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Sampling and determination of carbonyls in stack gas

Dai Tian-you, Wang Qin-hui*, Wei Fu-sheng

China National Environmental Monitoring Center, Beijing 100029, China

Tan Pei-gong, Liu Jin

Qingdao Environmental Monitoring Center, Qingdao 266003, China

Abstract—The GC determination of aldehydes and ketones in stack gas was reported. The stack gas was collected with the dust sampler by isokinetic sampling technique, 2, 4-dinitrophenylhydrazine in acidic solution was used to absorb aldehydes and ketones in stack gas specifically, to form their hydrazones, which were determined by GC with a capillary column of SE-54. The GC system can separate nine hydrazones of carbonyls interested with constant recovery rates of 94%—97%, giving lowest detectable limits of 0.05—1.0 ng. The standard gas of carbonyls were determined by this method with relative errors of −5% to −10%, percent coefficients of variation within 5%, and spiking recovery rates of 93%—97%. As an application of the method, the carbonyl pollutants were determined in stack gas samples of a chemical plant.

Keywords: aldehyde, ketone, 2, 4-dinitrophenylhydrazine absorption solution, stack gas, gas chromatography.

Some aldehydes and ketones are toxic and carcinogenic. To the pollution of aldehydes and ketones, a great attention has been paid all over the world. There are nine aldehydes and ketones listed in Tittle III of the New Clean Air Act Amendments of 1990 (SSESA Translating & Editing Committee, 1993). As such, it is necessary to study the collection and analysis of aldehydes and ketones in air and stack gas.

Up to now, there has not been a report about the determination for aldehydes and ketones in stack gas. Aldehydes and ketones can be absorbed by 2, 4-dinitrophenylhydrazine(2, 4-DNPH) in acidic medium quantitatively to form hydrazone derivatives. This reaction is highly specific(Katz, 1977; Kallio, 1977; Frachio; 1967; Sonkup, 1964; Fedeli, 1964). This study developed a technique for sampling and determination of aldehydes and ketones in stack gas. Aldehydes and ketones in stack gas are collected by isokinetic sampling method and absorbed with an acidic 2, 4-DNPH solution. The hydrazone derivatives formed are extracted qualitatively with carbon disulfide, and then analyzed by GC. This paper has studied sampling, hydrazones' recovery and GC conditions and so on, as illustrated by the application to analysis of stack gas in a chemical plant.

1 Experimental

1.1 Chemicals

Formaldehyde (36%—38% water solution), acetaldehyde (40% water solution), acrolein, butyraldehyde, valeraldehyde, benzaldehyde, acetone, butanone, acetophenone and 2, 4-dinitrophenylhydrazine are analytical reagent grade. Carbon disulfide(AR) should be distilled just before use.

* Present address: The First Hospital of Fangshan District, Beijing 102400, China

1.2 Sampling of stack gas

Isokinetic and non-isokinetic sampling technique are performed during the test. Gas sample is extracted from the cylindrical vent through a glass nozzle probe system. The sample gas stream is passed through a four-bottle impinger train. Following the impingers, the gas is directed through a sample pump, a dry gas meter and an orifice differential pressure meter.

Aldehydes and ketones in stack gas are absorbed by an aqueous acidic 2, 4-DNPH solution to form the hydrazone derivatives.

1.2.1 Absorption solution preparation

The DNPH absorption solution should be prepared and purified within 2 days of sampling. 2500 ml 2,4-DNPH saturated solution in 1 mol/L H_2SO_4 is prepared under ultrasonic wave. The NDPH solution is extracted twice with 1/10(v/v) CS_2. The clear DNPH solution is defined into amber bottles, which are tightly capped, and shipped to the test location.

1.2.2 Sampling train

Anderson Company's dust sampler is employed as the sampling device with four 1000 ml impingers connected in series as shown in Fig. 1. The first impinger contains 300 ml absorption solution, the second 100 ml, and the third is empty. Before the test run, Pitot tubes, nozzles, thermocouples, and dry gas meters are all calibrated and checked for leaking. The sampling flow rate, the nozzle size and sampling time *etc*. are chosen according to the preliminary determination of the vent and stack gas.

1.2.3 Testing field

In this paper, Qingdao Organic Chemical Plant was selected as a testing field spot. The

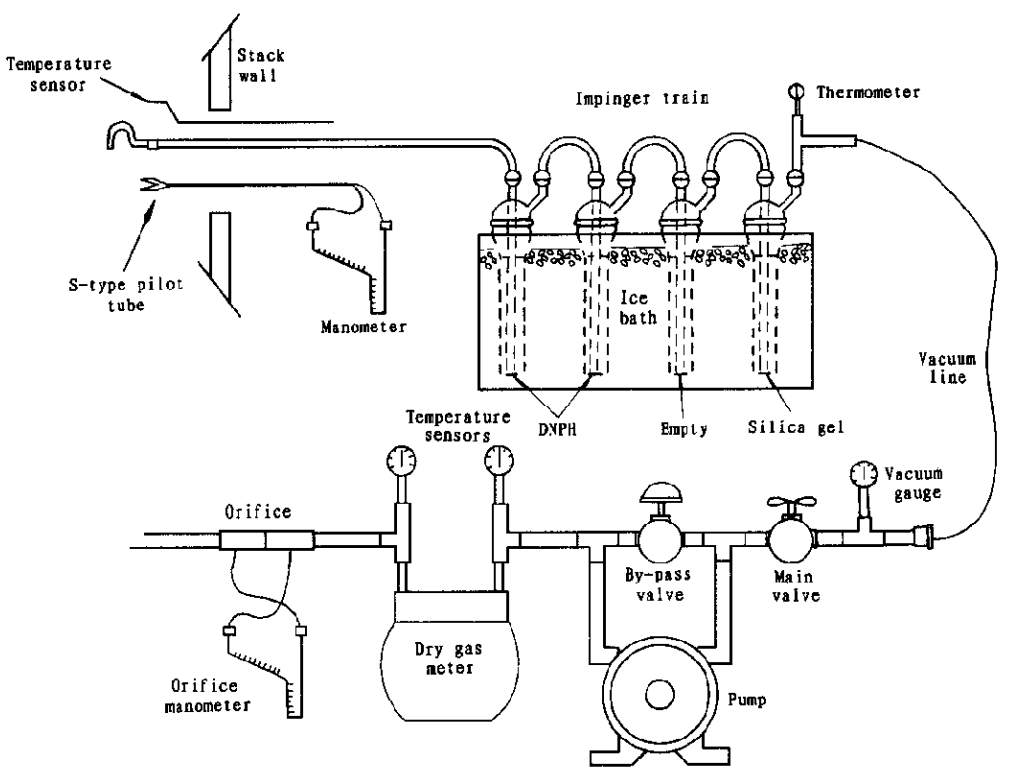

Fig. 1 Sampling train for aldehydes and ketones

formaldehyde workshop in this plant makes formaldehyde with methanol. The gaseous formaldehyde is absorbed by water to form water solution known as "Formalin", which is the final product. The stack gas of the absorption tower of formaldehyde workshop (containing nitrogen, hydrogen, carbon monoxide formaldehyde, water *etc*.) is discharged into a boiler through a cylindrical vent and then burned for making steam. So, hydrogen, carbon monoxide, formaldehyde, *etc*. are recovered as a combustible gas.

1.3 Sample recovery

The content of the first impinger and washing of the probe and its liner and the nozzle are collected in container 1; the content of the second impinger is collected in container 2; the content of the third impinger is collected in container 3. After the test run, the content of the impinger is moved to the container(recovery trailer) as soon as possible. The impinger is rinsed with a small portion of distilled water and CS_2, the washings are added to the corresponding container. Pilot tube and its liner, nozzles are rinsed with distilled water and CS_2, the washings are collected in container 1(the content of each container are analyzed separately to check for collection efficiency of each impinger).

The container is labeled, capped tightly and shipped to the laboratory.

The samples are stored in refrigerator of the laboratory to prevent decomposition of derivatives. Samples should be extracted within 12 days of collection and analyzed within 30 days of extraction(Dai, 1996).

1.4 Extraction

The contents of the container is transferred quantitatively to a 1000 ml separatory funnel and extracted twice with 1/10 (v/v) CS_2. The separatory funnel should be shaken for at least 3 minutes. The CS_2 extracts are added to a volumetric flask (100 ml or other appropriate size depending on the amount of CS_2 used in field recovery and extraction). The volumetric flask is filled to the line with CS_2 for analysis by GC.

1.5 Chromatographic analysis

1.5.1 Standard preparation

The standard gas of aldehydes or ketones are prepared by evaporating them into N_2 gas in an aluminum coated bag(made in China), which should be prepared just before use.

Multi-component stock carbonyl hydrazone derivative standards are prepared at concentration standard of 200 mg/L in CS_2. Two stock solutions are required, one as the calibration, standard, and the other one as the check standard. Calibration standards at hydrazones' concentrations of 10—100 mg/L are prepared. A check standard at hydrazone's concentration of 20 mg/L is prepared with another stock solution. The check standard is used to check the instrument response and the calibration curve.

1.5.2 GC system

The working parameters of the GC system for analysis of standards and samples are as follows. Instrument, PE9000 auto-system GC (made in USA); column, SE-54 capillary column, L25m, ID 0.32 mm; detector, electron capture detector, temperature, 375℃; column temperature, 220℃, stable; injection temperature, 270℃; N_2, 40 ml/min; split, 1:50; injection volume, 1μl.

1.5.3 Instrument calibration

Calibration standards are prepared at 5 levels as described above. Each calibration standard is injected in duplicate. After an initial calibration curve is obtained, the calibration check standard

should be analyzed. If the response of the check standard is within 10% of the target value, it should be injected periodically throughout the analysis of samples(i. e. after every 6—8 samples) and used for daily calibration . Otherwise, a new check standard should be prepared or the instrument recalibrated.

1.5.4 Sample analysis

Samples are identified by retention time and determined by calibration curve method. The width of the retention time window used for identification is based on the variations in retention time. If identification is questionable, GC/MS will be used as an additional qualitative technique to confirm compound identifications. The sample should be analyzed in triplicate on the GC. A CS_2 blank is analyzed at least once a day to ensure that the system is not contaminated. As stated above, a check standard should be analyzed prior to sample analysis. Some samples need to be diluted to make their concentrations within the calibration range.

2 Results and discussion

2.1 GC separation of hydrozones

Under the experiment conditions described above, excellent and rapid separations have been achieved for a variety of carbonyl hydrazone compounds. An example of the chromatographic separation of a mixture of hydrazones derived from some standard interested carbonyls is given in Fig. 2, while the corresponding retention time valucs arc listed in Table 1.

Table 1 Retention times and detection limits of carbonyl-DNPHs in SE-54 capillary column

Compounds	Retention time, min	Lowest quantifiable limit, ng
Formaldehyde-DNPH	6.41	0.05
Acetaldehyde-DNPH	8.47	0.05
Acrolein-DNPH	10.10	0.05
Acetone-DNPH	10.40	0.10
Butanone-DNPH	12.65	0.10
Butyraldehyde DNPH	13.21	0.10
Valeraldehyde-DNPH	15.87	0.10
Benzaldehyde-DNPH	18.02	1.0
Acetophenone-DNPH	28.04	1.0

As shown in Fig. 2, the separation of acrolein/acetone, butyraldehyde/methyl ethyl ketone, which are difficult to separate by a packed column(Sonkup, 1964), are well resolved in our system.

2.2 Quantitative analysis

Each calibration curve is made with 5 points of different concentraitons at least and fitted by the linear regression. The correlation coefficients for all calibration curves arc better than 0.998 (Table 2).

2.3 Detection limit

The lowest quantifiable limits (LQL) have been determined for 1 μl aliquots of calibration mixture samples by using a peak height integrator with a signal-to-noise ratio of 3. These LQLs are listed in Table 1.

2.4 Recovery of hydrazones

The recovery rate for extraction of hydrazones by CS_2 are determined by analysis with GC of known amounts of the calibration solution of hydrazones which is added to the absorption solution (200 ml). The results indicated that the recovery rates of 95%—97% for five hydrazones studied (Table 3).

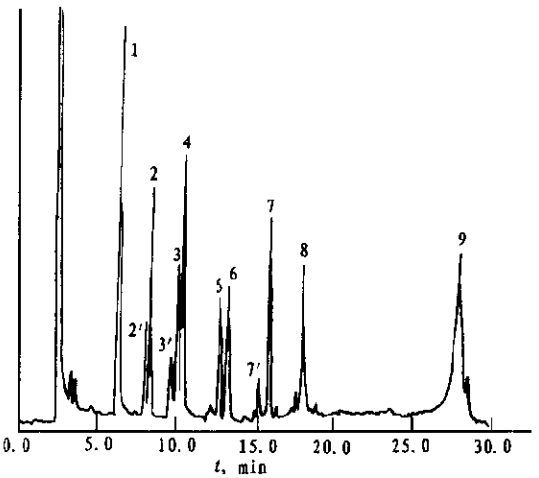

Fig. 2 GC separation of 2,4-dinitrophenylhydrazones of selected carbonyls in SE-54 column
1. Formal-DNPH; 2. acetaldehyde-DNPH; 3. acrolein-DNPH;
4. acetone-DNPH; 5. butanone-DNPH; 6. butyra ldehyde-DNPH;
7. *n*-valeraldehyde-DNPH; 8. benzaldehyde-DNPH; 9. acetophenone-DNPH

Table 2 The calibration curves of carbonyl-DNPHs

Compounds	Concentration, mg/L							Linear range, mg/L	Correlation coefficient
Formaldehyde-DNPH	0.83	4.15	8.3	16.6	33.2	83.0	116.2	0.83—116.2	0.9990
Acetaldehyde-DNPH	1.26	6.3	12.6	25.2	37.8	63.0	100.8	1.26—100.8	0.9995
Acrolein-DNPH	2.42	12.1	24.2	48.4	72.6	121.0	242.0	2.42—242	0.9990
Acetone-DNPH	1.72	8.6	17.2	34.4	51.6	86.0	137.6	1.72—137.6	0.9998
Butanone-DNPH	2.65	13.25	26.5	53.0	79.5	132.3	265.0	2.65—265	0.9990
Butyraldehyde-DNPH	2.26	11.3	22.6	45.2	67.8	113.0	226.0	2.26—226	0.9990
Valeraldehyde-DNPH	2.50	12.5	25.0	50.0	75.0	125.0	250.0	2.50—250	0.998
Acetophenone-DNPH	4.58	22.9	45.8	91.6	137.4	229	458	4.58—458	0.998

Table 3 Recovery rates of selected carbonyl-DNPHs by extraction with CS_2

Compounds	Test 1		Test2		Test 3	
	Concn., μg	Recovery rate, %	Concn., μg	Recovery rate, %	Concn., μg	Recovery rate, %
Formaldehyde-DNPH	200	97.5	1000	97.2	2000	98.0
Acetaldehyde-DNPH	180	96.2	900	95.8	1800	95.4
Acetone-DNPH	210	94.6	1050	93.8	2100	95.0
Butyraldehyde-DNPH	218	88.2	1090	87.0	2180	90.2
Butanone-DNPH	215	90.2	1075	89.6	2150	88.7

2.5 Reproducibility

In our experiment conditions, absolute retention times are reproducible within 2%. Reproducibility is also determined for quantitative analysis of calibration mixture and standard gas samples generated in the laboratory. Five replicate injections of calibration mixtures, respectively, yield RSDs of 2.4% for formaldehyde, 1.8% for acetaldehyde, 0.6% for acetone, and 2.0% for butanone. Good overall reproducibility (GC methods and sampling method) are also achieved for standard gas samples generated in the laboratory, five replicate analysis of these samples indicate

RSDs (or CVs) within 5% (Table 4).

Table 4 Results of replicate analysis for standard gas samples generated in the laboratory

Compounds	Concn. in standard gas, mg/m³	Analytical result, mg/m³					Mean	CV, %
Formaldehyde	70.0	64.84	67.67	65.70	68.25	65.35	66.36	2.3
	14.0	13.64	13.52	12.96	12.82	12.20	13.03	4.5
Acetaldehyde	80.0	73.50	76.80	75.44	76.80	75.62	75.99	2.5
Acetone	20.0	18.4	17.92	18.82	17.56	19.21	18.38	3.6
	20.0	17.69	18.60	19.24	18.81	17.80	18.43	3.6
	4.0	3.85	3.65	3.94	3.76	3.58	3.76	3.9
Butyraldehyde	15.0	14.46	15.20	14.30	13.96	13.14	14.21	5.3

2.6 Spike analysis

The spiking recovery for a given aldehyde or ketone is determined by the analysis with GC of known amounts of standard gas samples absorbed by the absorption solution to which a known quantity of the calibration solution of a hydrazone to be studied has been previously added. All standard gas samples are prepared in this laboratory. The spiking recovery rates (Rs) reported here are calculated as follows:

$$Rs = (C^* - C)/As \times 100\%,$$

where, $C(\mu g)$ is the concentration of the hydrazone in 100 ml absorption solution by which the standard gas of the carbonyl is added; $C^*(\mu g)$ is the concentration of the hydrazone in 100 ml absorption solution above to which the same hydrazone as a spiking standard is subjected additionally; $As(\mu g)$ means spiking amounts of the hydrazone.

The results yield relative errors of -5.0% to -8.0% and spiking recovery rates of 93%—97% for four carbonyls interested (Table 5).

Table 5 Spiking recovery rates of carbonyls for standard gas samples generated in the laboratory

Compounds	Concn. in standard gas, mg/m³	Hydrazone concn. result in absorbing solution, μg	Carbonyl concn. result in gas sample, mg/m³	Relative error, %	Spiking amount of hydrazone. μg	Spiking recovery, %
Formaldehyde	70.0	63.04	66.36	-5.2	60.0	97.1
	14.0	12.39	13.03	-6.9	10.0	96.2
Acetaldehyde	80.0	72.19	75.99	-5.0	70.0	95.6
	20.0	17.46	18.38	-8.1	15.0	94.6
Acetone	20.0	17.51	18.43	-7.8	15.0	93.6
	4.0	3.57	3.76	-6.0	4.0	95.4
Butyraldehyde	15.0	13.49	14.21	-5.3	15.0	940.2

2.7 Blanks

Laboratory method blanks: after DNPH preparation is completed, an aliquot of the solution is set in the laboratory. The DNPH solution is extracted twice with 1/10 CS_2, the extracts is injected into the GC system for analysis. The results indicated the lowest blank concentration of formaldehyde and acetone in the absorption solution to be 40 μg/L and 20 μg/L, respectively (other carbonyls are not detected).

Field blanks: at least one set of field blanks should be prepared. A sampling train is assembled in the staging area, and then taken to the sampling location. Its leakage is checked before and after the sampling. The sampling train is recovered in the same manner previously described. Two field

blank containers are used to the blank sample, each containing aliquots of sample recovery solvents (CS_2 and water) and unused DNPH absorption solution. The results of field blanks in Qingdao Organic Chemical Plant indicated 285 μg formaldehyde, 335 μg acetone in container 2 (containing 100 ml absorption solution) and 855 μg formaldehyde, 1000 μg acetone in container 1 (containing 300 ml absorption solution). While calculating the concentration of component in stack gas, field blank values should be eliminated.

2.8 Carbonyl sample's preservation in the aluminum-coated bag

The carbonyl sample's preservation study is performed with standard gas samples of carbonyls prepared in the aluminum-coated bag (made in China) with humidity of 50% at 20℃. The standard gas sample have preserved at 20℃ for definite hours and then is collected in 2, 4-DNPH solution. The carbonyl's initial concentration of the standard gas sample is determined by the same methods, while standard sample is collected from the bag instantly after preparation.

The recovery rate of the carbonyl compound is used to evaluate the stability of the carbonyl compound in the bag. The recovery rate (η_i) reported here is defined as the ratio of the carbonyl concentration of the standard sample collected in i hours of preservation(C_i) to that of the same compound in standard gas absorbed in 2, 4-DNPH solution instantly after preparation from the bag (C_o).

$$\eta_i = (C_i / C_o) \times 100\%.$$

The results (Table 6) indicated that under normal air humidity (ca. 50%) the carbonyl compounds can be preserved without attenuation for a limited period, i. e. 24 hours for formaldehyde and acetaldehyde, and 48 hours for acetone(Table 6).

Table 6 The stability of carbonyls in aluminum-coated bags

Compounds	Concentration of the standard gas sample (C_o), mg/m³	Recovery rate(η_i), %			
		24 h	48 h	96 h	144 h
Formaldehyde	11.73	97.5	83.4	48.7	22.8
Acetaldehyde	7.21	97.6	86.7	71.3	39.5
Acetone	14.8	98.9	101.4	80.9	58.9

2.9 Study of sampling method for stack gas

In this paper, the stack gas sample was absorbed in 2, 4-DNPH solution in the field test site with the Anderson Company's dust sampler by isokinetic sampling method. In order to make a comparison, aluminium-coated bags are also used for collection of the carbonyl samples. Before sampling, the bag should be washed with stack gas for several times. A pump was used to conduct the stack gas into the bag. After sampling, the bags were shipped to the laboratory as soon as possible.

Samples in the bag are absorbed in the 2, 4-DNPH solution and recovered in 12 hours and 24 hours of sampling, while recovery rates (η_i) of carbonyls interested are calculated as follows:

$$\eta_i = (C_i / C_0) \times 100\%,$$

where, C_i is the concentration of the carbonyl in the sample recovered in i hours of sampling; C_o is that of the same carbonyl in the sample collected by field absorption with 2, 4-DNPH solution at the same time.

The results indicated an obvious carbonyl's attenuation. Our laboratory has noticed that the stack gas in this plant contains large amounts of water, which was determined as 1.5% (V/V). It is possible that water make an important role in attenuation of carbonyls in bag samples(Table 7).

The results above indicated that a careful investigation for the field site must be done before

collection with the sampling bag.

2.10 Collection efficiency study

Since the present study used three serial impingers and determined three carbonyl compounds existing in the flue gas samples collected in Qingdao Organic Chemical Plant, the collection efficiency of each impinger for different carbonyls are examined. Collection efficiencies(η_i) reported (Table 8) are defined as the ratio of the carbonyl concentration of the impinger (C_i) to the sum concentration of all three impingers measured by GC:

$$\eta_i = [C_i/(C_1 + C_2 + C_3)] \times 100\%, \quad (i = 1, 2, 3).$$

Results of this study indicated good collection efficiencies of $\geqslant$ 98% for formaldehyde, $\geqslant$ 93% for acetaldehyde, and 100% for acetone to the first two impingers.

Table 7 The concentration of the carbonyl in stack gas determined by GC(mg/m³)

Compounds	Aluminum-coated bag sampling, recovery after		Field direct absorption collection
	12 h	24 h	
Formaldehyde	296	186.7	356
	285	190.6	351
	294	189.5	371
Acetaldehyde	493	303.1	580
	485	312.0	578
	489	300.5	590
Acetone	12.6		21.5

2.11 Stack gas sample analysis

Under the chromatographic conditions described in section 1.5.2, the stack gas samples collected from the formaldehyde workshop of Qingdao Organic Chemical Plant are determined. A typical chromatogram is shown in Fig. 2, and the results for carbonyls of the stack gas are shown in Table 8. The results indicated that there is a considerable amount of formaldehyde, acetaldehyde and acetone in the stack gas of this plant.

Table 8 The analytical results of carbonyls in stack gas of the formaldehyde workshop in Qingdao Organic Chemical Plant

Compounds		Hydrazone weight in each impinger, mg				Collection efficiency* (η), %	Volue of sample (standard), L	Carbonyl concn. in stack gas, mg/m³	Volue percent, %
		1	2	3	total				
Formaldehyde	I	35.569	0.501	0.101	36.171	99.7	13.0	397.5	0.0297
	II	52.090	1.130	0.120	53.35	99.7	23.1	329.9	0.0246
	III	35.937	0.509	0.072	36.518	99.8	13.3	392.2	0.0293
	IV	34.152	0.261	0.05	34.463	99.8	13.0	378.7	0.0283
	Mean					99.75		374.6	0.0279
Acetaldehyde	I	33.804	2.386	1.805	37.995	95.2	13.0	574.1	0.0292
	II	50.223	3.720	2.040	55.983	96.3	23.1	476.0	0.0242
	III	34.146	2.140	1.650	37.936	95.6	13.3	560.3	0.0285
	IV	43.642	1.944	1.760	47.346	96.3	13.0	715.3	0.0364
	Mean					95.8		581.4	0.0296
Acetone	I	1.580	No	No	1.580	100	13.0	29.6	0.0011
	II	1.606	No	No	1.606	100	13.3	19.4	0.00075
	III	1.78	No	No	1.178	100	13.0	22.1	0.00085
	Mean					100		23.7	0.00091

Note: * is the collection efficiency for the first two impinger, $\eta = (C_1 + C_2)/(C_1 + C_2 + C_3) \times 100\%$

3 Conclusion

The GC system equipped with SE-54 capillary column and the sampling of carbonyls by the absorption with an acidic 2, 4-DNPH solution to form their hydrazone derivatives are proposed as a method for determination of carbonyls in stack gas. Since the column as a strong ability to separate the carbonyl hydrazones, this method should be suitable for the separation of carbonyl hydrazone compounds isolated from samples of stack gas, as illustrated by the application to analysis of stack gas in the chemical plant.

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