

## **Analysis of Organic and Inorganic Compounds in Air Particulate Matters in Hong Kong**

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### **ABSTRACT**

Analytical procedures for the analyses of organic and inorganic compounds in air particulates collected on a single cellulose fibre filter were investigated using analytical facilities commonly available in a chemical laboratory. For the analysis of inorganic compounds, a DC arc emission spectrometer coupled with a photo-diode array detector was used to quantify the metal contents, including Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Si and V. The sample treatment method included pulverizing a portion of the filter and mixing it with thermochemical agents, which could enhance the sensitivity of the method for subsequent analyses. The recovery of the method was checked against SRM 1648 Urban Particulate Matters. The performance of various thermochemical agents was compared. The emission-time profiles show the possibility of differentiating refractory elements from the more volatile ones and thereby providing valuable information for use in the apportionment of major air pollution sources.

For the analysis of organic compounds, an elaborated procedure using Soxhlet extraction followed by liquid-liquid extraction with DMSO-hexane partition was developed for the determination of total polycyclic aromatic hydrocarbons (PAHs). A base-hydrolysis step was introduced to remove the interfering phthalates prior to total PAHs determination using the FTIR method. The applicability of the method is discussed in light of a preliminary roadside study of total PAHs in air particulates.

(Key words: Polycyclic aromatic hydrocarbons, DC arc emission spectroscopy, Metal analysis, Air particulate matters)

### **1. INTRODUCTION**

Chemical analyses of air particulate matters, in particular those in the respiratory regions (0.1 to 10  $\mu\text{m}$  size), have frequently been carried out in many field studies as the information obtained may well be used to apportion major air pollution sources to evaluate the potential

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risk of respiratory health problems and to provide a good indicator of the air quality sampled at receptor sites (Fung, 1989; Fung, 1993; Fung and Wong, 1993).

Problems inherent in the existing analytical methods for elemental analysis of air particulates are 1) the need to use high purity reagents and acids for the digestion of the particulates and filters, 2) the long time for sample preparation, and 3) the contamination problems in metal analysis. Thus, an analytical procedure using the DC arc for direct particulate analyses was developed in the present work to solve the above problems.

The results from chemical analyses of air particulates collected in Hong Kong and in many other cities have shown an increasing trend in the amounts of carbon content present at the particulate collected, and most of them were found to have come from vehicle exhaust and other fuel sources (HKEPD, 1989; HKEPD, 1990). Thus, concern has been expressed about the PAH content of the particulates, and this has necessitated the development of analytical methods. The existing methods often use expensive equipment with high running costs for PAH analyses, and especially in the analysis of individual PAH. Thus, the method for the determination of total PAHs would provide a suitable screening method. The problem for total PAHs analyses is that their responses are PAH dependent, and thus, the results obtained remain somewhat in doubt. As the response factor for the IR absorption of PAHs are shown to be more constant, they are more suitable for the determination of total PAHs (Fung and Cheung, 1993). Results from a preliminary investigation of the applicability of the method are presented and discussed here.

## 2. EXPERIMENTAL SECTION

### 2.1 Reagents and Chemicals

The thermochemical agents, sodium chloride, sodium carbonate, ammonium chloride and ammonium nitrate were of AR grade. The filter medium was Whatman 41 cellulose fibre filter, in dimension 8" × 10". The graphite electrodes from Bay Carbon (Bay City, Michigan 48706, USA) were SPK grade with a 6 mm diameter with a crater of 4 mm in diameter and 6 mm in depth. Blank tests were performed on all the above materials used in the DC arc emission spectroscopy to ensure that there was no interference at the analytical lines being monitored. The certified particulate matters were SRM 1648 Urban Particulate Matters from the National Institute of Standards and Technology (NIST), United States Department of Commerce.

All solvents used for extraction were purchased as "distilled in glass" grade. The dimethylsulfoxide (DMSO) used was the A. C. S. spectrophotometric grade and potassium bromide were of FT-IR grade. The PAHs standards such as phenanthrene, anthracene, fluoranthrene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(a)pyrene and benzo(g,h,i)perylene, were purchased from Aldrich, and were used without further purification. The PAHs were dissolved in a 1:1 methanol/acetonitrile solvent mixture.

### 2.2 Sample Collection and Preparation

The Sierra-Anderson PM-10 Size Selective Hi-Volume Air Sampler was used for the sampling of the 10 µm respiratory suspended particulates using 8" × 10" Whatman 41 filter papers. After 24-hour sampling periods, the dust-loaded filters were cut into two halves, with one portion used for the analysis of total PAHs and a portion of the other for grinding into powders using the heavy duty model #6 Wig-L-Bug Grinding Mill with a tungsten carbide capsule prior to analysis using the DC arc emission spectrometer.

### 2.3 Analysis of Metal Content Using the DC Arc Emission Spectrometer

The DC arc emission spectrometer consisted of a DC arc source and a 15 Ampere power (Rank Hilger) D. C. Arc Unit. The spectrometer (model WP1, Beijing Second Optical Instrument Company) used a 1-m Ebert-Fastie Type grating to provide suitable dispersion for atomic emission measurement. It also provided a plane surface for detection using the photodiode array (PDA) detector (Hamamatsu MOS Linear Image Sensor S3924-1024Q). The PDA consisted of 1024 photodiodes arranged linearly on a length of 25.6 mm with a height of 2.5 mm. The spectral response ranged between 200 and 1000 nm. The video data was fed into the Hamamatsu C2890 Data Processing Unit. Calculations and spectral displays were made through an IBM compatible 80486 computer. The exposure time could be varied from 0.1 ms to 12000 s. The change in the emission spectra over time could be monitored so that the variation in the peak emission intensity with time could be followed. The PDA was cooled to below  $-15^{\circ}\text{C}$  with a Peltier cooler, and condensation of the water was prevented by having the detector surface continuously purged with nitrogen dried through a column of molecular sieves.

Thermochemical agents/chlorinating carriers (Jambor, Otruba, and Sommer, 1988), were well mixed with the sample. 15 mg of the agent were powdered with the sample in a plastic vial using a mixer mill. For a mixture of thermochemical agents/chlorinating carriers, an equal mass ratio of each of the compounds was used to provide a total mass of 15 mg. The well-mixed sample was put into the crater of the graphite electrode. The gap of which was purged with an argon stream at 1.5 l/min to exclude nitrogen, thereby eliminating the CN band, and supporting a more stable plasma.

To check the recovery of trace metals using the above procedures, SRM 1648 Urban Particulates were used as standards and were treated according to the same procedures as those used for the particulates collected with the Hi-vol sampler.

### 2.4 FTIR Determination of PAH

A summary of the procedures under optimized conditions for sample clean-up using liquid-liquid extraction and base-hydrolysis prior to FTIR analysis is given in Figure 1. Half of the sample collected on the cellulose filter was extracted with dichloromethane for 16 hours using the Soxhlet apparatus. The resulting mixture was evaporated under nitrogen. The residue was re-dissolved into n-hexane. The liquid-liquid extraction procedure using DMSO as introduced by Natusch and Tomkins (1978) was used to extract the PAHs from aliphatic hydrocarbons, acids and bases, whilst base-hydrolysis using a 0.1 M KOH-DMSO (2:1) mixture for 15 minutes was used to destroy the phthalates. The DMSO after cleanup was back-extracted using hexane. 50 mg p-chloranil used as the internal standard was then added. The mixture was evaporated under nitrogen in a 12 mm diameter  $\times$  25 mm height glass vial. 55 mg KBr powder and 2 glass balls were added prior to pulverization using the SPEX 3110 Wig-L-Bug laboratory mill. The powder obtained was pressed to form a 13 mm diameter pellet.

In the FTIR measurement, the area ratio of the absorbance peak observed between 3015 and 3090  $\text{cm}^{-1}$  and the absorbance peak of p-chloranil at 3360  $\text{cm}^{-1}$  was calculated. A mixture consisted of equal mass ratios of phenanthrene, anthracene, fluoranthrene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(a)pyrene and benzo(g,h,i)perylene was used as the standard for comparison with the sample spectrum to quantify the total PAHs.

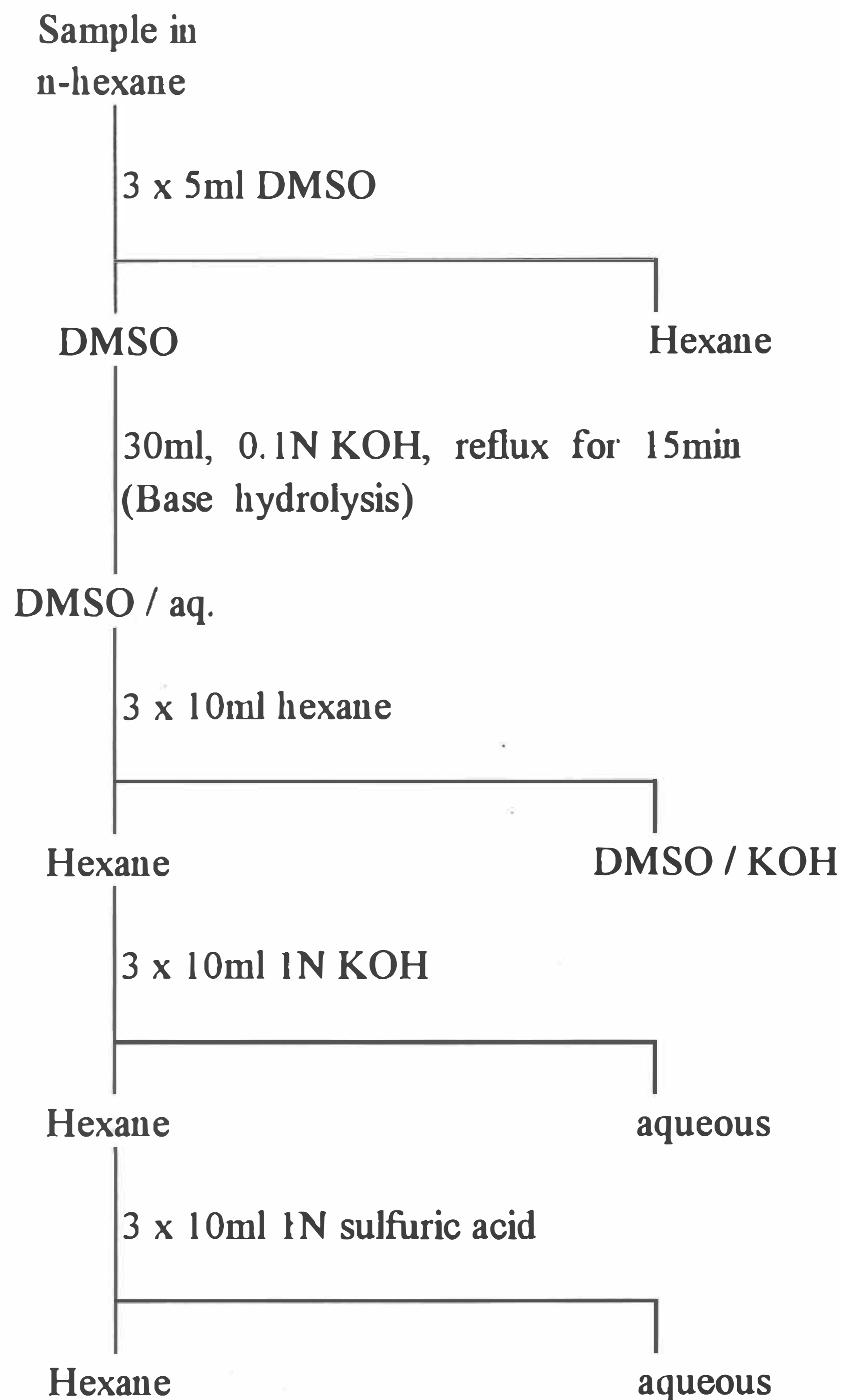


Fig. 1. General Extraction Scheme for the Isolation of PAHs after Soxhlet Extraction.

### 3. RESULTS AND DISCUSSION

#### 3.1 Inorganic Analysis Using DC Arc Emission Spectroscopy

A typical emission spectrum using the DC arc emission method for the analysis of trace metals in air particulates is given in Figure 2. The spectrum was obtained as the result of an integration of the output signal throughout the ignition period of one and a half minutes. The emission peaks are clearly well separated as shown in the UV region from 298.9 to 318.9 nm. Thus, most of the trace metals could be analyzed directly and simultaneously using a photodiode array detector covering the UV region in one frame with good resolution (1024 elements).

The reliability of the method was evaluated using SRM 1648 Urban Particulate Matters. The results obtained are shown in Table 1. This method was found to be able to cover a wide range of elements at concentrations normally present in air particulates for elements like Al, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Si and V. With the exception of metals like Pb and Mg, most other metals found in the SRM 1648 standard had recovery ratios lower than 40% when their peak heights were compared with those obtained using standards prepared from simple metal salts.

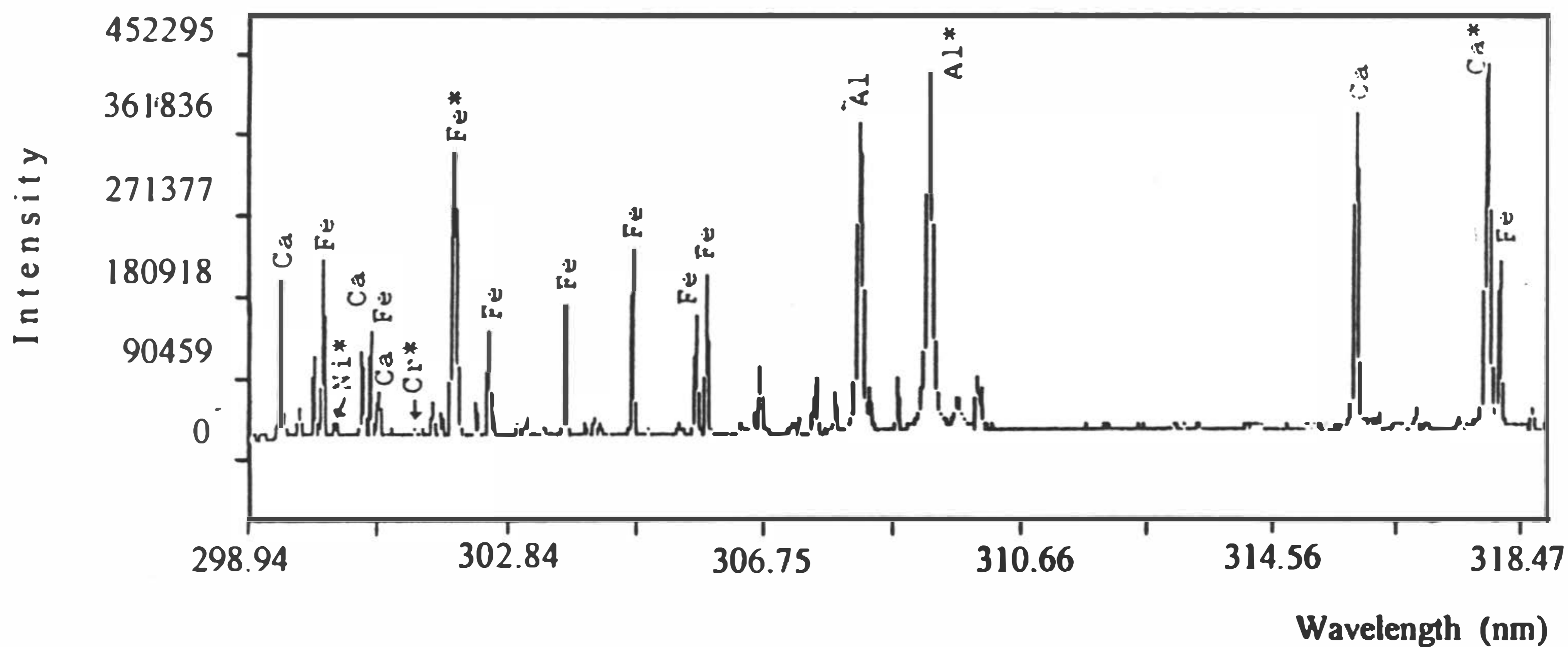


Fig. 2. A Typical Emission Spectrum of SRM 1648 Urban Particulate Matters.  
\* analytical peaks

Table 1. Comparison of the concentrations of elements found (using the simple chloride salts of the corresponding elements) in SRM 1648 urban particulate matters with the certified values.

Element	Concentration (ppm)		Ratio (%)
	Certified	Found	
Al	34,200	10,400	30.4
Ca	-	10,800	-
Cd	75	ND	-
Cr	403	ND	-
Cu	609	204	33.5
Fe	39,100	10,700	27.4
Mg	8,000	5,050	63.1
Mn	860	220	25.6
Ni	82	ND	-
Pb	6,550	4,900	74.8
Si	-	19,000	-
V	140	ND	-

The analytical signals were integrated for 90 sec. ND=not detected.

The cause of the rather low recovery was mainly due to the matrix effect of the air particulates. This could be shown clearly by comparing the emission profiles of Fe, Ca and Al upon heating using the urban particulates as compared with the simple chloride salts of the compounds (Figures 3 to 5). With the simple salts, Fe, Ca, and Al were vaporized quickly from the graphite electrode within a short time. This is because the metals were more volatile in the absence of particulate matrices. However, with the particulates sample, they came out slowly and showed two maxima within the experimental times. Volatile species came out at the beginning as in the case of simple salts, but the non-volatile ones could only be released when the crater temperature became much higher. Such a phenomenon indicated that the method was able to reflect the chemical environment of the trace metal. Since the same

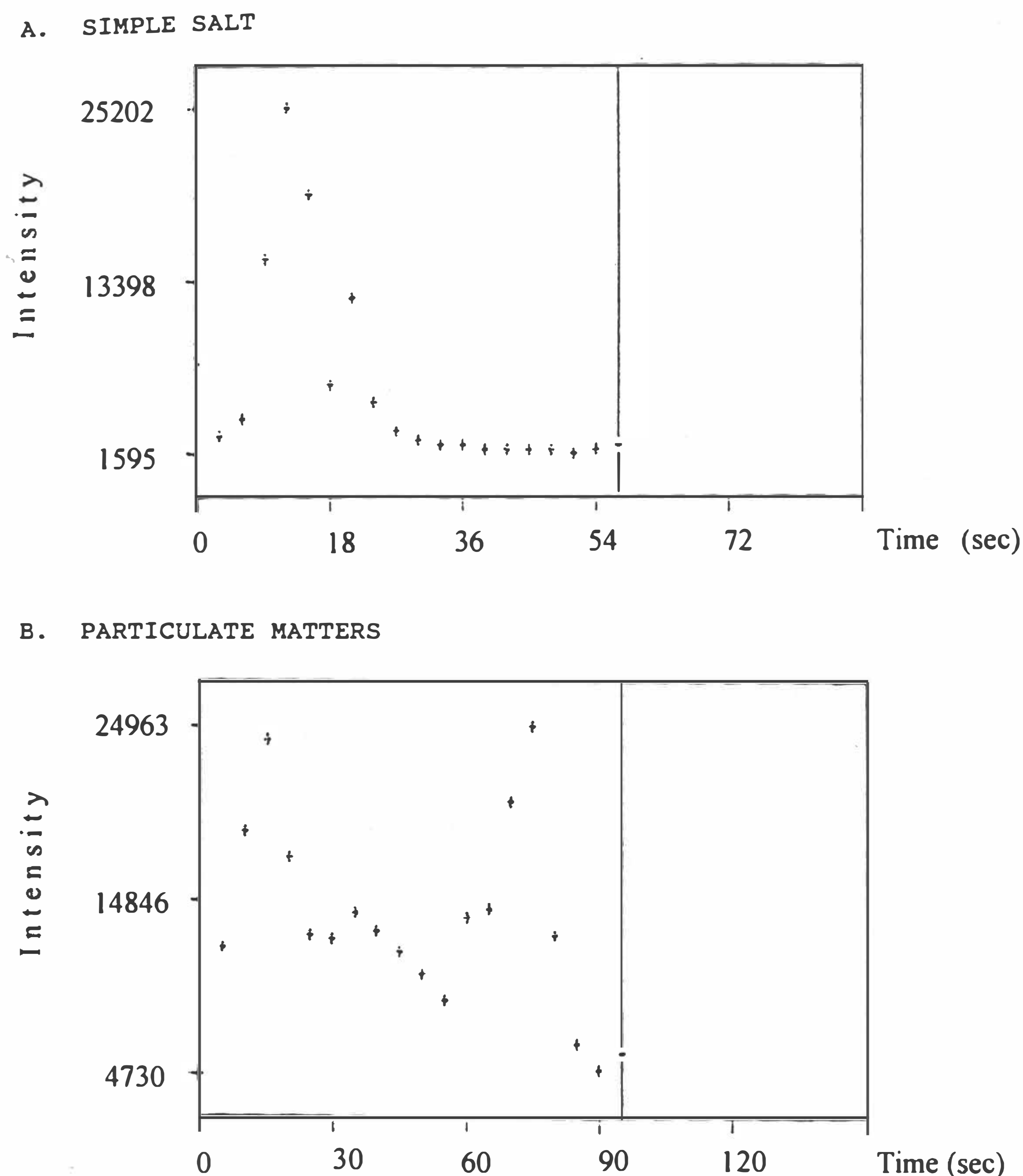


Fig. 3. Comparison of the Emission Time Profile for Iron using Simple Chloride Salt and Particulate Matrices. (A. Simple Salts, B. Particulate Matters)

element coming from different sources might have different volatilities, the use of DC arc analysis could provide information to indicate the source of the trace metal.

In general, the sensitivity of the method in terms of the quantity of sample used was shown to be much better than the AAS and ICP methods. Only a tiny fraction of the sample filter (1% of the sample weight for each determination) was used for the DC arc spectroscopic analysis whilst a quarter or half of the paper was often required for analysis after digestion using the AAS or ICP methods with comparable sensitivities for the three methods used.

The sensitivity and recovery could be enhanced using different thermochemical agents/chlorinating carriers in place of sodium chloride. The peak heights of the emission lines of Cr, Fe, Al, Ca, V and Sn were compared with those obtained when NaCl was used as the thermochemical agent. The results are given in Table 2. The addition of  $\text{Na}_2\text{CO}_3$  led to poorer sensitivity and recovery. However, the addition of  $\text{NH}_4\text{Cl}$  and  $\text{NaNO}_3$  gave rise to the improvement in both the sensitivity and recovery. The best results were obtained when a mixture of  $\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{NaNO}_3$  (1:1:1) was used for this gave the highest sensitivity and recovery for most of the elements tested. The improvement was due to the oxidizing power and the chlorinating carrier properties of the mixture which gave a more complete destruction of the sample matrices and impacted a higher volatility to the metal

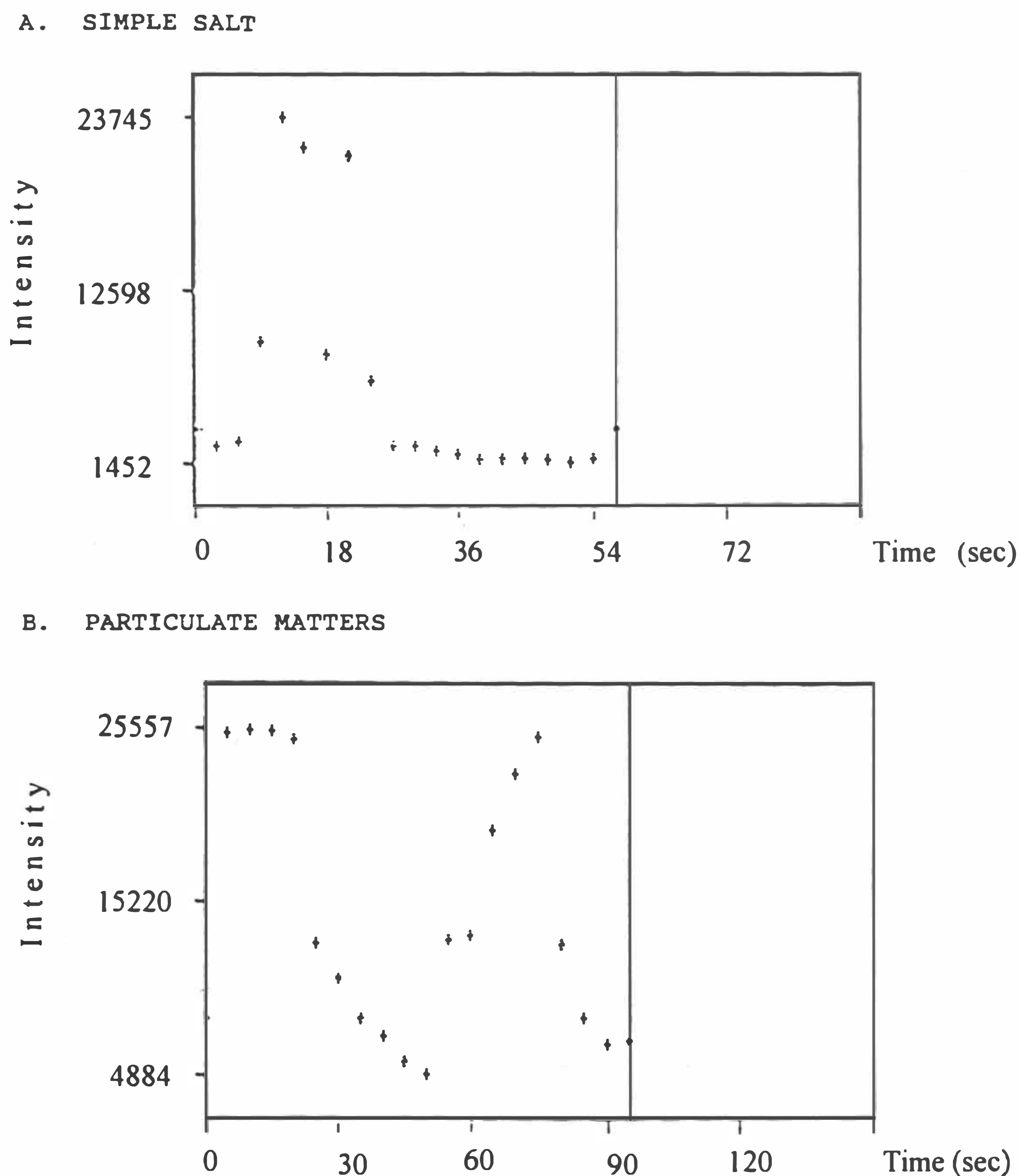
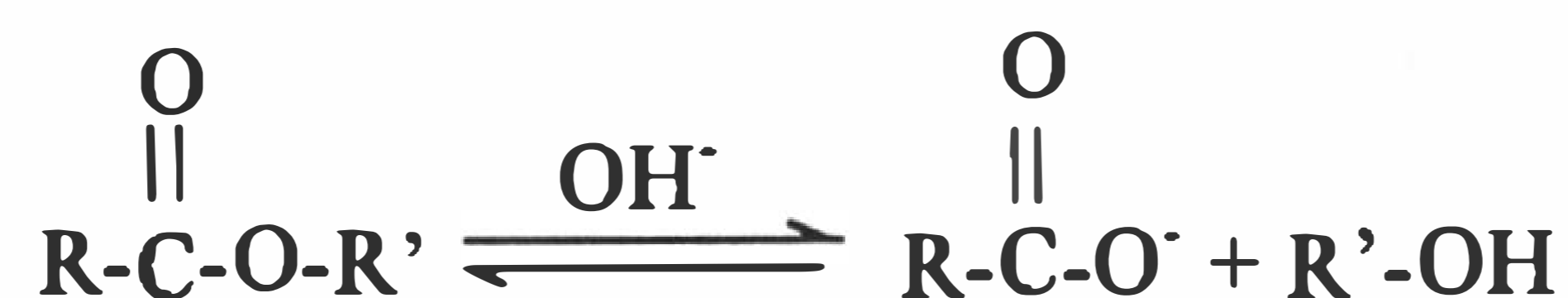


Fig. 4. Comparison of the Emission Time Profile for Iron using Simple Chloride Salt and Particulate Matrices. (A. Simple Salts, B. Particulate Matters)

element formed during heating. The recoveries of the metals investigated (Cr, Fe, Al, and V) using the certified air particulate matters were shown to increase to above 50% using  $\text{NaCl} + \text{Na}_2\text{CO}_3 + \text{NaNO}_3$  as the thermochemical agents.

### 3.2 Total PAHs Determination Using FTIR

The rather lengthy procedures, shown in Figure 1, deal with the removal of interfering compounds in the extract after Soxhlet extraction. According to the liquid-liquid extraction method, as developed by Natusch and Tomkins (1978), the DMSO could interact strongly with PAHs to separate them from the aliphatic hydrocarbons. However, in the complex extract of the particulate matters, phthalates and bases were also recovered together with PAHs. Phthalates, originating from industrial exhausts, gave positive interference at the aromatic C-H stretching region of the FTIR spectrum. Therefore, a hydrolysis procedure was developed to exclude phthalates from the final extract. Phthalates undergo base-catalyzed hydrolysis as shown on the following equation:



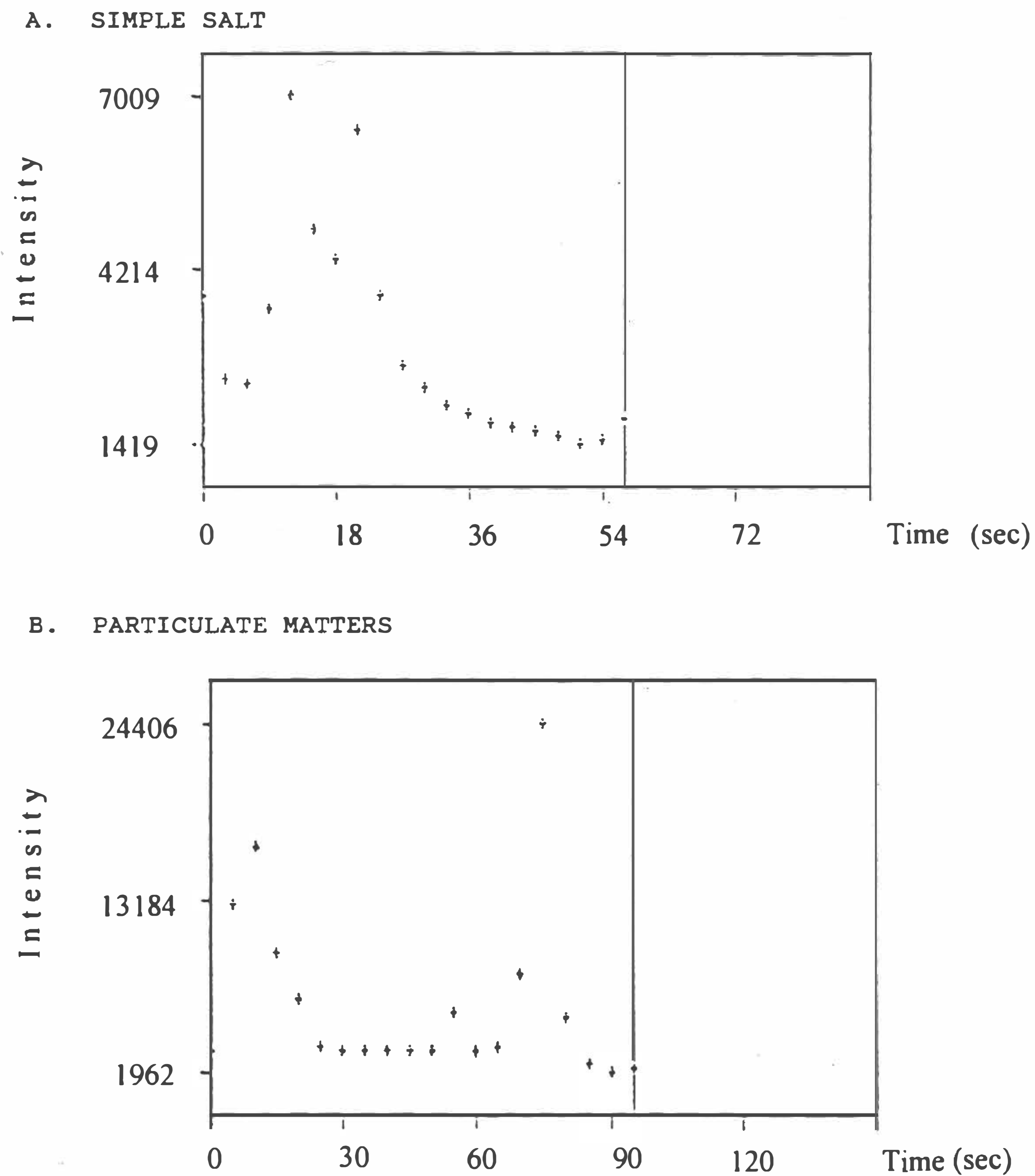


Fig. 5. Comparison of the Emission Time Profile for Calcium using Simple Chloride Salt and Particulate Matrices. (A. Simple Salts, B. Particulate Matters)

Table 2. Effect of thermochemical agents/chlorinating carriers on the peak height and the corresponding percentage recovery of metals from SRM 1648 urban particulates.

Element	NaCl		NaCl Na <sub>2</sub> CO <sub>3</sub>		NaCl Na <sub>2</sub> CO <sub>3</sub> NH <sub>4</sub> Cl		NaCl NaNO <sub>3</sub>		NaCl Na <sub>2</sub> CO <sub>3</sub> NaNO <sub>3</sub>	
	Rel. peak ht.	Rec. (%)	Rel. peak ht.	Rec. (%)	Rel. peak ht.	Rec. (%)	Rel. peak ht.	Rec. (%)	Rel. peak ht.	Rec. (%)
Cr	1.00	ND	0.30	ND	1.34	ND	2.45	45.0	4.33	62.0
Fe	1.00	27.4	0.07	2.7	1.06	29.0	1.88	47.0	2.46	57.6
Al	1.00	30.4	0.14	5.8	1.87	51.9	2.74	68.8	3.19	75.7
Ca	1.00	-	0.09	-	1.48	-	2.18	-	2.63	-
V	1.00	ND	0.00	ND	0.83	ND	1.72	38.9	2.80	56.0
Sn	1.00	-	0.12	-	0.91	-	0.57	-	1.12	-

\* The peak height using NaCl was taken as 1. Samples containing 0.60 mg of SRM 1648 urban particulates were tested. Rel. peak ht.=relative peak height. Rec.(%)=Percentage recovery. ND=not detected.



To study potential interferents, standard solutions containing different functional groups of organic compounds in hexane were prepared. Hydrolysis using conditions as shown in Table 3 was performed on the standard solutions. The concentrations of the base used and the hydrolysis time were optimized. The use of 0.1 N KOH as the base and a hydrolysis time of 15 minutes were capable of removing phthalates and retaining PAHs. The recovery of PAHs was reduced by either increasing the hydrolysis time to 50 minutes or increasing the concentration of KOH to 1 N. By following the DMSO-hexane liquid-liquid extraction procedure, and coupling with the optimized base-hydrolysis conditions, the final concentration of each analyte was monitored using capillary gas chromatography. The recovery of phenanthrene and pyrene were shown to be higher than 90%.

Table 3. Comparison of the percentage recoveries of different groups of compounds under different base-hydrolysis conditions in the DMSO-hexane liquid-liquid extraction procedure.

	Just boiled			15min hydrolysis			50min hydrolysis		
	0.01N	0.1N	1.0N	0.01N	0.1N	1.0N	0.01N	0.1N	1.0N
4-Chloro-N-methylaniline	4	4.9	3.8	1.3	0	0	0	0	0
2-Methyl naphthalene	70	90	52	49	29	44	50	35	31
Dibenzothiothene	94	99	78	88	98	72	76	56	64
5,6-Benzoquinoline	0	0	0	0	0	0	0	0	0
1-Naphthyl amine	0	0	0	0	0	0	0	0	0
Alpha-naphthol	5	3.6	2.2	2	2	0.8	0	1	0
10-Methylanthracene-9-carboxaldehyde	71	41	13	66	34	11	49	5	1.5
Naphthyl benzoate	0	0	0	0	0	0	0	0	0
Dibutyl phthalate	36	0.4	0	2.5	0	0	0	0	0
Diethyl phthalate	16	33	12	15	0	0	2.4	0	0
Phenanthrene	96	99	78	95	97	75	77	62	67
Pyrene	97	99	73	97	92	73	80	84	79

[KOH]: 0.01N to 1N, hydrolysis time: 0 to 50 minutes.

The applicability of the method in the field monitoring of total PAHs was studied in a selected residential area in Hong Kong. Over a weekly cycle, sampling was performed, and the results are shown in Table 4. The average concentration was found to be fairly constant over the period of study. The concentrations detected on the weekend and Sunday did not differ very much when compared to those obtained on weekdays. The above results agree well with the pattern of traffic observed at the sampling site.

#### 4. CONCLUSION

An analytical procedure was developed in the present work using a DC arc diode array spectrometer for trace inorganic analysis and FTIR for the determination of total PAHs in urban particulates. The DC arc method was shown to provide a rapid means for the elemental analysis of particulate matters due to the simple sample preparation required prior

Table 4. The variation of concentrations of total PAHs sampled at a road-side station over a one-week cycle in a residential area in Hong Kong.

Date (1993)	Total PAH (ug)	Avg. conc. (ug/m <sup>3</sup> )
July 8(Thu)	252	0.195
9(Fri)	172	0.142
10(Sat)	157	0.128
11(Sun)	207	0.185
12(Mon)	165	0.154
13(Tue)	159	0.135
14(Wed)	202	0.166

to determination. As a result of this, any contamination problems due to the acid used or the long digestion time could be eliminated. The sensitivity of the method was found to be high and only a tiny fraction of the homogenized sample was used for the determination (about 1% of the sample from the 8" × 10" filter used for each determination). Thus, the same sample could be used for parallel method determination or for analysis of other parameters. The method for the determination of total PAHs was developed using an FTIR procedure which gave a more reliable result due to the constancy of the IR signal for different PAHs. Optimized solvent extraction procedures were given, and the method was shown to give satisfactory results in the field study at a residential area in Hong Kong over a weekly cycle.

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