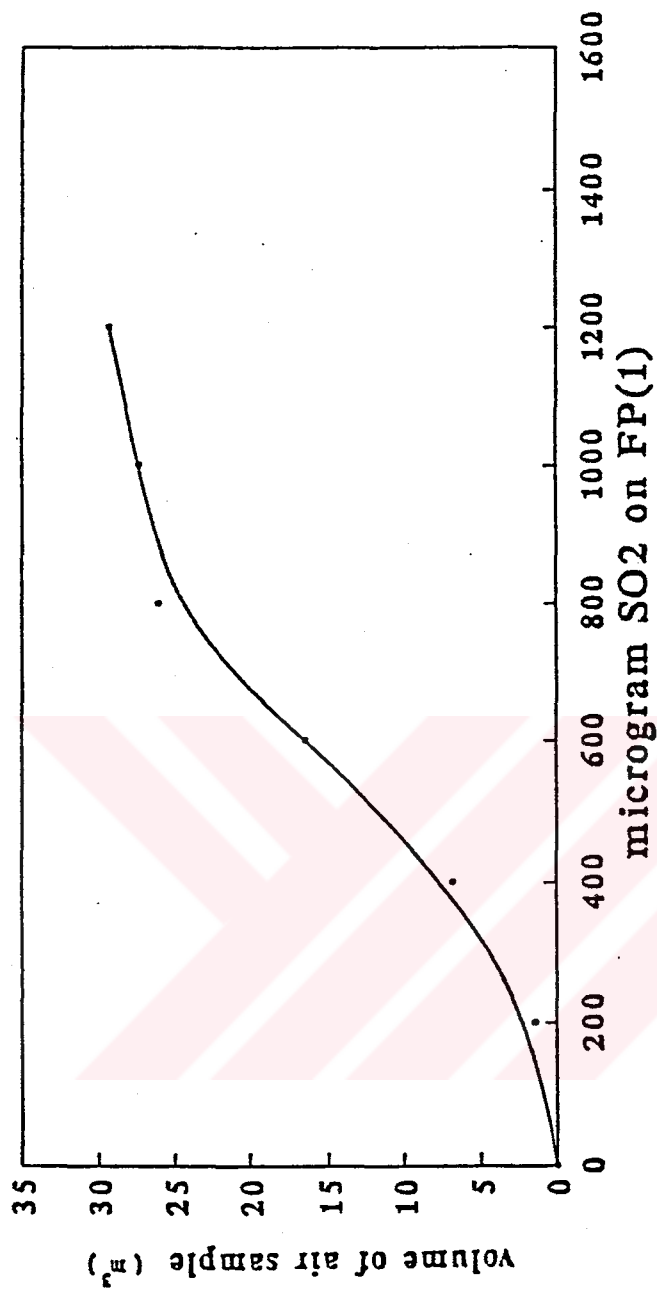


Figure 3.1.a. The collection capacity of the first carbonate filter with the changes in the volume of air sample containing $76.5 \mu\text{gm}^{-3}$ of SO_2 .

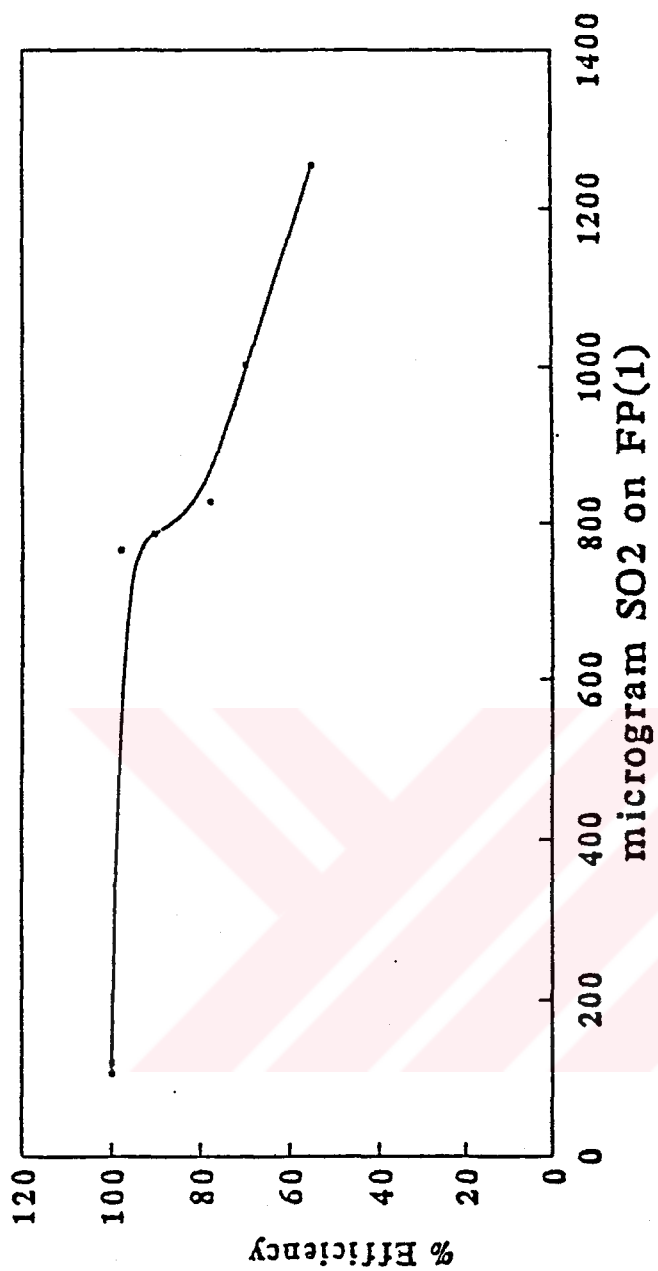


Figure 3.1.b. Percent collection efficiency change with the change in the absorbed amount of SO₂ on the first filter.

In this case the impregnate concentration can be increased to the required amount to solve the saturation problem. The results obtained from laboratory studies can be seen in Figure 3.1.a and Figure 3.1.b. After 15 hours collection periods the first carbonate filter starts to saturate with SO_2 coming from the permeation tube after diluting with the atmospheric air. The change in collection efficiency with the collection time for these experiments are shown in Figure 3.2. Around 15 hours collection time there is no significant decrease in the percent collection efficiency of the first carbonate filter, that is, the decrease is approximately 10%.

After the above observations, we performed field experiments in METU Campus in May, 1993 and it was observed that the collection efficiency of the carbonate filter papers was not varied with the collection times of 1 hour to 24 hours. This result was in agreement with the observations from laboratory studies. Since the collection efficiency of the carbonate filters does not change with the daily sampling periods, more than 24-h samplings can be done by using the carbonate treated filter papers with a filter pack system.

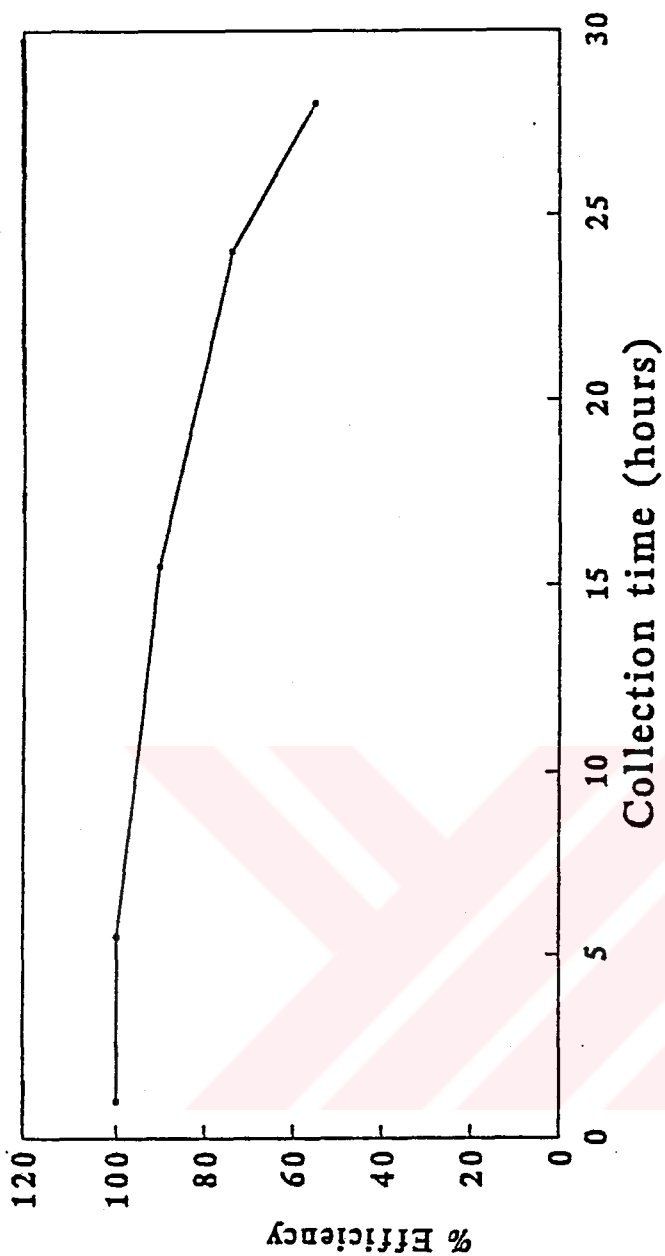


Figure 3.2. The change in the collection efficiency of the carbonate filters with the sampling time.

Average collection efficiencies of greater than 95% were observed for hourly and daily samplings. The flow rates applied for the sampling was between 15 to 25 L/min. Approximately the same percent collection efficiencies with laboratory results were observed for the SO₂ at this flow rate range.

At field studies, the saturation of carbonate treated filter papers by SO₂ was not observed even after three days sampling time. As shown in Figure 3.3 where concentrations of SO₂ on filter(1) and on filter (2) were plotted as a function of collection time, for 5 to 24 hours samplings. The increase in the concentration of SO₂ on the second filter paper indicates the decrease in collection efficiency which in turn indicates the saturation of the first filter. Field studies did not indicate any saturation at a concentration of 5 to 20 µg/m³ SO₂ which was measured during samplings. As mentioned before, field sampling was carried out during May 1993 in Ankara. However, higher concentrations during winter months may cause saturation of the filters.

Blanks of filters used in collection is quite important. Blanks can be a problem particularly at rural atmosphere where the SO₂ concentrations are low. To lower the blanks of the filters prior to impregnation, we followed procedure suggested by R. J. Ferek et al., (1991), [14]. Cleaned cellulose filters were leached for 2-days in double distilled deionized water (DDW)

followed by an overnight leaching in 0.1 M HCl. A comparison of the mean values of total sulfate loadings on filter blanks obtained by various precleaning procedures are given in Table 3.1.

It was observed that using high purity glycerol solution in the impregnation procedure lowers the amount of background sulfate from cellulose filters [14]. In this research, both the first and the second precleaning procedures were used, but both of these two procedures were not significantly changed our results. The reason for this observation was the detection limit of ion chromatography that we used in the analysis. The detected values of 0.014 and $0.009 \mu\text{g}/\text{m}^3$ SO_2 given in the Table 3.1 are smaller one and two orders of magnitudes, respectively than the detection limit of our ion chromatography which was $0.14 \mu\text{g}/\text{m}^3$. For the filter paper precleaning we used the first procedure given in the Table 3.1 [14].

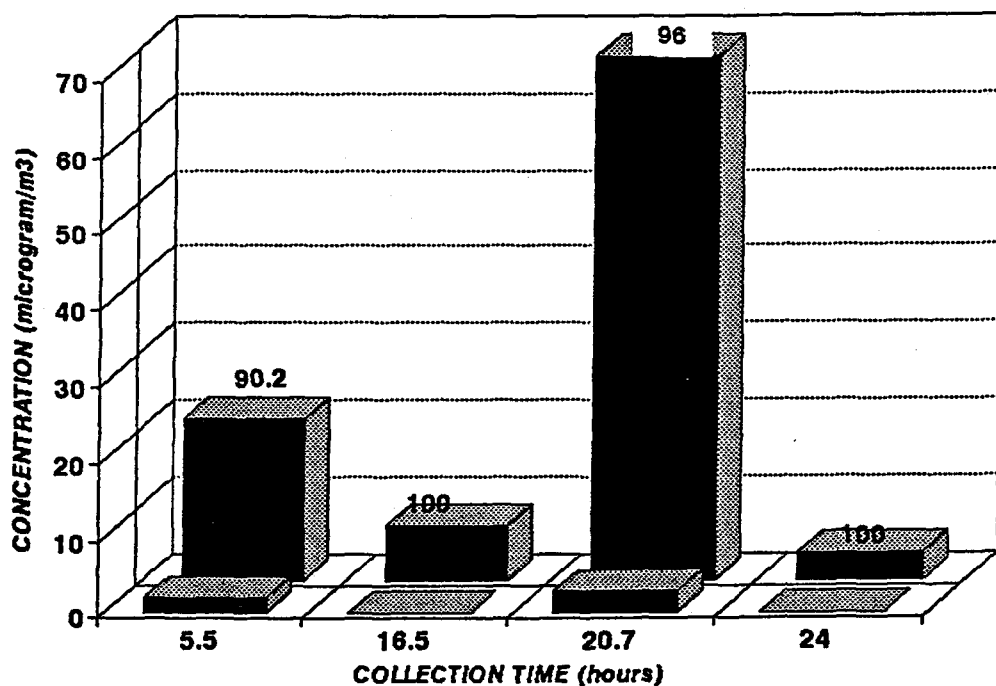


Figure 3.3 The Collected Amounts of SO₂ by the First and Second Filter Papers (numbers over the bars indicate the % collection efficiencies; large and small bars show the collected amount of analyte by the first and second filters, respectively).

Table 3.1. Mean Values of the Total Sulfate Loading on Blank Carbonate-Impregnated Filters From the Three Preparation Procedures and the Corresponding Measurement Uncertainties and Detection Limits**.

Precleaning procedure	Mean Mass of SO_4^{2-} ($\mu\text{g SO}_4^{2-}$) on filters ($\bar{x} \pm 1s, n$)	Implied 2s measurement uncertainty* ($\mu\text{g SO}_2/\text{m}^3, \text{pptv}$)	Corresponding 3s Detection-Limit ($\mu\text{g SO}_2/\text{m}^3, \text{pptv}$)
Soak in distilled water only	1.52±0.57, 6	0.127, 44	0.190, 66
Leached in 0.1 M HCl and impregnated with reagent-grade glycerol	0.62±0.041, 10	0.009, 3	0.014, 5
Leached in 0.1 M HCl and impregnated with ultrapure glycerol	0.57±0.029, 8	0.006, 2	0.009, 3

x: the mean, s: standard deviation, n: the number of samples

*: assuming a 6-m^3 sample of air; $1\text{pptv} = 0.00286 \mu\text{g SO}_2/\text{m}^3$

** : R. J. Ferek et al.,1991, [14].

In addition to SO_2 , HNO_3 and HNO_2 are also collected by carbonate filters. But, these species do not interfere with the SO_2 during the analysis by ion chromatography and they do not cause any reduction in the collection efficiency of the SO_2 by the carbonate filters. In addition to these, the nitric acid and nitrous acid collection efficiency on the first filter was very small compared with the SO_2 collection efficiency on the same filter paper. In SO_2 collection higher than 95% efficiency was observed but for nitric and nitrous acids the efficiency was less than 10% .

The most important point that must be noted in the analysis of SO_2 , is the use of extraction solution of 3 (w/v)% H_2O_2 with a pH of less than 5 (pH = 3.0 prepared from phosphoric acid, as given before). This pH value is enough to oxidize the all SO_3^{2-} to SO_4^{2-} and suitable for the ion chromatographic analysis without any problem.

In literature it is reported [11] that in the atmosphere, SO_2 as well as O_3 and a variety of reduced sulfur gases including carbonyl sulfide, OCS , dimethyl sulfide, $(\text{CH}_3)_2\text{S}$, hydrogen sulfide, H_2S , methyl hydrogen sulfide, CH_3SH and carbon disulfide, CS_2 , are present. The reduced sulfur species could potentially be oxidized to sulfate on the coated filters to produce artificially high sulfur dioxide concentrations. In addition, the presence of O_3 in

the sample could enhance the oxidation of the sulfur compounds. To evaluate the effect of these other chemical species on the SO_2 collection efficiency, air streams were generated with known amounts of SO_2 , SO_2 and O_3 , SO_2 and reduced sulfur gases, and reduced sulfur gases and O_3 . It was observed [11] that all of these trials, statistically, did not alter the collection efficiency of carbonate filters observed from a sample stream containing only SO_2 [11].

3.1.2 Efficiency of Sodium Chloride Impregnated and Nylon Filters For HNO_3 Collection

This study is one of the first ones which collect the atmospheric gaseous pollutants by means of using treated filter papers with a filter pack system in Türkiye. The filter paper system is cheaper than the automated instruments and is efficient as much as commercial samplers. In literature it was reported that the atmospheric gaseous nitric acid can be collected both by NaCl impregnated cellulose and nylon filters at the efficiencies of greater than 95% [10,21]. Greater than 95% collection efficiency was observed in this research, that is, 98% on the average.

3.1.2.1 Collection of Atmospheric Gaseous Nitric Acid by NaCl

Impregnated Whatman 41 Filter Papers

The nitric acid vapor evaporated from 1.5 M HNO_3 was sampled on two sodium chloride impregnated filter papers which were connected in series at an air flow rate of 15 to 25 L/min. The analysis were done colorimetrically by reducing nitrates to nitrite, using saltzman reagent. The efficiency of the collection of nitric acid vapor by the filters was estimated using the Equation (3.1) and the efficiencies of greater than 95% were observed as given in Figure 3.4. In this Figure first two experiments were done using 30(w/v)% NaCl as impregnate. Because of the possible effects of high chloride concentration on analyses, the other experiments were done by using 5(w/v)% NaCl solution as impregnate. As can be seen from the Figure, the collection efficiencies are about 96%. The first experiment has very low efficiency which is probably due to a leakage in the sampling.

In order to optimize the the NaCl-impregnated technique to the filter pack system, the following experiments were performed:

Collection efficiency and the collection capacity of NaCl filters were determined by considering the following factors; adsorption of $\text{HNO}_3(\text{g})$ by

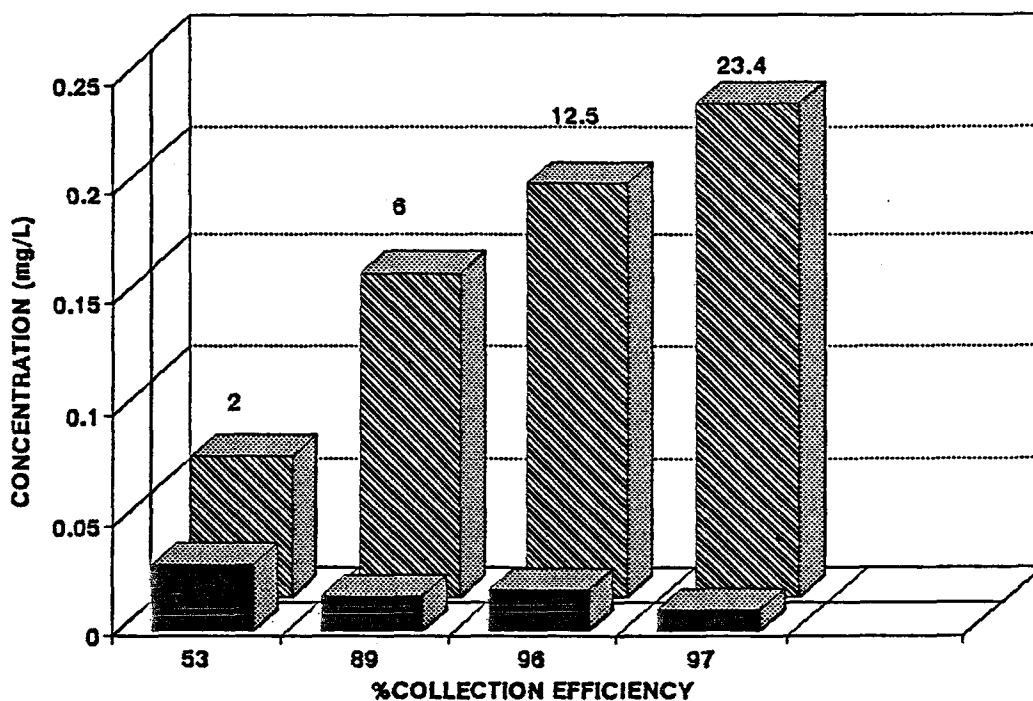


Figure 3.4 Percent Efficiency and the mg/L of HNO_3 Collected by the First and Second NaCl-Filters During the Different Sampling Periods (the bars corresponding to 53 and 89% collection efficiencies indicate the concentration differences between the two filters that were impregnated with 30(w/v)% NaCl solution and the numbers over the bars indicate the collection times in hour).

prefilter, collection capacity of NaCl filters, adsorption of NO_2 by NaCl filters, adsorption of NO_2 by prefilter and released or retained as HNO_3 , adsorption of SO_2 by NaCl filters, and volatilization of NH_4NO_3 .

To determine the breakthrough of nitric acid vapor, the nitric acid was evaporated from 1.5 M HNO_3 solution and collected by two NaCl filters and two nylon filters placed after a particulate teflon filter, in separate experiments having same experimental conditions. The results of these experiments are shown in Figure 3.5. Both NaCl and nylon filters reached to saturation point after approximately 30 hours sampling time. However, the first nylon filter collected 98% of the incident HNO_3 for this time interval which indicates that the collection capacity of nylon filter is higher than the collection capacity of NaCl filter that the first filter collected about 75% of the incoming nitric acid vapor. The loss of nitrate from the first filters can be understood well from the slopes of two lines given in Figure. The collected nitric acid was measured as total nitrate using IC for nylon filters and spectrophotometer for NaCl filters.

Adsorption of nitric acid on the prefilter is known to be significant and requires empirical corrections at high humidities, like 90%. Sulfuric acid aerosol, which had been preloaded on prefilters, cause nitrate losses that increased with contact time [10]. In our experiments the humidities never exceed 60%.

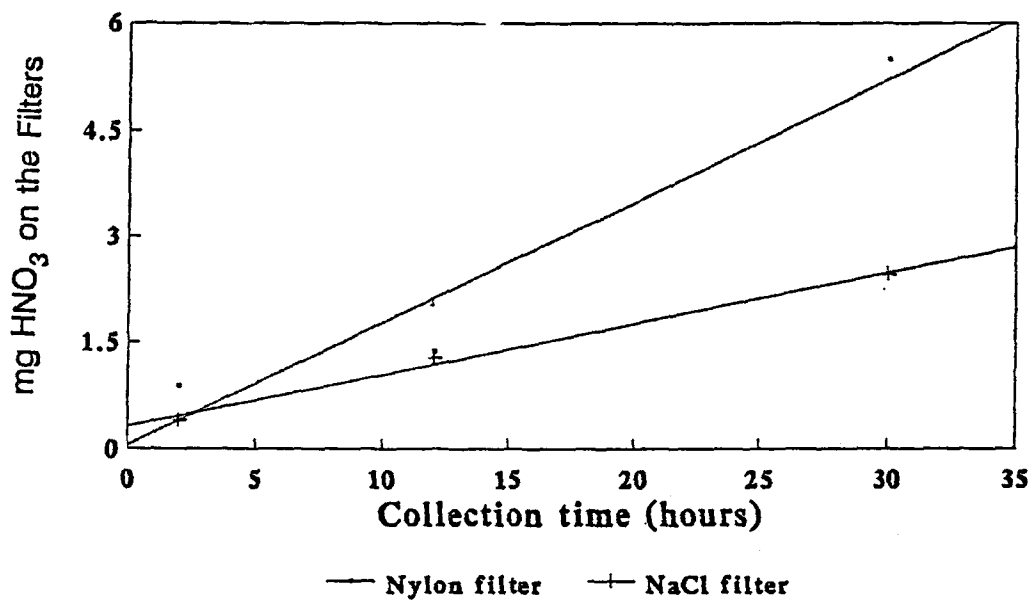


Figure 3.5 Comparison of NaCl and Nylon Filters in terms of Their Collection Capacities with the Sampling Time.

As a result adsorption of nitric acid on the prefilter was not a significant problem. On NaCl filter, the collected amount of nitric acid was 22.4 μg and on the prefilter it was 1.1 μg which may be particulate nitrate.

To observe possible adsorption of nitrogen dioxide by NaCl - impregnated filters, we did experiments by using NO_2 permeation tubes. In laboratory conditions, we evaporated nitric acid and collected in normal procedure. Same experiment was repeated by placing NO_2 permeation tube to the mouth of sampling tube and we collected sample with the same collection time interval. After analysis we observed approximately the same amounts of NO_3^- from two experiments. We repeated this experiment three times and the observed NO_2 retention, expressed as $\mu\text{g}/\text{m}^3 \text{NO}_3^-$, was less than 0.5% (Table 3.2). On the average the observed amount of nitrate was 1675 μg which was collected from concentrated reagent vapor without using NO_2 permeation tube. When the permeation tube was used with the concentrated reagent vapor in the same conditions, the collected amount of nitric acid was 1681.7 μg , on the average. The difference between these two average results was about 1.2 $\mu\text{g}/\text{m}^3$ (6.7 μg HNO_3 for 5.6 m^3 air sample) which assumed as nitrate produced by the NO_2 . In these experiments we assumed the outdoor air as a clean air, since there was no detectable amount of nitric acid in the atmosphere even sampled for 20-h with a flow rate of 20

L/min. However, the atmospheric NO_2 generated more nitric acid than the NO_2 from permeation tube, that was about $3.2 \mu\text{g}/\text{m}^3$ ($17.9 \mu\text{g HNO}_3$).

Table 3.2. NO_2 Retention on NaCl-Filter (as $\mu\text{g}/\text{m}^3 \text{NO}_3^-$)*

Number of observation	Observed concentration of $\text{HNO}_3(\mu\text{g}/\text{m}^3)$	
	Ambient air	Permeation tube**
4	3.2 ± 0.3	1.2 ± 0.8

* Flow rate = 23 L/min, 4-h exposures. Analyzed as nitrite after reducing with hydrazine and corrected with blank filters.

** Permeation tube was calibrated gravimetrically and was producing $870 \mu\text{g NO}_2/\text{m}^3$ of air sample.

As a result it was concluded that NO_2 at ambient levels do not show any interference during the sampling of nitric acid.

The ammonium nitrate particles collected on the particulate filter may be partially volatilized as HNO_3 during extended sampling periods, but it is then retained by the NaCl filters. Data from ambient sampling with the prefilter-NaCl filters system indicated that gaseous nitric acid concentrations as collected on NaCl filters during summer usually exceeded the levels of particulate nitrate found on particulate filters (quartz or teflon). J. Forrest et al., (1979), [10], reported that the loss was ranged from 0 to 72%, being greatest during low relative humidities (<60%). The one case with no loss occurred after three hours of sampling at 100% R.H. Qualitatively, these results are in accordance with the expectation that the vapor pressure of NH_3 and HNO_3 above NH_4NO_3 would decrease when it exits as a liquid, droplet above the deliquescent point of 62% at 25°C .

As a result positive HNO_3 interferences occur when NH_4NO_3 collected on the particulate filter dissociates into the gases HNO_3 and NH_3 . This is particularly a problem during long sampling periods and high ambient temperatures. Negative HNO_3 interferences also occur due to the adsorption or reaction of HNO_3 on the surface of the collected particles by the prefilter [10].

In this investigation we determined the amount of nitrate (particulate or gaseous) on the particulate teflon filter. It was approximately the same as the amount of nitrate collected on the second filter paper. For 24-h sampling period, in laboratory conditions, we observed $22.4 \mu\text{g NO}_3^-$ on the first NaCl filter, $0.9 \mu\text{g NO}_3^-$ on the second NaCl filter, and $1.1 \mu\text{g NO}_3^-$ on the teflon filter. At field studies it also will not cause any significant amount of error in our results obtained by filter pack system technique. We concluded that our result is in agreement with the results reported in literature.

Collection of SO_2 by NaCl filters was tested by analyzing HNO_3 collected on NaCl filters by the procedure used for analysis of SO_2 samples and we did not observe any significant amount of SO_2 in the form of SO_4^{2-} . A small peak that could not be identified by IC was observed. The detection limit of ion chromatography for sulfate is 0.049 ppb/24 hours in the air or 0.1 mg/L in the solution. The sulfate peaks corresponding less than this concentration limit could not be detected. As a result the adsorbed SO_2 on NaCl filters can be neglected without causing any error.

It is noted in literature [10] that NaCl-impregnated cellulose filters show no loss of nitrate after the three weeks of post-collection storage in sealed polyethylene bags placed in a silica-gel containing desiccator. In this research

the samples were analyzed right after the collection. For that reason loss of nitrate during storage was not tested.

3.1.2.2 Use of Nylon Filters For the Sampling of Atmospheric

Gaseous Nitric Acid

The one of the disadvantages of the NaCl filters was the difficulty of analysis by ion chromatography. The chloride peak overlaps the nitrate peak and for that reason we analyzed the nitrate samples collected by sodium chloride filters spectrophotometrically. But this was the time consuming and containing many treatment procedures for the analysis which may cause contamination errors.

To overcome the contaminations and to save time we also optimized nylon filters for the sampling of atmospheric gaseous nitric acid. The collection efficiency and capacity of nylon filters for HNO_3 were tested considering the factors like in the case of NaCl impregnated filters. The positive and negative HNO_3 interferences were assumed to be the same with NaCl filters. The other interferants were not significant, but adsorption and oxidation of HNO_2 may take place on the nylon filters that causes positive errors in the analysis. This error would not alter the collection efficiency of nylon filters with respect to the

gaseous nitric acid, since $\text{HNO}_2(\text{g})$ is generally oxidized to HNO_3 by O_3 or other oxidants in the atmosphere.

As a result, nitric acid at ambient concentrations can be measured with >95% efficiency using nylon or NaCl impregnated filters. NO_2 at ambient levels shows no interference in HNO_3 sampling at 90% R.H. [21]. But atmospheric particulate matter on teflon prefilters retains HNO_3 . This implies a need for short term sampling to minimize errors. Loss of NH_4NO_3 from the prefilter by volatilization can cause a large positive error in HNO_3 measurements. But the concentrations of NH_3 and HNO_3 at sampling site must be sufficient to cause a saturation with respect to NH_4NO_3 aerosol formation; to cause an error. The artifact is negligible on nylon filters which are usually operated at large flow rates, while it may be a significant source of errors in the use of nylon denuders, which are characterized by high exposed surface and low operative flow rates as it is mentioned in literature [22], also.

Figure 3.6 shows the HNO_3 collection efficiency of the nylon and sodium chloride impregnated Whatman 41 filter papers. Results show that the collection efficiency of sodium chloride filters impregnated in 5(w/v)% NaCl solution is approximately the same that of nylon filters. The collection efficiency of sodium chloride filters is same as the collection efficiency of the nylon filters

around 3000 μg HNO_3 collected by the first filters. However, the collection efficiency of nylon filters do not change significantly about 5000 μg of HNO_3 collected. The collection capacity and the efficiency of the NaCl filters can be increased as nylon filters by increasing the impregnate concentration but this may cause pressure drops or a decrease in flow rate during the sampling periods. The comparison of these two filters' efficiencies are estimated by looking at correlation line as shown in Figure 3.7. It can be seen from the figure that the two filters are not differing in collection efficiency, significantly. The slope of the line is 2.5 which indicates the compatibility of two filter types. As it was mentioned before it is practical to use nylon filters as it does not require any pretreatment.

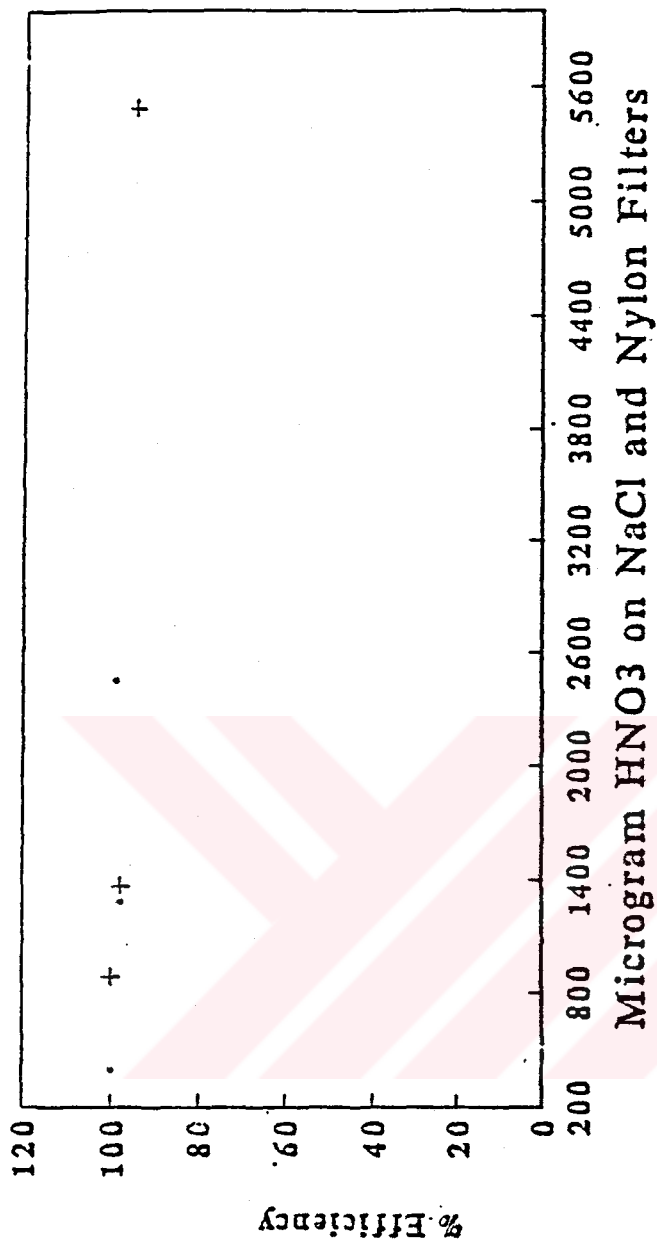


Figure 3.6 Comparison of Collection Efficiencies of NaCl and Nylon

Filters

+ Nylon filters, . NaCl filter Papers

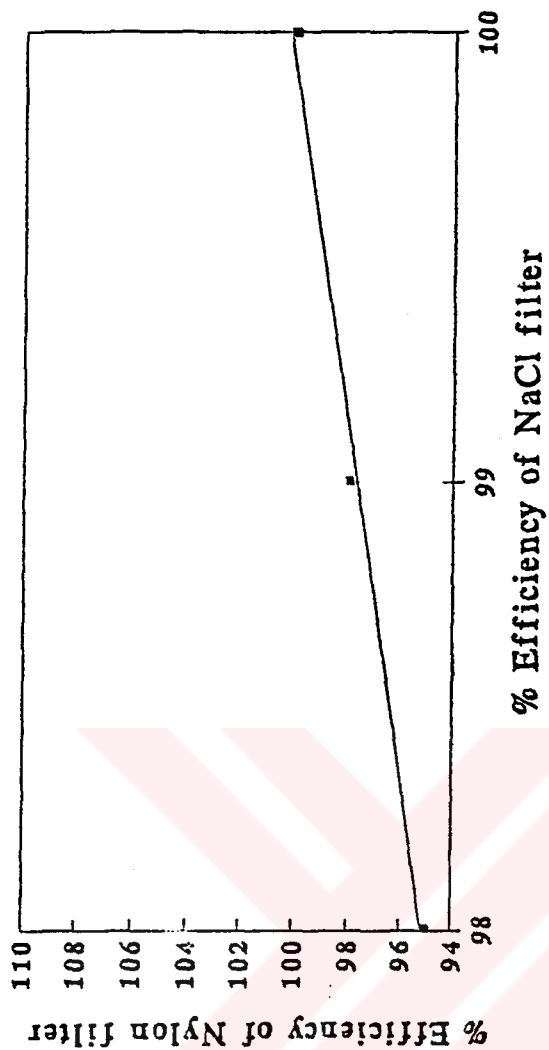
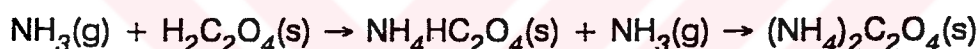


Figure 3.7 Comparison of NaCl and Nylon Filters with respect to Their Percent Efficiencies ($n=3$; $r^2=0.986$; intercept = -149.8 and slope = 2.5).

3.1.3 Collection of Atmospheric NH₃ on Oxalic Acid

Impregnated Filter Papers

Atmospheric ammonia can be collected on oxalic acid impregnated Whatman 41 filter papers at collection efficiencies close to 100%. However, the collection efficiency of the NH₃ may decrease by a factor of 3 as the relative humidity was decreased from 75 to 33% [11]. While the air sample was passed with a flow rates of 15 to 25 L/min, the below stepwise neutralization reaction thought to occur on the oxalic acid impregnated filter papers;



The collection efficiency of ammonia system was calculated by the Equation (3.1) that was used for SO₂ and HNO₃.

The saturation concentration of NH₃ which is a measure of the capacity of oxalic acid impregnated filters was tested by sampling NH₃ vapor from concentrated reagent bottle at different sampling periods in the laboratory conditions. Three oxalic acid treated filters were used in sequence and concentration of NH₃ on each filter were determined. Observation of substantial amount of NH₃ gas on the second and third filters is the indication

of the saturation of the first filter. The result of this experiment is summarized in Figure 3.8. The first three experiments corresponding to about 200 $\mu\text{g NH}_3$ collected on filter(1) are 3-hours samplings and the other corresponding 700 $\mu\text{g NH}_3$ is 11-hours sampling. As it can be seen from the Figure up to about 700 $\mu\text{g NH}_3$ amount almost no leak to the second and third filters is observed. Again this concentration is very large for ambient air conditions, indicating that one can easily use oxalic acid treated filters in both rural and urban atmospheres for the sampling of NH_3 without any doubt about the capacity.

The estimate of the collection efficiencies were plotted against total ammonia collected on the filters and is given in Figure 3.9. Collection efficiency is around 95% up to around 300 μg total NH_3 and drops to 85% at about 700 μg total NH_3 . These results show that oxalic acid filters can be used safely for the collection of atmospheric gaseous NH_3 .

The collected NH_3 on oxalic acid filters are stable for several weeks if they are kept at an ammonia free atmosphere and below 4°C.

There is evidence of volatilization of NH_4NO_3 and NH_4Cl [10,25,26] in our filter pack sampler, leading to an over estimation of HNO_3 and NH_3 and an underestimation of the corresponding particulate species. In most air

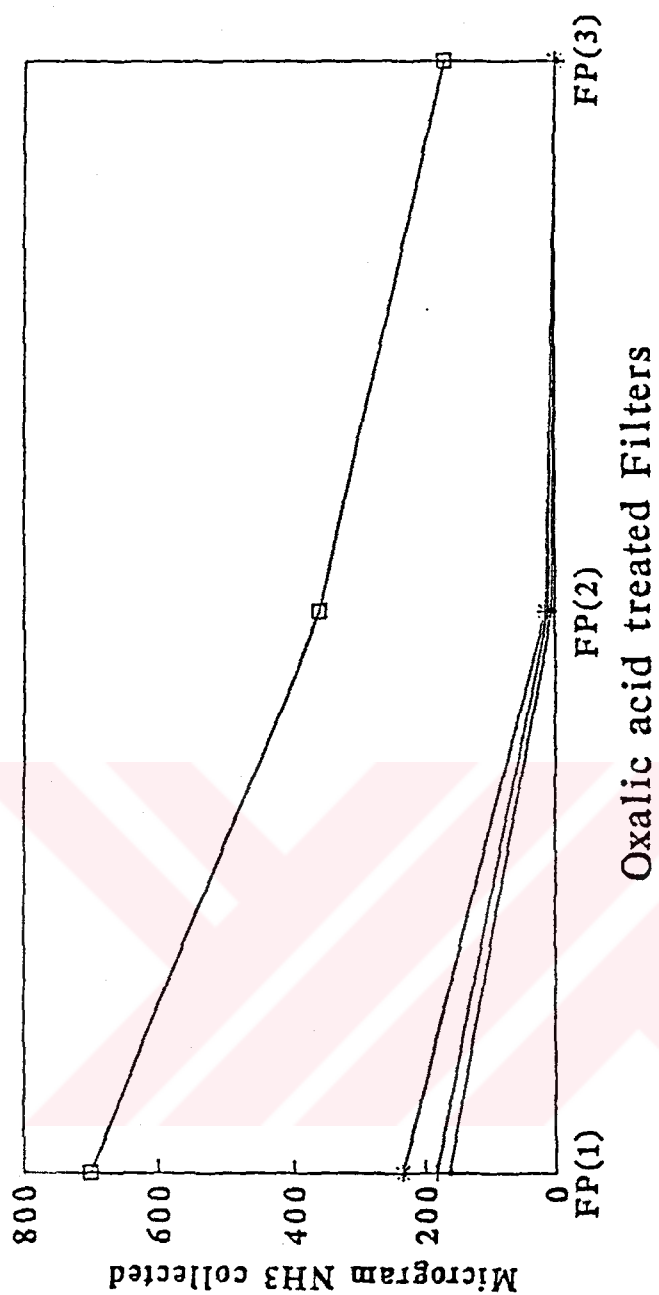


Figure 3.8 The Change in the Collected Amounts of NH_3 with the Filter

Numbers

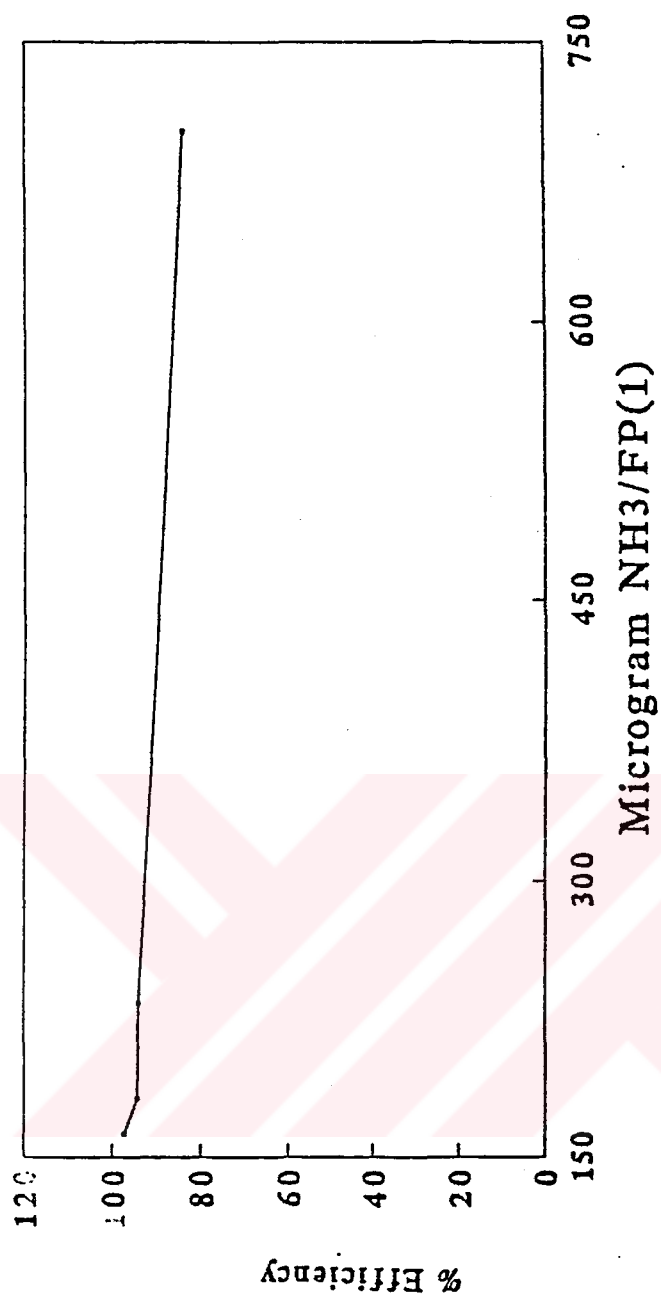


Figure 3.9 The Effect of Collected NH_3 on the Collection Efficiency of the Oxalic Acid Impregnated Filter paper(1)

sampling applications, this error is likely to be of minor consequence and it may be preferable to use filter pack procedure in view of its greater convenience.

The possible interferences of ammonia during analysis are; glycine, hydrazine and some amines that will react with Nessler's reagent to give the characteristic yellow color in the time required for the test. If the sample contains chlorine, the chlorine must be removed prior to the ammonia determination by pretreatment of the sample. The turbid samples may be clarified, by coprecipitation, with ZnSO_4 and NaOH solution; the precipitated $\text{Zn}(\text{OH})_2$ is filtered off [17]. No color change and turbidity was observed in our experiments. Accordingly estimation of interferences were not studied.

3.1.4 Collection of Atmospheric NO₂ and Total Nitrogen Oxides (NO_x) with Triethanolamine Treated Filter Papers

Triethanolamine (TEA) absorbs NO₂ (but not NO) and converts to nitrite (NO₂⁻). The formation rate of TEA-NO₂ complex is not fast enough to collect all NO₂ on the first treated filter paper. For this reason we reduced the flow rate of air sample and we used three TEA treated filters after a particulate filter. The sampling flow rate was reduced from 15 l/min to 1-2 L/min that gave the collection efficiencies of around 85%. The collection efficiencies of this system was calculated by the equation;

$$\% \text{ COLLECTION EFFICIENCY} = \frac{(C_1 + C_2 - C_3)}{(C_1 + C_2)} * 100 \quad (3.2)$$

Where C₁, C₂ and C₃ are the µg/m³ of NO₂ or NO_x (as NO₂) on the filter papers 1, 2, and 3, respectively.

In literature the atmospheric nitrogen dioxide has been sampled by means of passive samplers. This study is the first in literature at which NO₂ is collected using nonpassive sampler. We first tried high flow rate collections to

make the system compatible with the system that will be used in the field for the simultaneous sampling of sulfur dioxide, gaseous nitric acid and ammonia.

The results of experiments at high flow rates are summarized in Figure 3.10 shows the absorbed amounts of nitrogen dioxide or total nitrogen oxides (as NO_2) per filter papers that placed in series. It can easily be seen from the figure that collected NO_2 on each filter are not significantly different even at the reduced flow rate of 4-6 l/min. Since the collection efficiency calculated as the concentration ratio of filters these results indicate that the collection efficiency of triethanolamine treated filter papers is not significant at the flow rate of 5 l/min. This result can be explained by the very slow absorption rate of NO_2 by triethanolamine.

Although the collection efficiency which is around 60% of above experiments was not as satisfactory as the previous collectors, we compared filter pack system with automated NO_x samplers. For this purpose Air Monitoring Station which was equipped with SO_2 , and Meteorological Event Analyzers in addition to NO_x analyzer was used. This station was one of the seven stations located at Izmir area and operated by Dr. Gürdal Tunçel and his group (1992).

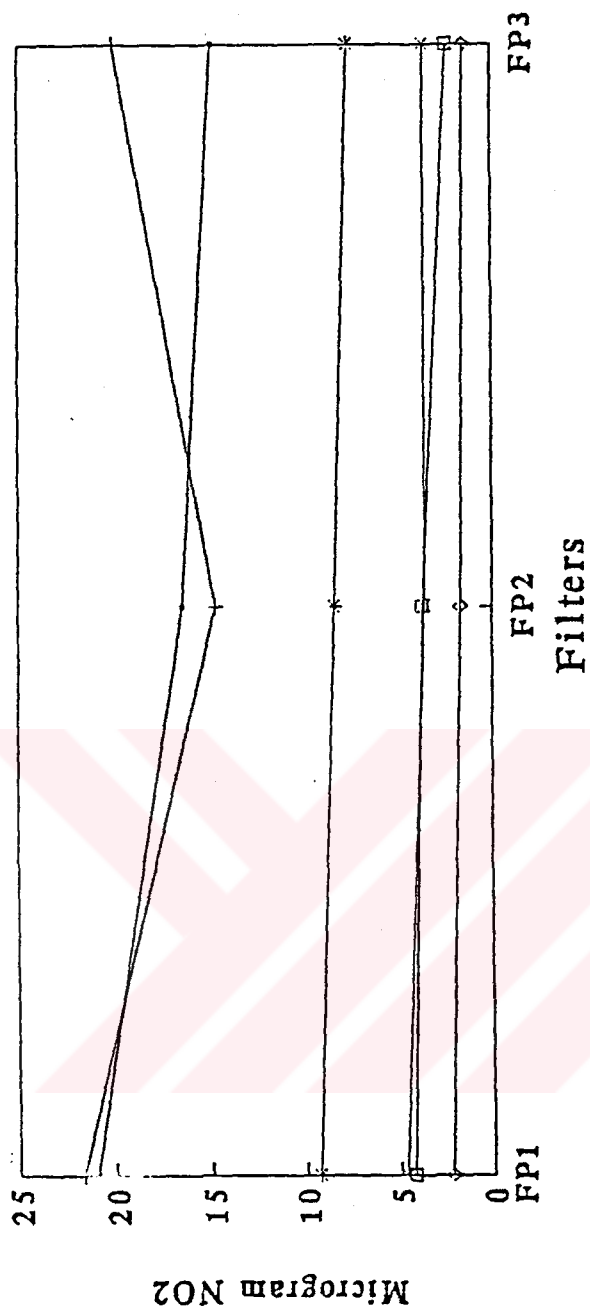


Figure 3.10 Comparison of Collected Amounts of NO₂ by the First, Second, and Third Filters When Flow Rate = 4-6 l/min

Efficiency of filter pack system was estimated by performing parallel samplings with automated analyzers. In these estimates, automated analyzers were assumed to be working with 100% efficiency. The results of these experiments are given in Table 3.3. As it is seen from the table, the results obtained for NO_2 are closer to the automated analyzer as the ratio of $\mu\text{g}/\text{m}^3$ NO_2 in automated sampler to the filter pack system is around 1.3 ± 0.7 . But the comparison for NO_x which is given in the first two rows of the Table 3.3 is not very good indicating the saturation of filters in the ambient concentrations. The further experiments for NO_x are being discussed in the following pages.

Table 3.3. Comparison of results obtained by filter pack* and automated NO_x analyzer.

$\mu\text{g}/\text{m}^3$ NO ₂ by Autoanalyzer	$\mu\text{g}/\text{m}^3$ NO ₂ by Filter pack	Date
12.3 (NO+NO ₂)	7.2 (NO+NO ₂)	24.06.92
24.6 (NO+NO ₂)	6.1 (NO+NO ₂)	26.07.92
2.1	1.3	27.06.92
2.1	2.1	28.06.92
2.1	0.8	29.06.92
2.2	2.3	30.06.92
2.2	2.4	01.07.92
2.2	2.5	02.07.92

* Experiments were done in Izmir-Menemen, The flow rate was 4-6 L/min.

Additional experiments were performed at reduced flow rates in order to improve the collection efficiency of the TEA filters. Obtained results are shown in figure 3.11, 3.12, and 3.13. When Figure 3.11 is compared to the Figure 3.10 which was obtained from high flow rates, the amount of NO_2 on the first, second and third filters in the Figure 3.11 are significantly different, that is, the first and the second filters collect more NO_2 compared to the third filter. This result shows that the collection capacity increases as the sampling flow rate reduces. Figure 3.12 shows that as the atmospheric concentration of NO_2 decreases the collection efficiency increases. As a result, at low polluted areas the TEA filters can be used efficiently if the atmospheric NO_2 concentration is lower than 5 or 6 $\mu\text{g}/\text{m}^3$. From the Figure 3.13 it can be seen that the amount of NO_2 collected on the first filter affects the collection efficiency, since the absorption of NO_2 on the TEA filters increases as the incoming amount of NO_2 decreases, as reported in literature [23], also. Two things that affect the collection efficiency are; flow rate of sampling and the atmospheric concentration of NO_2 at the sampling site. We can conclude that the collection capacity of TEA filters is very high compared to the other absorbents or adsorbents for the SO_2 , HNO_3 , and NH_3 collections. A 10(v/v)% TEA-impregnated filter still absorbing NO_2 after 91 hours collection time at an average atmospheric NO_2 concentration of 9.63 $\mu\text{g}/\text{m}^3$. The reached, maximum collection efficiency of the TEA filters was 85-90%.

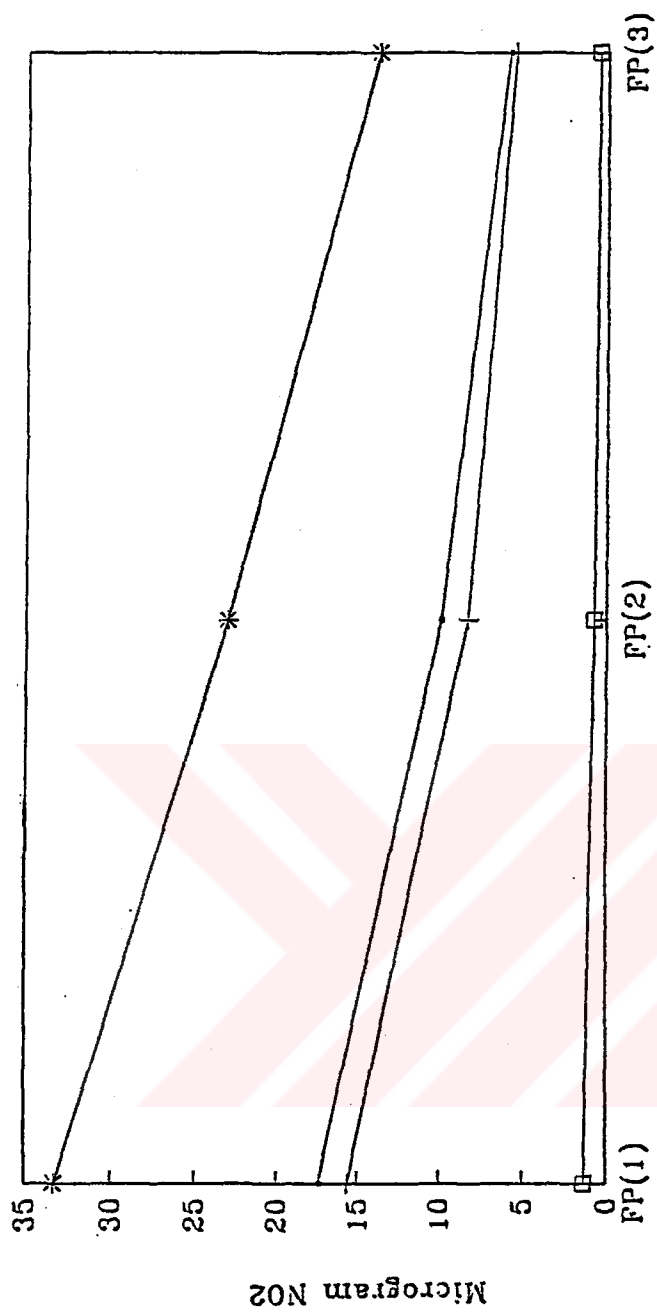


Figure 3.11 Comparison of Collected Amounts of NO₂ by the First, Second, and Third Filters When Flow Rate = 1-2 l/min

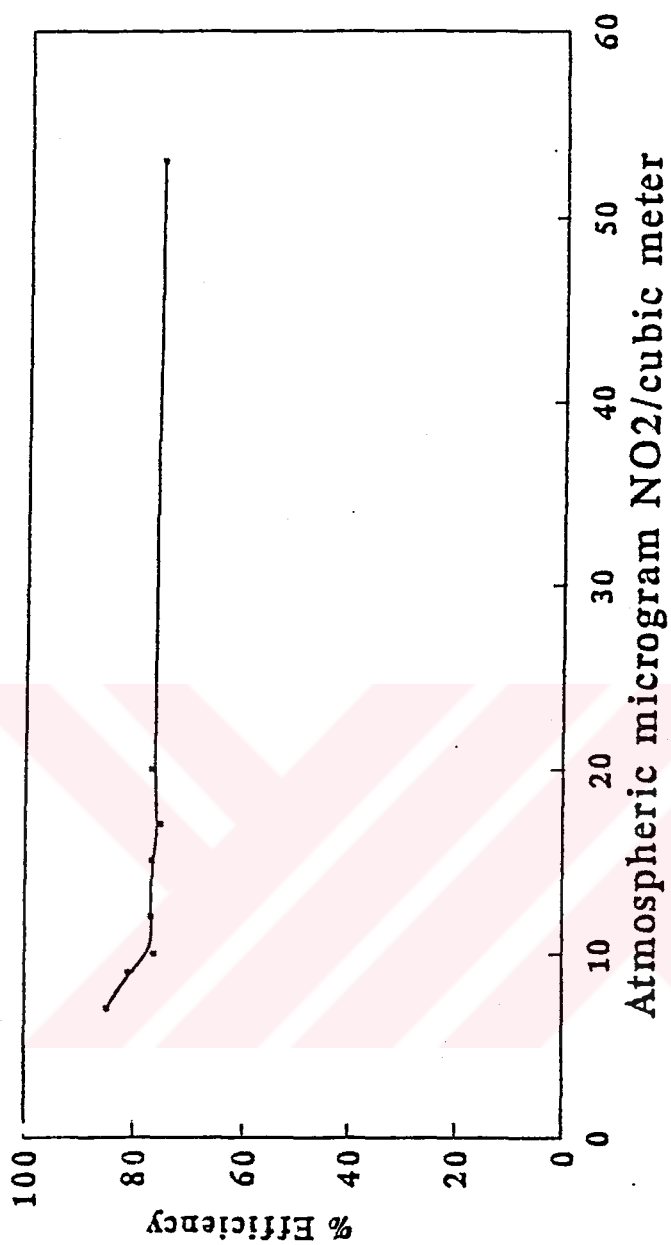


Figure 3.12 The Effect of Atmospheric Concentration of NO₂ to the Collection Efficiency of the TEA Treated Filter papers

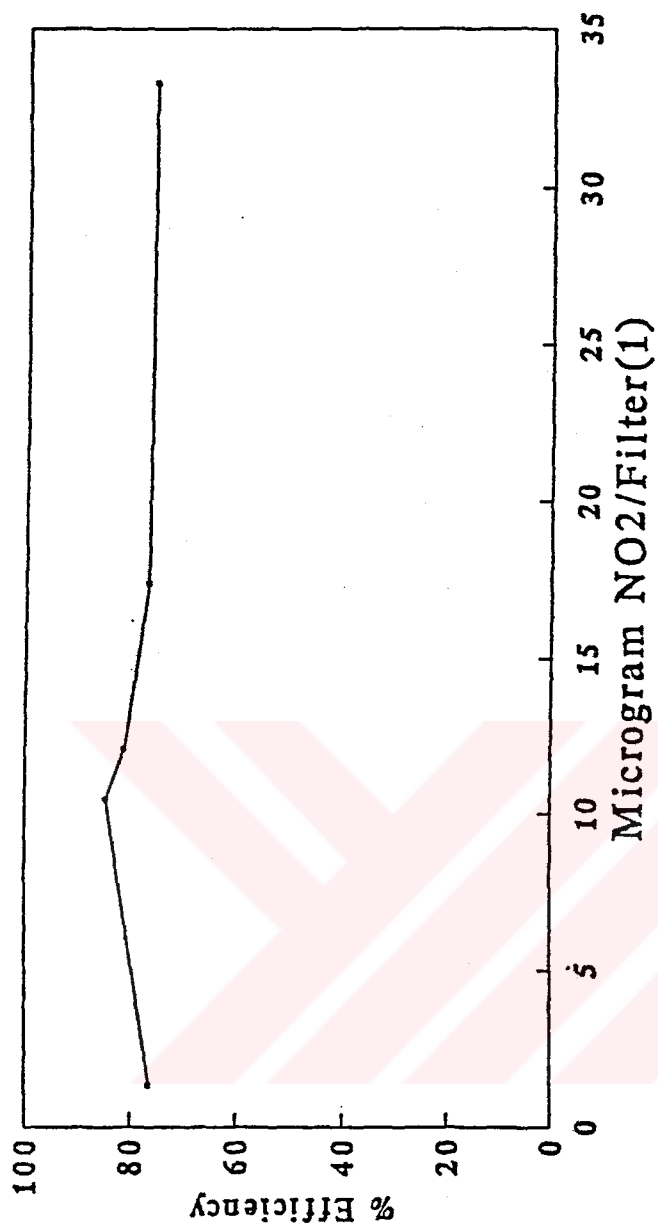


Figure 3.13 The Change in the Percent Efficiency of the Filter Pack System with the Changes in the amounts of NO₂ Absorbed by the First Filter Paper.

To collect NO_x with TEA impregnated filter papers, a modification was done to the NO_2 sampling system. Before the filter pack system an oxidizer bottle containing acidic 25(w/v)% KMnO_4 solution was filled. Then a prefilter and three TEA filters were placed in series. The air sample was passed with a flow rate of 1 L/min. Atmospheric NO_2 is not affected by the KMnO_4 solution but NO is oxidized to NO_2 . By this way total nitrogen oxides can be sampled with the efficiencies of around 85%. In field studies 100% efficiency can be reached by using four or five TEA filters in series. But in this case it would not be practical and would cause a decrease in the flow rate makes it similar with a passive sampler.

The advantages of using TEA was fourfold in our procedure; (1) it captures NO_2 efficiently in a nonpassive sampling system, (2) it has a high viscosity and low vapor pressure making it possible to coat solid materials to give stable sampling surfaces, (3) The TEA- NO_2 complex is quite stable so that the trapped NO_2 can be stored for considerable periods prior to analysis, and (4) the TEA (absorber) has a relatively life time. Tests have showed that the absorber was still removing NO_2 after 150 hours of sampling at 0.15 ppm [23].

TEA absorbs SO_2 also, but this problem can be solved by adding H_2O_2 solution to the NO_2 sample to be analyzed colorimetrically. But it should be noted that for air pollution analysis, hydrogen peroxide should be added prior to the addition of sulfanilic acid or sulfanilamide and N-1-Naphthylethylene-diamine-dihydrochloride (NEDA), to reduce or eliminate the SO_2 interference.

3.1.4.1 Conversion of Trapped NO_2 to NO_2^-

As in all NO_2 methods depending on diazotization, there is a question of the fractional conversion of NO_2 to NO_2^- . It has been shown in Figure 3.12 that the fraction of NO_2 converted to nitrite increases as the concentration of NO_2 sampled decreases and that as the concentration of NO_2 sampled approaches to zero the efficiency of conversion of NO_2 to NO_2^- approaches unity [23]. This result can be estimated from Figure 3.12 which indicates that as the atmospheric NO_2 concentration approaches zero the collection efficiency of the TEA filters approaches 100%. The 100% collection efficiency means that all incoming NO_2 is converted to nitrite on the TEA filters. The ambient air in Ankara atmosphere always contains at least $7 \mu\text{g}/\text{m}^3$ of NO_2 . For this reason we did not have chance to carry out experiments at lower NO_2 concentrations.

As it was mentioned before, efficiencies could be estimated by using the results obtained from the parallel samplings of filter pack with an automated NO₂ analyzer. The NO_x sampler in Ankara Hifsiissiha Institute was used for this purpose. Efficiencies of filters were estimated by assuming 100% collection efficiency for the automated analyzer. These results are presented in Table 3.4. Measured efficiencies are varied from 79 to 88% on the averages.

The compatibility of filter pack system with autoanalyzer was tested through the estimate of correlation curve. Figure 3.14 shows the results of this calculation. As can be seen from the Figure, the agreement in between autoanalyzer and filter pack system is quite good with $r^2 = 0.998$ and intercept = -102.1. The slope of the line is larger than unity.

Table 3.2. Comparison of atmospheric concentrations of NO₂ obtained by filter pack (FP) and by an automated Analyzer*

$\mu\text{g}/\text{m}^3$ NO ₂ by FP	$\mu\text{g}/\text{m}^3$ NO ₂ by Autoanalyzer	%Efficiency of FP
46.2	52.5	88.0
44.6	52.8	84.5
40.5	51.4	79.0

* Experiments were parallel daily measurements from 15.06.93 to 17.06.93 at Hıfıssıha Institute, ANKARA.

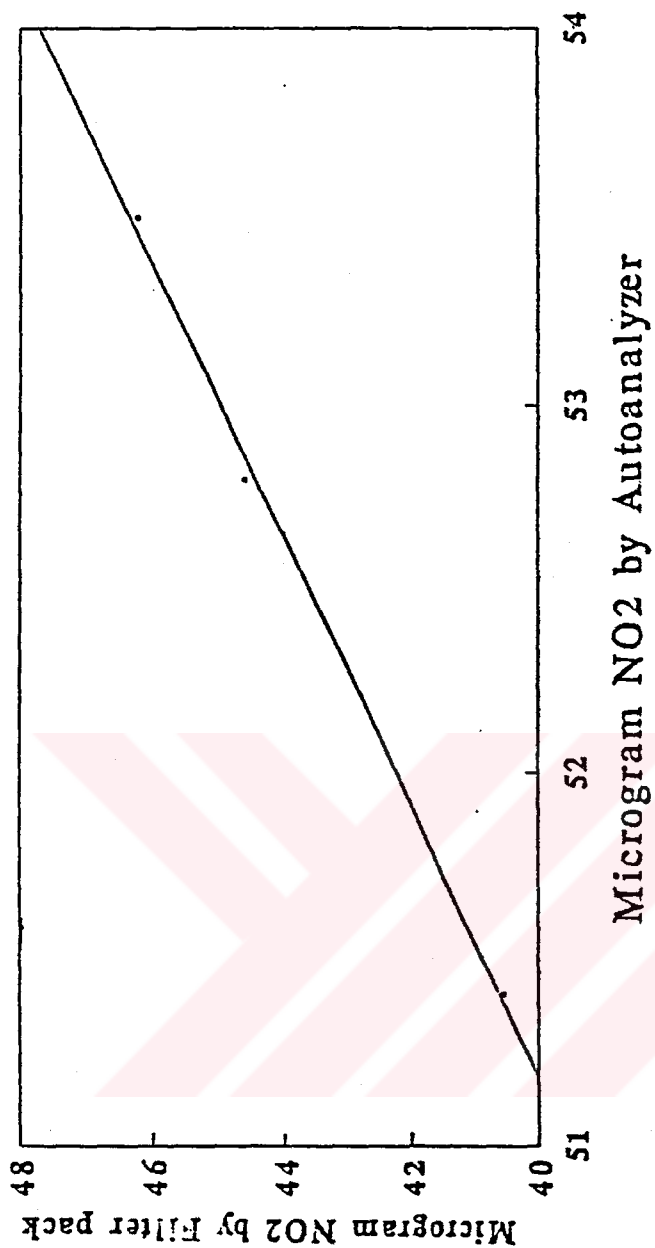


Figure 3.14 Comparison of Filter Pack System with an Automated NO₂ Analyzer ($n=3$; $r^2=0.998$; intercept= 5300.1 and slope=-102.1).

3.5 Simultaneous Sampling of SO_2 , HNO_3 , and NH_3

In order to investigate simultaneous sampling capacity of the individually optimized filters, experiments were performed with the filter pack assembly shown in Figure 2.3. In this assembly a teflon particulate filter was placed to the first cell of the filter pack system. To the following three cells; one nylon or NaCl filter, one oxalic acid filter and one sodium carbonate filter were placed in the order shown in Figure 2.3. The air sample was passed with flow rates which were optimized in individual experiments (15 to 25 L/min).

In order to check the interference in between the sampled gases on each filter, the analyses for each filter were done for each sampled gases by dividing the filter into three parts. The results are summarized in Table 3.5. As it is given in the table, only nylon filter collects $1.90 \mu\text{g}$ of NH_3 . When we changed the places of oxalic acid filter and nylon filter, this time the oxalic acid filter absorbed both ammonia and nitrate in the form of ammonium nitrate and caused lack of nitrate on the nylon filter. Interference of the sampled gases to each other are minimized by placing the oxalic acid filter to down stream of nylon filter. In this order the only possibility was the collection of NH_3 on nylon filter. The analysis of nylon filter for NH_3 showed that the collected ammonia was around 1% which is insignificant as an interferant.

Table 3.5. Observation of Retention or Loss of the Pollutants on the Impregnated Filter Papers**.

<u>Parameters</u>	<u>Na₂CO₃ Filter</u>	<u>Nylon Filter</u>	<u>Oxalic Acid Filter</u>
SO ₂	117.2µg	BDL	BDL
HNO ₃	5.1µg*	162.3µg	BDL
NH ₃	BDL	1.90µg	143.1µg

*All nitrate are background and coming from the impregnate, Na₂CO₃.

**Filters were placed down stream of a Teflon particulate filter in the order of (a) Nylon filter, (b) Oxalic acid filter, and (c) Na₂CO₃ filter.

BDL = below detection limit

To determine the detection limits of combined filter pack system by taking the 24 hours as the optimal sampling time for each analyte, the blank filters and the detection limit of ion chromatography that we used in the analyses, were used. For SO₂ and HNO₃, the detection limit of ion chromatography was 0.1 mg/L that corresponds to 0.049 ppb SO₂ and 0.050 ppb HNO₃ for 24 hours sampling (about 25 m³ of air sample). For the

detection limits of NH_3 and NO_2 , treated but not exposed five filter papers (blank filters) in five separate experiments were treated in Nessler's reagent and Saltzman reagent, respectively. The absorbances were read and concentration of analytes corresponding to 3s absorbance value was obtained from the calibration curves and converted to atmospheric concentrations for 24 hours sampling, that are, the detection limits of NH_3 and NO_2 . These results are summarized in Table 3.6. As can be seen from the table detection limits are quite good for atmospheric research.



Table 3.6. Detection Limits for the SO₂, NO_x (as NO₂), HNO₃, and NH₃ in the Analysis in ppb/24-hours.

Measured Parameter	Detection Limit (3s), ppb/24-h
SO ₂ [*]	0.049
HNO ₃ [*]	0.050
HNO ₃ ^{**}	0.054
NH ₃ ^{**}	0.030
NO _x ^{**}	0.074

* Analysis done by ion chromatography

** Analysis done by spectrophotometry.

For the determination of precision of combined system, three 1-hour samplings were performed in the laboratory conditions by using SO_2 permeation tube which was calibrated gravimetrically and evaporating the concentrated reagents of HNO_3 and NH_3 . The results are shown in Table 3.7. It can be seen that the precisions of three filter types are good enough to understand the reliability of the combined filter pack system. The accuracy tests for the nitric acid and ammonia were not done because of lack of permeation devices. But for SO_2 we did the accuracy test by comparing with the permeation tube. The amount of SO_2 released from the permeation tube was between 115 to 120 μg for 1-hour corresponds to 1.4 m^3 of air sample. And we observed 117.2 μg of SO_2 on the average of three experiments which was approximately the same as expected amount. This result caused -0.3% error when we assumed the average amount of SO_2 coming from the permeation tube as 117.5 μg (averages of 115 μg and 120 μg).

Table 3.7. Precision determinations for the simultaneous sampling of SO₂, HNO₃, and NH₃.

<u>Analytes</u>	<u>No. of Exp.</u>	<u>Coll.Time</u>	<u>Mean(μg)</u>	<u>s(μg)</u>	<u>%RSD</u>
SO ₂	3	1 hour	117.2	6.2	5.3
HNO ₃	3	1 hour	162.3	11.9	7.3
NH ₃	3	1 hour	143.1	11.5	8.0

As mentioned before, the NO_x system is not compatible to combined system, the atmospheric NO_2 was sampled individually at lower flow rates. To test the precision and accuracy of the NO_x collection we used the parallel sampling results that were obtained with our filter pack system and automated collectors at Hifsssiha Institute. The results of these experiments are summarized at Table 3.8. Application of the F-test indicated that the precision of filter pack system is not significantly different than the automated analyzers at 95% probability level. But in the case of accuracy filter pack system gives negative deviations from the values obtained by the autoanalyzer. This error is, on the average, -16.7%. This amount of error is due to the collection efficiency of the TEA filters. The collection efficiency was around 85% when compared to the autoanalyzer. In the experiments we used 3-TEA filters that collected the 85% of the NO_2 but if we would use 5-TEA filters this efficiency value would be around 100%. So by increasing the number of filters accuracy of the filter pack system can be improved more, but increasing the number of the filter is not practical, since it causes more reductions in the sampling flow rate which makes our nonpassive system similar to passive ones. If the flow rate is kept constant at 1-1.5 L/min, after placing 5-TEA filters then the system can be used efficiently in field studies.

Table 3.8. Comparison of the Accuracy and the Precision of the Filter Pack System with the Automated Instrument.

	<u>No. of Exp.</u>	<u>Mean($\mu\text{g}/\text{m}^3$)</u>	<u>s($\mu\text{g}/\text{m}^3$)</u>	<u>%RSD</u>
NO ₂ by Filter Pack				
(with 3 TEA Filters)	3	43.8	2.9	6.6
NO ₂ by Autoanalyzer	3	52.6	1.1	2.1

CHAPTER IV

CONCLUSION

In this study a sampler was developed as an alternative to the automated ones, for the collection of atmospheric gaseous pollutants, namely, sulfur dioxide, gaseous nitric acid, gaseous ammonia, and atmospheric nitrogen oxides. The air pollution caused by the parameters under consideration were monitored, in a simple, cheap and efficient way. The efficiencies of SO_2 , HNO_3 , and NH_3 are around 100% after optimizations and the collection capacities are 800 μg , 6000 μg , and around 300 μg , respectively. The collection capacity of the nylon filter with respect to gaseous nitric acid is larger than the capacity of NaCl filter. In addition to this it is practical and far from the contamination risks (because of lack of pretreatments and little extraction process). For these reasons we used nylon filters in this study.

In the case of sampling of atmospheric nitrogen oxides we could reach approximately 87% collection efficiency and it was concluded that the system used for the sampling of atmospheric nitrogen oxides is not compatible with the sampling system used for the other three analytes, because of low flow rate of sampling. So nitrogen oxides should be sampled individually. By increasing the number of TEA filters it is possible to reach the 100% collection efficiency in lower polluted areas with a sampling flow rate of 1 L/min.

The simultaneous sampling system for the SO_2 , HNO_3 , and NH_3 can be used efficiently in the field works. But if the field is polluted at high levels, then the sampling time should be reduced to a suitable period. For longer collection periods there is a danger of clogging of particulate filter with particulate matters that causes loss of gaseous pollutants by means of absorption, adsorption, or volatilization.

The simultaneous sampling experiments showed that a negligible amount of SO_2 was collected by the nylon filter and some of the atmospheric nitric acid absorbed by the oxalic acid filter. The latter problem can be solved by placing the oxalic acid filter to the downstream of Nylon filter. To prevent the adsorption of SO_2 on the nylon filter, the filter material should be selected carefully and it should be tested for the SO_2 and SO_4^{2-} before use.

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