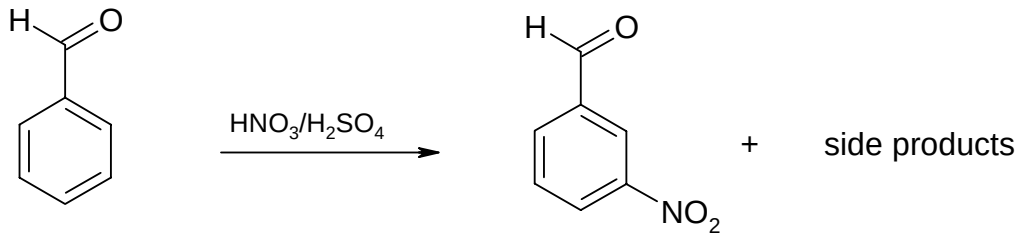
1003 Nitration of benzaldehyde to 3-nitrobenzaldehyde



C_7H_6O (106.1)	HNO_3 (63.0) H_2SO_4 (98.1)	$C_7H_5NO_3$ (151.1)

Classification

Reaction types and substance classes

electrophilic substitution of aromatics, nitration of aromatics
aromatics, nitroaromatics, aldehyde

Work methods

stirring with magnetic stir bar, extracting, shaking out, recrystallizing, filtering, use of an ice cooling bath

Instruction (batch scale 100 mmol)

Equipment

500 mL three-neck flask, 1 L beaker, internal thermometer, addition funnel with pressure balance, magnetic stirrer, magnetic stir bar, rotary evaporator, separating funnel, suction flask, Buechner funnel, ice bath

Substances

benzaldehyde (freshly distilled) (bp 179 °C)	10.6 g (10.1 mL, 100 mmol)
H_2SO_4 (conc.)	90 mL (1.7 mol)
HNO_3 (fuming)	45 mL (0.95 mol)
tert-butyl methyl ether (bp 55 °C)	125 mL
aqueous $NaHCO_3$ solution (5%)	125 mL
sodium sulfate for drying	about 5 g
toluene (bp 111 °C)	
petroleum ether (bp 60-80 °C)	

Reaction

89 mL (1.7 mol) concentrated H_2SO_4 are filled in a 500 mL three-neck flask equipped with an internal thermometer and an addition funnel with pressure balance. Whilst cooling with an ice bath 45 mL (0.95 mol) fuming HNO_3 are added carefully under stirring, the temperature

must not exceed 10 °C. To this nitrating acid, 10.6 g (10.2 mL, 100 mmol) benzaldehyde are added under further cooling so that the temperature can be constantly kept at 15 °C (about 1 hour). The ice bath is removed and the reaction mixture is stored over night at room temperature.

Work up

The reaction mixture is poured in a 1 L beaker on 500 g crunched ice, the yellow precipitation is sucked off at 16 hPa over a Buechner funnel and washed with 200 mL of cold water. Crude yield (humid): 14.4 g

The humid crude product is dissolved in 125 mL *tert*-butyl methyl ether and then shaken out with 125 mL of a 5% $NaHCO_3$ solution. The organic phase is dried over sodium sulfate, filtered and the solvent evaporated at a rotary evaporator. The residue is recrystallized from toluene / petroleumether (60-80 °C) by dissolving it in toluene whilst heating and then adding the double amount of petroleum ether in portions under ice cooling. The crystalllized light yellow **3-nitrobenzaldehyde** is sucked off over a Buechner funnel. The product is dried over silica gel in an evacuated desiccator.
Yield: 8.0 g (53 mmol, 53%); mp 56 °C

Comments

In the experiments Number 2003 and 5004 the product is used as educt.

Waste management

Recycling

The evaporated *tert*-butyl methyl ether is collected and redistilled.

Waste Disposal

Waste	Disposal
aqueous filtrate from crude product	solvent water mixtures, halogen free
aqueous phase from shaking out	solvent water mixtures, halogen free
petroleumether toluene mixture (mother liquor)	organic solvents, halogen free
sodium sulfate	solid waste, free from mercury

Time

3-4 hours, without recrystallization

Break

Before shaking out

Degree of difficulty

Medium

Instruction (batch scale 20 mmol)

Equipment

250 mL three-neck flask, 500 mL beaker, internal thermometer, addition funnel with pressure balance, magnetic stirrer, magnetic stir bar, rotary evaporator, separating funnel, suction flask, Buechner funnel, ice bath

Substances

benzaldehyde (freshly distilled) (bp 179 °C)	2.12 g, (2.02 mL, 20.0 mmol)
H_2SO_4 (conc.)	19 mL (350 mmol)
HNO_3 (fuming)	8.7 mL (200 mmol)
tert-butyl methyl ether (bp 55 °C)	25 mL
aqueous $NaHCO_3$ solution (5%)	25 mL
sodium sulfate for drying	about 1 g
toluene (bp 111 °C)	
petroleum ether (bp 60-80 °C)	

Reaction

19 mL (350 mmol) of conc. H_2SO_4 are filled in a 250 mL three-neck flask equipped with an internal thermometer and addition funnel with pressure balance. Whilst cooling with an ice bath 8.7 mL (200 mmol) fuming HNO_3 are added carefully under stirring, the temperature must not exceed 10 °C. To this nitrating acid 2.12 g (2.02 mL, 20.0 mmol) benzaldehyde are added under further cooling so that the temperature can be constantly kept at 15 °C. The ice bath is removed and the reaction mixture is stored over night at room temperature.

Work up

The reaction mixture is poured in a 500 mL beaker on 150 g of crunched ice. The yellow precipitation is sucked off over a Buechner funnel and washed with 50 mL cold water. Crude yield (humid): 2.87 g

The humid crude product is dissolved in 25 mL *tert*-butyl methyl ether and shaken out with 25 mL of a 5% $NaHCO_3$ solution. The organic phase is dried over sodium sulfate, filtered and the solvent evaporated at a rotary evaporator. The residue is recrystallized from toluene/petroleum ether (60-80 °C) by dissolving it under heating in a few mL of toluene and then adding the double amount of petroleum ether in portions under ice cooling. The crystallized **3-nitrobenzaldehyde** is sucked off over a Buechner funnel and dried in the evacuated desiccator.

Yield: 1.57 g (10.4 mmol, 52%); mp 56 °C

Comments

In experiments Number 2003 and 5004 the product is used as educt.

Waste management

Recycling
The evaporated *tert*-butyl methyl ether is collected and redistilled.

Waste disposal

Waste	Disposal
aqueous filtrate from crude product	solvent water mixtures, halogen free
aqeuous phase from shaking out	solvent water mixtures, halogen free
petroleumether toluene mixture (mother liquor)	organic solvents, halogen free
sodium sulfate	solid waste, free from mercury

Time
2-3 hours, without recrystallisation

Break
Before shaking out

Degree of difficulty
Medium

Analytics

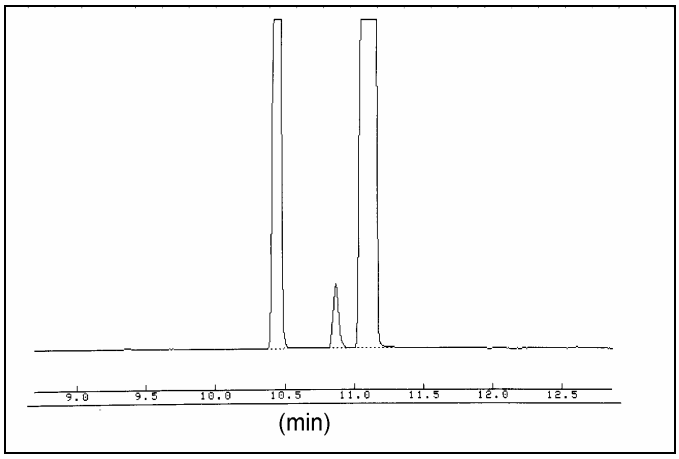
GC

GC-Conditions:

column:	5CB Low Blend/MS, length 30 m, internal diameter 0.32 mm, Film 0.25m
inlet:	injector temperature 210 °C, splitinjection
carrier gas:	H_2, pre-column pressure 50 kPa
oven:	60 °C (2 min), heating rate 10 °C/min, isotherme 240 °C (50 min)
detector:	FID, 310 °C,
integrator:	Shimadzu

Percent concentration was calculated from peak areas.

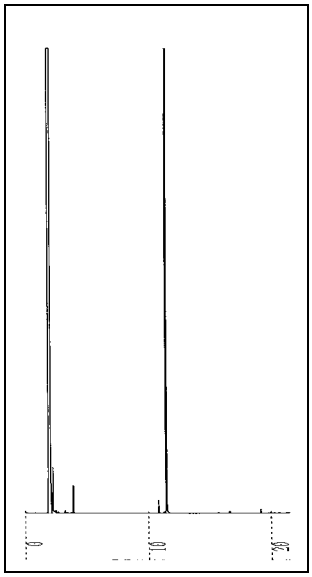
GC of the crude product



Retention time (min)	Substance	Peak area %
10.5	2-nitrobenzaldehyde	8.80
10.9	4-nitrobenzaldehyde	0.92
11.1	3-nitrobenzaldehyde	90.3

No educt detected

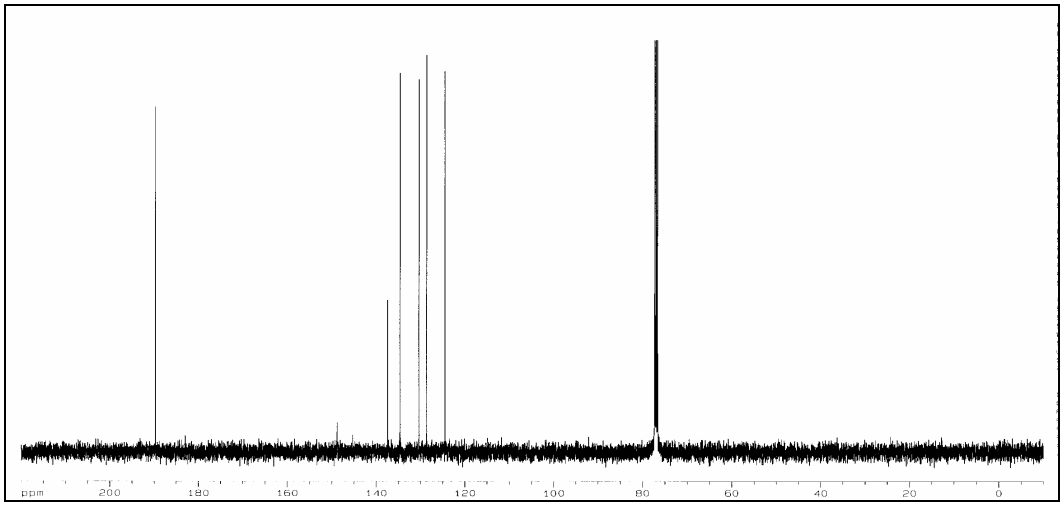
GC of the pure product



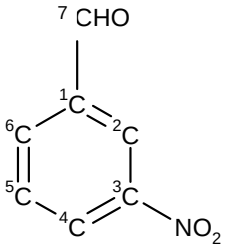
Retention time (min)	Substance	Peak area %
11.4	3-nitrobenzaldehyde	> 99

The peaks below 10 min are from solvents.

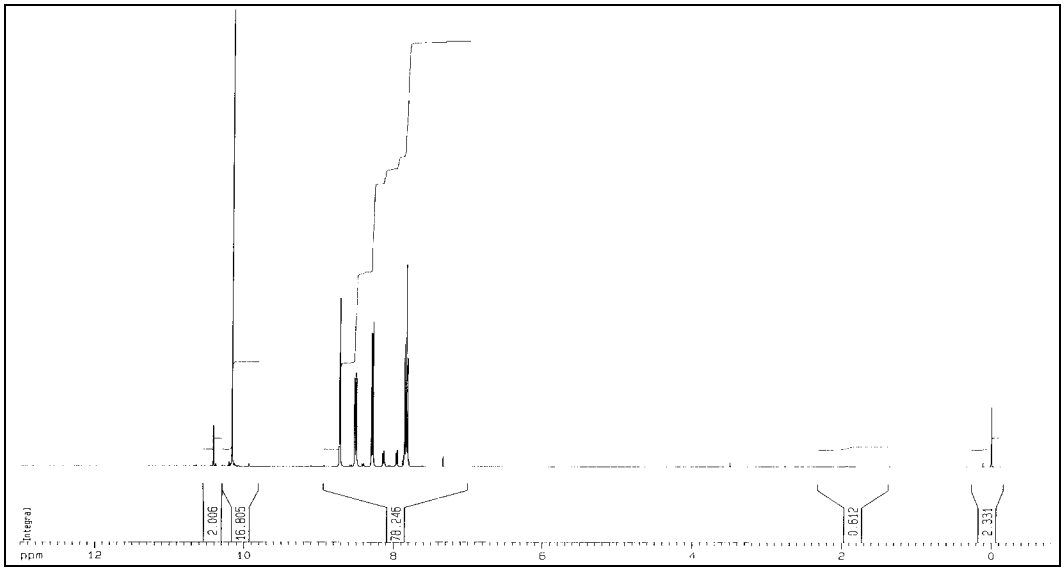
^{13}C NMR spectrum of the pure product (100 MHz, $CDCl_3$)



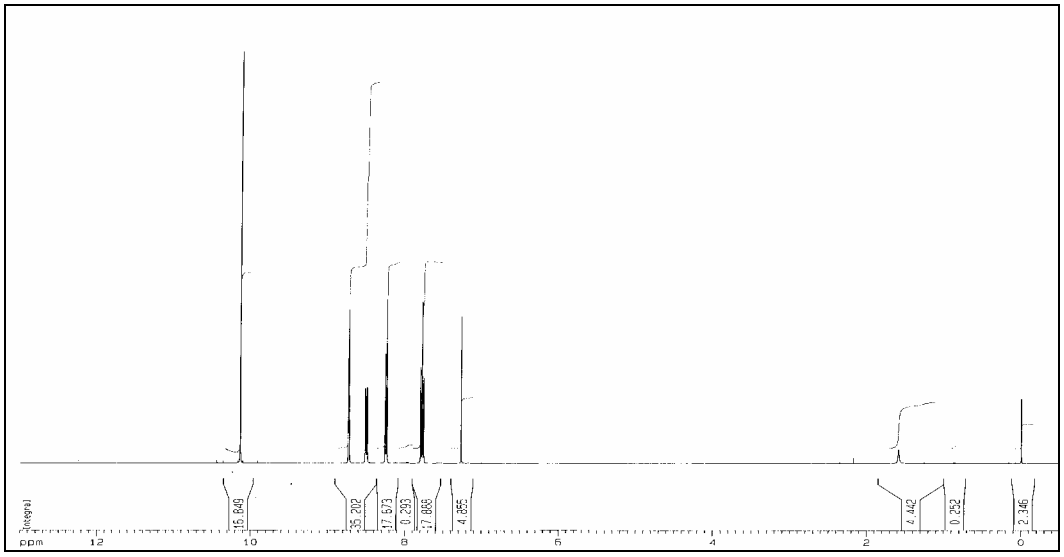
δ (ppm)	Assignment
124.49	C-2
128.57	C-4
130.36	C-5
134.58	C-6
137.39	C-1
148.79	C-3
189.67	C-7
76.5-77.5	solvent



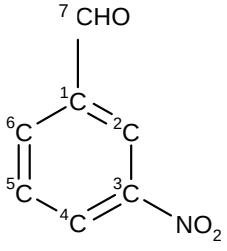
1H NMR spectrum of the crude product (400 MHz, $CDCl_3$)



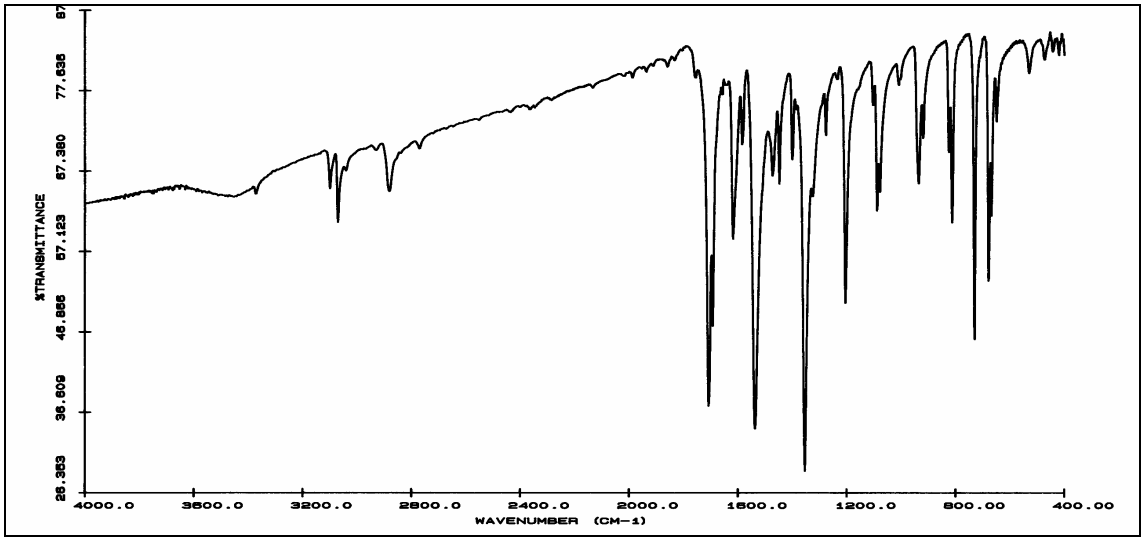
1H NMR Spectrum of the pure product (400 MHz, $CDCl_3$)



δ (ppm)	Multiplicity	Number of H	Assignment
7.76 - 7.80	t	1	5-H
8.23 - 8.25	m	1	6-H
8.48 - 8.51	m	1	4-H
8.72 - 8.73	m	1	2-H
10.13	s	1	7-H
7.26			solvent



IR spectrum of the pure product (KBr)



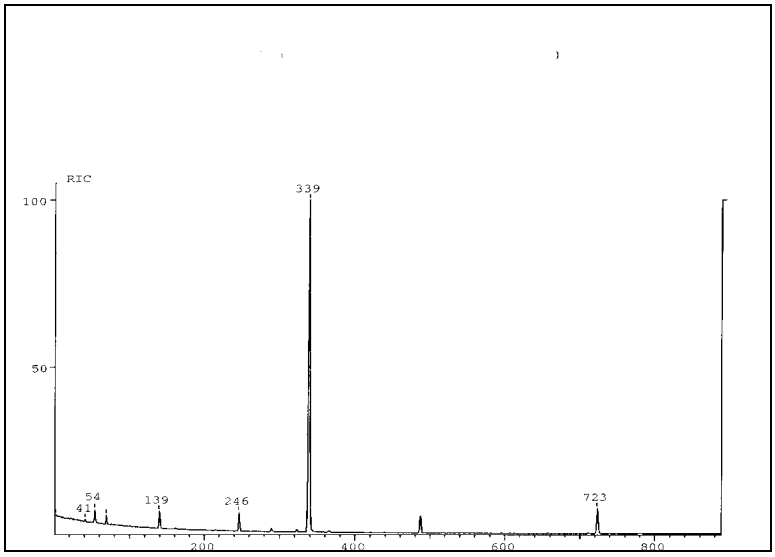
(cm^{-1})	Assignment
3100	C-H-valence, arene
2840	OC-H-valence, aldehyde
1690	C=O-valence, aldehyde
1580	C=C-valence, arene
1540, 1350	N=O-valence, asymm. and symm.

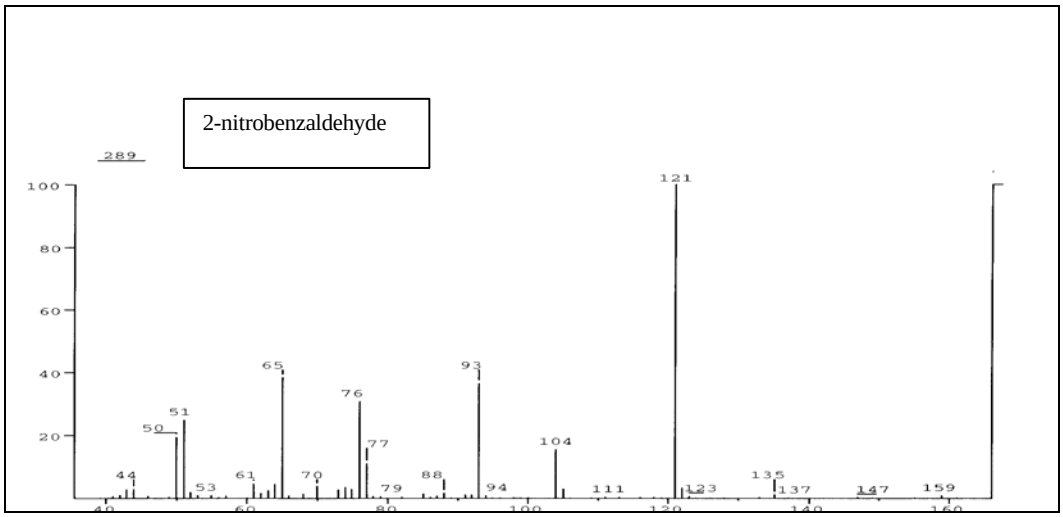
GC/MS of the crude product

GC-conditions:

column:	ZB-1, length 30 m
inlet:	splitinjection 1 : 20
oven:	70 – 300 °C, 6 °C/min

The GC/MS measurings confirm the formation of 3 Isomeres:




2-nitrobenzaldehyde
289
100
80
60
40
20
121
65
93
76
51
50
77
104
44
61
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88
79
94
111
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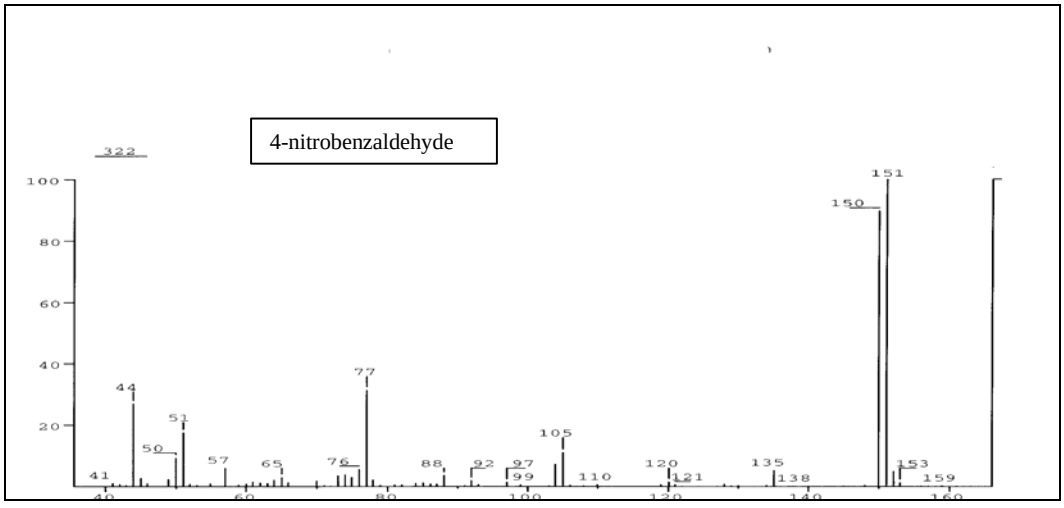
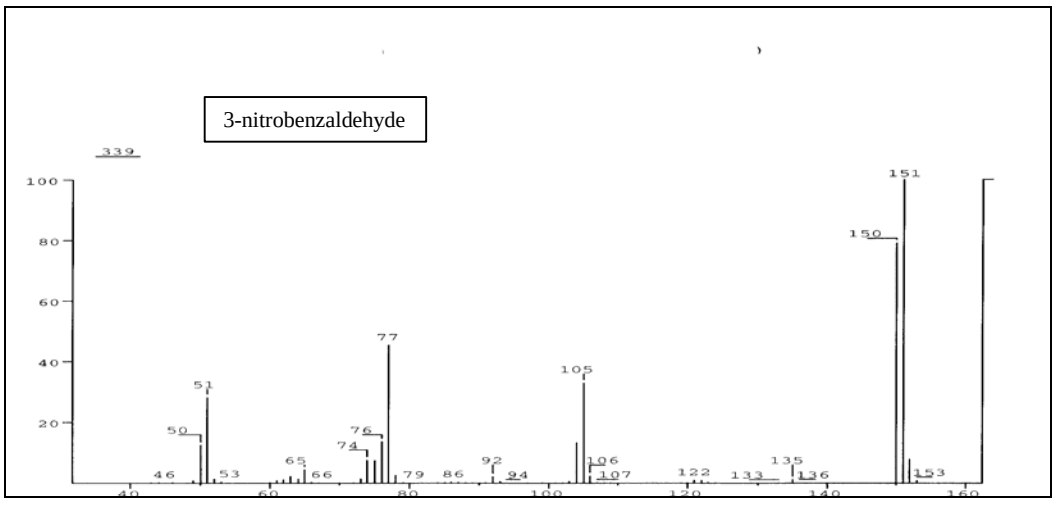
135
137
147
159
40
60
80
100
120
140
160


4-nitrobenzaldehyde
322
100
80
60
40
20
151
150
77
44
51
105
50
57
65
76
88
92
97
99
110
120
121
135
138
153
159
41
40
60
80
100
120
140
160


3-nitrobenzaldehyde
339
100
80
60
40
20
151
150
77
105
51
50
76
74
65
66
46
53
79
86
92
94
106
107
122
133
135
136
153
40
60
80
100
120
140
160