Qatar Univ. Sci. J. (1994), 14 (2): 229-233

MULTIELEMENT ANALYSIS OF SUSPENDED PARTICULATES IN DOHA (QATAR) AIR BEFORE AND DURING THE GULF WAR

By

H. ABOU-LEILA, L. AL-HOUTY and H. EL SAMMAN
Department of Physics, Faculty of Science University of Qatar, Doha, Qatar

قياس تركيز عناصر مكونات الغبار الجوي في الدوحة ـ قطر قبل واثناء حرب الخليج

حسين أبو ليله و لطيفة الحوطي و حسين السمان

يحتوى البحث على دراسة لقياس نسبة تركيز العناصر الموجودة في الغبار الجوى في مدينتى الدوحة والخور قبل حرائق أبار البترول في الكويت ومقارنتها بقياسات على الغبار الجوي بالدوحة أثناء الحرائق . كما يحتوى على دراسة لقياس تركيز العناصر الموجودة في بعض عينات من البترول القطري والكويتي . وقد تمت الدراسة بإستخدام طريقة التألق بالأشعة السينية وبينت الدراسة وجود عناصر الألومنيوم والسيليكون والكبريت والكلور والبوتاسيوم والكالسيوم والحديد والزنك بتركيزات مختلفة في الغبار الجوي ، بالاضافة إلى تسعة عناصر اخرى في الغبار المتجمع بواسطة مرشحات تكييف الهواء بجامعة قطر وهى عناصر التيتانيوم والفانديوم والكروم والمنجنيز والاسترانشيوم والكادميوم والقصدير والزئبق والرصاص . وقد تمت ملاحظة زيادة في نسب مركبات الكبريت والزنك أثناء الحرائق .

Keywords: X-ray fluorescence, Air quality, Burning of Kuwait oil fields during Gulf war.

ABSTRACT

Efforts have been made to study the effect on Qatar atmosphere from the burning of Kuwait oil fields during the Gulf war. Analysis of suspended air particulates was done by X-ray fluorescence technique. Eight elements were detected in particulates collected before and during the war. These are Al, Si, S, Cl, K, Ca, Fe and Zn. Only the concentration of Zn and S was increased in samples collected after the burning of Kuwait oil fields. Nine other elements were traced in dust particulates with different concentrations. These elements are Ti, V, Cr, Mn, Sr, Cd, Sb, Hg and Pb. Results were also compared with those from Kuwait oil and Qatar oil samples.

INTRODUCTION

Qatar is a peninsula of area about 11500 km^2. It is situated on the western coast of the Arabian Gulf about 500 km south-east of Kuwait. The degree of air pollution in Qatar has not been yet studied. A considerable effort is needed to establish a data base concerning air pollution in order to develop a national air quality standard for Qatar. Suspended particulate matter in air is considered as a major pollution which can have considerable effects on health and environment. Some of these pollutant are generated in localized urban areas while others can be carried from greater distances. Data on gamma background radiation in Qatar was previously established[1], moreover contamination of air quality from the Chernobyl accident was monitored in Qatar[2]. The quality and pollution of air in the Arabian Gulf area has been studied by several authors [3-5]. The burning of oil fields in Kuwait has had a dramatic pollution effects on the whole area[6-11]. Smoked clouds as well as oil odors have been noticed in Doha air with different concentration degree. At that time ,the future effects of this pollution was very difficult to be predicted.

Nowadays, some efforts are done to follow any possible effects on the environment which could be attributed to the highly polluted atmosphere during the war period. For these efforts data on the degree and nature of pollution during war are highly needed. No such data is available in literature for Qatar.

This work, presents a search for toxic trace elements such as V, As, Se, Sb, Hg, Pb.....etc. in some oil samples from Kuwait burning fields and in suspended particulate in Doha air before and during the Gulf war.

EXPERIMENTAL TECHNIQUE

X-ray fluorescence (XRF) spectrometer was used in the present work for the following reasons; a) The technique is switchable for large number of samples (up to 24 samples) automatically, b) It is a non destructive method, thus samples can be retained for further future study, c) It's detectability is fairly uniform across the periodic table. All elements higher than Na can be easily analyzed.

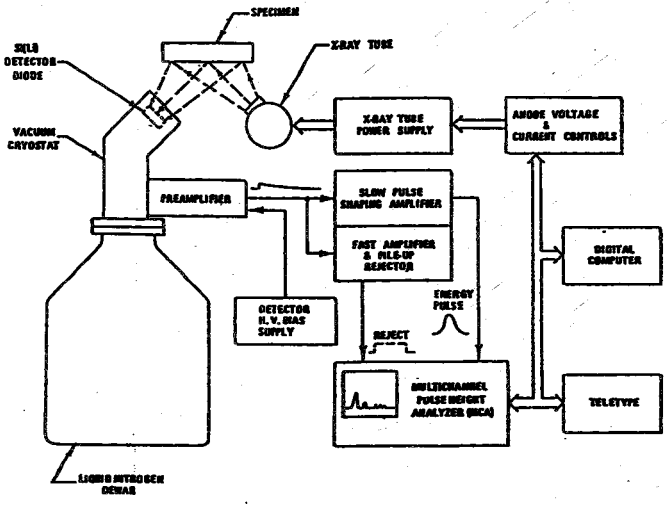

Fig. 1: Block diagram of the XRF spectrometer.

An ORTEC 6110 Tube Excited X-ray Florescence Analyzer TEFA was used for this analysis. Figure 1 shows a schematic representation of the major parts of the spectrometer. The excitation conditions can be varied by changing the anode voltage from 10 to 50 kV while the anode current can be changed from 5 to 200mA. Two types of anodes W or Mo can be used. The X-ray from the excited tube can be directed to the sample through an Al or Cu filter if needed. The characteristic X-ray results from the sample are detected using a high resolution , low energy Si(Li) detector (FWHM is 165 eV at 5.9 keV from Mn K_a). The output of the detector is fed to a linear amplifier and 1024 channels multichannel analyzer. Two different software packages were used for the analysis purpose. The first is an ORTEC XRF software ATAC[12] which provides a linear least square fit of element concentration versus florescence X-ray intensities (for different excitation conditions). This program requires variety of standard samples for calibration purpose. The second software is a fundamental parameter technique FPT[13]. This program can run without any standard. With this software, an unknown sample elemental composition is computed by theoretical predication of characteristic line intensities from a computed representation of the X-ray output, from basic elemental coefficients and from a model of X-rays generation and interaction. The program can also run by either one dissimilar or one similar standard. The dissimilar standard can have only one matrix. The similar standard can have a matrix similar to the matrix of the sample and could be used to analyze different samples in different excitation conditions. Table 1, shows the composition of a similar standard used in the present work. After the analysis of the standard sample , the net counts per second for each photopeak is computed and corrected for the detector efficiency. From the corrected counts per second and the concentration of each sample in the standard, a senstivity factor is derived and used to calculate the element concentration in unknown samples.

Table 1
The standard analysis report of FPT program, obtained using known concentration of different elements

Elem.	Conc.	Line	Measured CPS	Detector Efficiency	Predicted Intensity	Sensitivity Factor
Al	7.34%	Kα1	61.73	64.35%	5.602E+00	1.713E+01 (1)
Si	9.26%	Kα1	127.32	75.48%	0.000E-01	1.000E+00 (1)
S	13.33%	Kα1	509.26	75.93%	2.690E+01	2.493E+01 (1)
Ca	13.48%	Kα1	1266.82	90.81%	9.108E+01	1.532E+01 (1)
Y	7.78%	Kα1	1674.22	95.78%	1.110E+02	1.575E+01 (1)
Cr	5.78%	Kα1	31.89	96.68%	1.099E+02	3.002E-01 (1)
Fe	5.12%	Kα1	1093.17	97.89%	1.382E+02	8.079E+00 (1)
Ni	5.28%	Kα1	1573.67	98.62%	1.964E+02	8.125E+00 (1)
Zn	13.89%	Kα1	6649.33	99.07%	6.134E+02	1.094E+01 (1)
Cd	7.49%	Kα1	501.08	91.65%	8.054E+01	6.788E+00 (1)
Hg	10.13%	Lα1	1928.30	99.38%	1.972E+02	9.841E+00 (1)
Pb	10.38%	Lα1	2786.50	99.46%	2.339E+02	1.198E+01 (1)

Sample Preparation

Three types of samples were analyzed:

1) Suspended particulate in air were collected on 10 cm diameter filter paper using a high volume air sampler collector model 302 from (Nuclear Associates) . The samples were collected at several locales in Doha. Each sample was collected during a period of 6 hours with a flow rate of the order of 48.6 m^3/h. The filters were weighted before and after collection. The amount of dust collected in each filter was of the order of 0.04 - 0.06 g. The filter with the accumulated dust were exposed directly to the X-ray beam without any treatment .

2) Dust particulate were collected from air conditioning filters of Qater University which is located about 15 km from Doha. Dust of weight 10 g was then pelletized at 20 kN/cm^2. The pellets of 3 cm diameter were exposed to X-ray beam for analyses.

3) Oil samples from Kuwait oil field as well as from Qater oil field were prepared by putting one drop of oil in the center of the filter paper. Efforts have been made to distribute the oil drop to perform a homogeneous area of the filter. The filters were then analyzed by exposing them directly to the X-ray beam.

Preparation of standards

Two types of standards were prepared:

1) Standards for filter paper samples:

Salt solutions of known concentrations of each of the elements : Al, Si, S, Cl, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Sb, Sr, Cd, Hg and Pb were prepared. Different ratios of

these solutions with known element concentration were then mixed together using a micropipet. One drop of the final solution was put in the center of the filter paper and left to dry.

2) Standards for pellets samples:

Known masses of the above mentioned elements were mixed together very well and a sample of 10 g by weight was pelletized at 20 kN/cm^2 having the same size and diameter as the sample of dust pellets mentioned before.

RESULTS AND DISCUSSION

Several runs have been taken to analyze each sample at different conditions. The concentration of the elements present in each sample was estimated using both the FPT and ATAC procedures and prepared standards . The average value of all these measurements was taken. The average percentage error is found to be 5 % of each value. The main objective of the study of oil samples was to identify the elements present in each sample, estimate their relative concentration and then search for the presence of these elements in air filters used to collect suspended particulate in atmosphere and in the dust samples collected from the air conditioning filter during the war. Fig. 2, shows a typical spectrum of one of the dust sample.

Oil Samples

I- Kuwait Oil

Table (2) summarizes the analyzed data of two oil samples. The first is crude oil sample from Burgan (I) and the second is a light oil sample from a refinery (API 30.6, Swt 2.46), (II). From the results one can reveal the following points:

1) Al, Si, S, Cl, K,Ca, Cu, and Sr are present in both samples with relative intensities ranging between 0.1 %, to about 88 % . The concentration of each element varies from sample to sample

2) Ti, V, Fe and Se were found with relatively high concentrations in the crude oil samples as compared to some part per million (PPM) in the light oil samples

3) Br is detected in a relatively high concentration in the light oil samples (0.19 %) while no traces was found in the crude oil sample

4) Some PPM of Ni, Zn, As, Cd, Sb and Hg were detected in both samples

5) No traces of Cr, Mn or Pb were detected in both samples

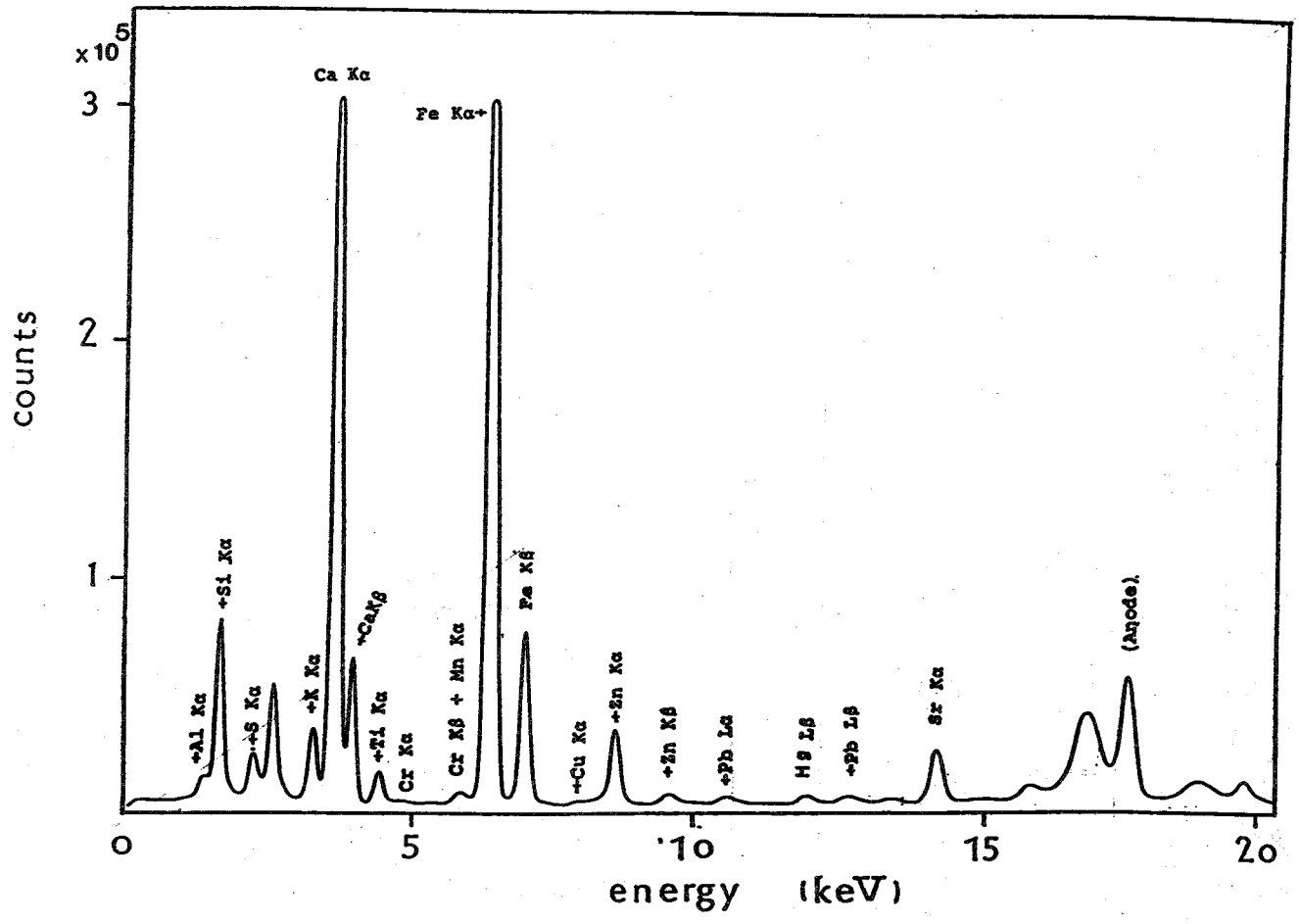

Fig. 2: Typical spectrum obtained with the XRF spectrometer for a dust sample.

II- Qatar Oil

Table (2) summarizes the analyzed data of a Qatar oil sample (III). Comparing these results with the results obtained from Kuwait oil we can reveal the following:

Table 2
Relative concentrations of different elements detected in oil samples from Kuwait (I & II) and from Qatar (III)

Elements	Samples		
	I CONC %	II CONC %	III CONC %
Al	0.11	1.25	0.47
Si	2.06	18.37	0.00
S	1.90	42.18	55.00
Cl	88.05	32.52	30.29
K	4.96	0.57	0.00
Ca	2.07	1.15	0.37
Ti	332 PPM	0.8	3.42
V	251 PPM	0.11	818 PPM
Cr	0.00 PPM	0.00 PPM	0.00 PPM
Mn	0.00 PPM	0.00 PPM	0.35
Fe	330 PPM	0.17	1.85
Ni	56 PPM	394	0.22
CU	0.27	2.05	6.65
Zn	47 PPM	245	0.27
As	124 PPM	287 PPM	0.49
Se	450 PPM	0.29	0.66
Br	0.19	0.00 PPM	0.00 PPM
Sr	0.12	0.33	0.64
Cd	1.00 PPM	145 PPM	0.00 PPM
Sb	39 PPM	424 PPM	0.00 PPM
Hg	108 PPM	759 PPM	0.22
Pb	0.00 PPM	0.00 PPM	735 PPM

1) Si, K and Cd are absent from Qatar oil samples. While Mn is absent from Kuwait samples. The presence of Si and K from Kuwait samples can be mainly attributed to the contamination of samples with sand and soil. Since only few samples from each country are analyzed, no conclusion can be drawn confirming the existence or none existence of trace elements such as Sb or Mn in one country sample or another.

2) Al, S, Cl, Ca, Ti, V, Fe, Ni, Cu, Zn, As, Sr and Hg are present in both samples.

3) Although some traces of Pb are found in Qatar oil, no Pb was found in Kuwait samples. The possible toxic elements such as Hg and Cd are present in Kuwait samples only as PPM.

Air Filters Samples

Several air filters samples collected during the war were analyzed and compared with other filters taken before the war. Table (3) shows a sample of the results of analysis for two filters taken 10 years before the war (samples A and B) . One of these filters presents elements detected in air particulate collected from the atmosphere of Doha city while the second one presents elements detected in particulate collected at the sea shore near Al-Khor city about 50 km North of Doha. From these data, it is clear that the atmosphere was rather clean. Al, Si, S, Cl , K, Ca, Fe and Cu were present in both cities in concentrations ranging from ≈1 to ≈37%. Zn was present in Al-Khor with concentration in the order of 2.18% while only some parts per million (PPM) were detected in Doha city. No Pb or other heavy trace elements were detected.

Table (3) represents also the data for some samples taken during the Gulf war in February and March 1991. Comparing these results with those obtained ten years before the war, we can summarize the following :

Table 3
Relative concentration of elements observed in air filter samples collected from the atmosphere in Doha city before and during the war

Element	Samples					
	A CONC %	B CONC %	C CONC %	D CONC %	E CONC %	F CONC %
Al	5.70	2.68	1.71	3.41	4.89	2.50
Si	19.98	11.44	5.34	7.40	16.39	5.77
S	36.58	24.01	46.20	67.75	27.14	58.53
Cl	1.01	21.28	29.85	9.46	18.90	18.11
K	1.59	1.87	1.64	1.03	1.27	1.23
Ca	31.94	35.31	13.56	8.45	29.23	14.48
Fe	2.42	2.27	9.97	1.26	1.45	0.81
Cu	0.76	1.14	0.29	0.26	721 PPM	0.19
Zn	105 PPM	2.18	0.43	0.97	0.15	0.38

A : sample collected on Feb. 1981 (Doha city)
b : sample collected on Feb. 1981 (Ras Lafan)
c : sample collected on Feb. 12 1991 (Doha city)
D : sample collected on Feb. 24 1991 (Doha city)
E : sample collected on Mar. 6 1991 (Doha city)
F : sample collected on Mar. 17 1991 (Doha city)

1- No other elements except the nine previously mentioned elements were detected.

2- Only the concentrations of Zn and S were increased . No other elements previously detected in oil samples were noticed. The high turbidity noticed in Doha atmosphere during Kuwait oil burning could be mainly attributed to volatile organic hydrocarbons.

Dust particulate samples

Dust particulate samples are expected to give more information about elements present in air particulate as compared with air filter samples. This is due to the fact that they are collected by suction by high air flow rate during long time reaching nearly one weak. In the present work , one sample was taken just before the burning of oil fields in Kuwait, and three samples were taken during March - April 1991 (one sample is collected during March and two samples were collected during April). The analysis of the results show that in addition to the elements previously detected in air filter samples, nine other elements were detected in

the collected dust samples. These elements are Ti, V, Cr, Mn, Sr, Cd, Sb, Hg and Pb. Table (4), shows the average concentration of each of these elements before and during oil fields burning.

Table 4

The average concentration of elements detected in dust samples collected from the filter of air-conditioning in Doha city and not seen in air filter samples

Element	A		B	
Ti	2.56	2.15		
V	7	PPM	6	PPM
Cr	0.35		0.31	
Mn	0.56		0.47	
Sr	0.39		0.26	
Cd	13	PPM	14	PPM
Sb	296	PPM	680	PPM
Hg	48	PPM	44	PPM
Pb	214	PPM	121	PPM

A) average concentration % during burning of oil fields.
B) concentration % before the burning of oil fields.

CONCLUSION

The data presented in the present work could be considered as the first step to establish a data base for air pollution in Doha. Although, the results presented in this work are not to be conclusive, however, some indications could be drawn. Comparison between data on air quality before and during the Gulf war has shown that :

1- There is an increase in Zn and S compounds. The increase in S could be attributed to the burning of the Kuwait oil fields. We can not define the origin of the increase of Zn. In fact only two samples from burning Kuwait oil fields were available in this study. These samples contain only some PPM's of Zn. Other Kuwait's oil fields could have higher concentrations of Zn. In addition , the increase in Zn might be due to Zn compounds particulates carried with smoke clouds passing through north of the country where Zn concentration is slightly high (Table 3).

2- Except for Cr, the elements detected in the dust samples are present in the oil samples from Kuwait and/or from Qatar. The concentrations of these elements are small to notice any effect from the oil burning, (Table 2 and Table 4). In addition, there is no significant difference in the concentration of those elements in dust samples before and during the oil burning. Moreover, the presence of Ti with moderate concentration might be due to air pollution from the Qatar oil.

3- One could conclude that the observed turbidity in Doha air was mainly due to volatile hydrocarbons.

ACKNOWLEDGEMENTS

The authors are grateful to Prof. Dr. Abdel-Fattah Bastawi Farag , Chemistry Department, University of Qatar for his helpful discussion and preparing the standard samples used in this work.

REFERENCES

[1] **Al-Houty, L., H. Abou Leila and S. El Khameesy, 1987.** Nature of gamma rays background radiation in new and old buildings of Qatar University, Environment International 13: 393-398.

[2] **Al-Houty, L., S. El-Khameesy and H. Abou Liela, 1988.** Radioactive contamination of the atmosphere of Doha Qatar from Chernobyl accident, Nucl. Science J. 25: 21-30.

[3] **Mohamed, M.A., and A.A. Al-Shamlan, 1977.** Organic matter content in Kuwait Bay Sediments as an index of pollution, J. of the University of Kuwait (Science) 4: 215-222.

[4] **El-Samara, M.I., and K.Z. El Deeb, 1988.** Horizontal and vertical distribution of oil pollution in the Arabian Gulf and the Gulf of Oman, Marine pollution Bulletin 19: 14-18.

[5] **El-Sabh, M.J. and T.S. Murty, 1988.** Simulation of the movement and dispersion of oil slicks in the Arabian Gulf, Natural Hazards 1: 197-219.

[6] **El-Baz, F., 1992.** Preliminary observations of environmental damage due to the Gulf war, Natural Resources Forum 16: 71-75.

[7] **Corss, A.M., 1992.** Monitoring marine oil pollution using AVHRR data, Observations off the coast of Kuwait and Saudi Arabia during January 1991, Int. J. of Remote Sensing 13: 781-788.

[8] **John, V.C., 1992.** Circulation and mixing processes and their effect on pollutant distribution in western Arabian Gulf, Applied Ocean Research 14: 59-64.

[9] **Browning, K.A., R.J. Allam, S.P. Ballard and R.T.H. Barnes, 1992.** Environmental effects from burning oil wells in the Gulf, Weather 47: 201- 212.

[10] **Jenkins, G.J., D.W. Johnson, D.S. McKenna and R.W. Saunders, 1992.** Aircraft measurements of the Gulf smoke plume, Weather 47: 212-220.

[11] **Shaw, W.S. 1992,** Smoke at Bahrain during the Kuwait oil-field fires,Weather 47: 220-225.

[12] **EG&G ORTEC,** Materials Analysis Division, Software program ATAC Version 4, Dec. 1981.

[13] **EG&G ORTEC,** Materials Analysis Division, Software program FPT Version 08.29, Jan. 1983.