Analyses of Soil Samples from Green's Point Light Station in Letite Passage, New Brunswick, Canada

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ABSTRACT

Zitko, V. 2000. Analyses of soil samples from Green's Point Light Station in Letite Passage, New Brunswick, Canada. Can. Manuscr. Rep. Fish. Aquat. Sci. 2543: iii + 14 p.

The soil samples from the Green's Point Light Station site contain mixtures of organic compounds, extractable by dichloromethane, at concentrations of 0.09-99.7 mg g^{-1}. The mixtures consist of some hydrocarbons, two dyes, and numerous other compounds, mainly organic acids and, possibly, esters, some phenols, and other compounds some of which are tentatively identified as organophosphites. The composition of the mixtures is site-dependent and varies from a mixture resembling diesel fuel at one side of the generator building (Map 1) to the above-described mixture with different proportions of the components at another side of the building and at more distant locations, and to a 'black goo' in an area of previous storage of unlabeled drums. The presence of carboxyl or ester groups is always prominently indicated by the infrared spectra of all samples. The origin of the contamination may be a combination of organic compounds from diesel fuel, waste lube oil, waste diester lube oil, and exterior red paint.

RÉSUMÉ

Zitko, V. 2000. Analyses of soil samples from Green's Point Light Station in Letite Passage, New Brunswick, Canada. Can. Manuscr. Rep. Fish. Aquat. Sci. 2543: iii + 14 p.

Les échantillons de sol pris sur le site de la station de phare de Green's Point contiennent des mélanges de composés organiques extractibles au dichlorométhane, à des concentrations de 0,09-99,7 mg g^{-1}. Les mélanges sont constitués de quelques hydrocarbures, de deux colorants et de nombreux autres composés, surtout des acides organiques et, peut-être, des esters, des phénols et d'autres composés dont certains sont identifiés, pour le moment, comme des organophosphites. La composition des mélanges dépend de l'endroit sur le site et va d'un mélange ressemblant à du carburant diesel à une extrémité du bâtiment des groupes générateurs (Carte 1) au mélange décrit ci-dessus avec des proportions différentes des composés d'un autre côté du bâtiment et en un point plus éloigné, et à une « gelée » noire dans un secteur où des barils non étiquetés avaient été entreposés. La présence de carboxyle ou de groupes d'esters est toujours manifeste par les spectres infrarouges de tous les échantillons. L'origine de la contamination peut être une combinaison de composés organiques provenant de carburant diesel, d'huile de lubrification usée, d'huile de lubrification diester usée et de peinture extérieure rouge.

INTRODUCTION

Arrangements are in progress to facilitate public access to the lighthouse and associated facilities at Green's Point. Public Works and Government Services undertook an environmental survey [MGI Limited 1998], which identified several areas of soil contaminated with metals and hydrocarbons. I was asked to comment on the results of the survey.

In the MGI report, the soil around the generator building (Map 1) was given the highest priority for remediation, because of hydrocarbon contamination, with hydrocarbon concentration of 410 mg kg^{-1}. Other areas were identified as impacted by arsenic, lead, zinc, copper, barium, and tin. Consequently, before commenting on the MGI report, I visited the site. The 'metal-impacted' areas do not look particularly hazardous and are covered by vegetation. Paint chips, visible in places on the ground, can be easily removed, and leaching of metals and the resulting risk to the public, visiting the area, appear minimal.

The 'hydrocarbon-impacted' area around the generator building does not look 'quite right' and I took a composite sample (about top 5 cm) from both sides of the building. The presence of two dyes, hydrocarbons and other compounds was detected in this sample. Consequently, additional samples were collected around the generator building and, later, at several other locations. This report describes the results of the analyses.

EXPERIMENTAL

A composite sample of soil (34 g, from approximately top 5 cm) was collected on May 6, 2000 on both sides of the generator building (fill pipe and exhaust side, I, Map 1). Additional samples (15-40 g, sites 1-6, Map 1), were collected on June 4, 2000, and the sampling was completed by taking samples 1A-4A (Map 1) on June 17, 2000.

Most of the samples were passed through a 1.00-mm sieve and the weight losses at 105°C and 550°C were determined. Because of lack of material, aliquots of samples 2 and 3 were combined for the weight loss determination. These samples appeared very similar and it is not likely that the pooling introduced a significant error. Samples 1A, 2A, and 4A appeared very wet and were freeze-dried before sieving and extraction. Portions of the samples, 3-30 g, weighed to the nearest 0.01 g, were extracted first with dichloromethane and then with methanol, in 38 x 2.2 cm id glass columns. Ultraviolet and visible (UV/vis) spectra of the extracts were determined, the extracts were evaporated to dryness, and the residues of the dichloromethane extracts were weighed. Finally, infrared (IR) spectra of the extracts were determined. The residues were also examined by thin layer chromatography (TLC) on Whatman Silica Gel 150A, K5F, 5 x 20 cm plates. The solvents were benzene and a mixture petroleum ether-diethyl ether-glacial acetic acid 80:20:1 v/v. Compounds on the plates were examined under UV light, after charring with sulfuric acid, and after reaction with silver nitrate or with Fast Black K salt (FBK, Ojanperä et al. 1990). Preparative TLC was carried out on the same adsorbent and with the same solvents, but on 20 x 20 cm plates. Zones of interest were detected by UV light, scraped, and extracted with dichloromethane or methanol.

Test for phosphates by ammonium molybdate and benzidine, and for halogens by the Beilstein test, were performed as described by Feigl (Feigl 1958; Feigl 1966, respectively).

A Hewlett-Packard Diode Array spectrophotometer Model 8452A with a 2-nm resolution was used to scan the ultraviolet and visible (UV/vis) spectra. Infrared (IR) spectra were determined by a Perkin-Elmer Model 700 spectrophotometer on 3M Disposable IR Cards for the dichloromethane-extracted residues or a film in sodium chloride cells, and in KBr pellets for the methanol-extracted residues.

RESULTS AND DISCUSSION

CONCENTRATION OF ORGANIC COMPOUNDS IN SOIL SAMPLES

Weight losses at 105 and 550°C, and the concentration of dichloromethane-extractable substances are presented in Table 1. The concentration of methanol-extractable materials was not determined quantitatively, because of interference of co-extracted chlorides and sulfates (identified by their IR spectra and precipitation by silver nitrate) caused by moisture of the soil samples.

Table 1. Concentration of dichloromethane-extractable compounds and weight losses of soil samples.

Sample	Dcm, mg g^{-1} Dw	Dcm, mg g^{-1} Ww	Loss at 550°C, %, Ww	Loss at 550°C, %, Dw	Loss at 105°C, %
Initial		6.90	46.00		
1	9.19	5.42	69.19	47.72	41.06
2+3			23.06	13.87	10.67
4			28.94	14.80	16.60
5	6.51	5.34	24.91	8.50	17.94
6	9.52	3.06	93.09	78.50	67.84
1A	6.82				
2A	7.48				
3A		0.09			
4A	99.72			25.5	

Dcm = dichloromethane-extractable substances; Dw, Ww = dry weight (based on weight loss at 105°C), and wet weight basis, respectively.

As can be seen from Table 1, the concentration of dichloromethane-extractable compounds, as well as the weight losses, are considerable and much higher than the reported concentration of hydrocarbons (0.41 mg g^{-1}, MGI Limited 1998).

ANALYSIS OF THE INITIAL SAMPLE

The UV/visible spectrum of the dichloromethane extract of the initial sample is quite featureless, with relatively strong absorption in the UV (Fig. 1a). A 'shoulder' at 288 nm may indicate the presence of phenols. The extract also contains a small amount of chlorophyll from the vegetation (absorption maximum at 666 nm, Fig. 1b). The infared (IR) spectrum of the dichloromethane extract of the sample (Fig. 2) shows the presence of hydroxy groups (3350 cm^{-1}), ester or carboxyl groups (1700-1730 cm^{-1}), and, possibly, benzene rings (1600 and 1500 cm^{-1}). On the whole, the spectrum is similar to that of a polyol ester (Coates and Setti 1985). The UV/visible spectrum of the methanol extract has a maximum at 228 nm and a shoulder at approximately 272 nm (Fig. 3). These may also indicate the presence of phenols.

The dichloromethane extract contains a red and an orange dye, as shown by thin layer chromatography (TLC) on silica plates, developed in benzene (Fig. 4). In addition to the dyes, the extract contains some hydrocarbons as relatively minor constituents. The bulk of the extract consists of a number of more polar compounds. Two zones have a strong blue and light blue fluorescence, respectively.

The dyes were isolated by TLC and their spectra are in Fig. 5. Their main absorption maxima are at 514 nm (the red dye) and at 488 nm (the orange dye). The red dye is identical with the dye in the red paint of the door and stairs of the light tower, but its composition is not yet known. The dye is not listed in Green (1990).

Two zones from the more polar section were isolated as well. Their spectra are in Fig. 6. A narrow fluorescent zone had a featureless UV spectrum. It is likely that the amount recovered from the plate was not sufficient for a good spectrum. The spectrum of a broader, brown zone just above start has a pronounced shoulder at about 280 nm, which may indicate the presence of phenols.

More polar compounds in the dichloromethane extract and in the methanol extract were resolved by TLC on silica, developed in petroleum ether-diethyl ether-acetic acid (Fig. 7). The presence of phenols, indicated by the UV spectrum of one of the more polar fractions of the dichloromethane extract, was confirmed by detecting such compounds by Fast Black K salt (Fig. 8). Increasing the polarity of the developing solvent to ethyl acetate did not result in improved resolution (Fig. 8).

Some more polar compounds in both extracts also reacted with silver nitrate (Fig. 9). A positive reaction with this reagent may indicate the presence of halogens, but other compounds may react as well. No halogens were detectable in the extract by the Beilstein test. Phosphate was detectable in the ash

(550°C) of the methanol extract by the ammonium molybdate-benzidine reaction, and triethyl, tributyl, and triphenyl phosphite behaved similarly on TLC to the more polar silver nitrate-positive compounds.

The presence of hydroxyl groups is also demonstrated by the IR spectrum of the methanol extract (Fig. 10, maximum at 3350 cm^{-1}). The spectrum also shows the presence of ester or carboxyl groups (1710 cm^{-1}) and, possibly, phosphites or phosphates (1080 cm^{-1}).

ANALYSIS OF ADDITIONAL SAMPLES

The dyes are present in samples 1(trace), 3A (trace), 2-4, taken at the left-hand side of the generator building (Map 1, Fig. 11), 6 (trace) and, in a very high concentration, in sample 2A. In all instances the red dye is present in much higher concentration than the orange dye. Sample 5 contains primarily hydrocarbons, and sample 6 other organics (Fig. 12). The composition of samples 2-4 and 2A is similar, except that samples 3 and 1A and 2A contain a higher concentration of the second most polar compound(s), which appear(s) to have phenol groups, according to the positive reaction with FBK (Fig. 12, 13, sample 1A not shown). Practically all other major spots on TLC plates of all samples except 4A, 5 and 6 react with FBK (Fig. 13). Consequently, these samples contain a mixture of phenols.

All samples taken around the generator building, as well as sample 6, contain the silver nitrate-positive compounds tentatively identified as organophosphites (Fig. 14). These compounds are not detectable in samples 1A, 2A, 3A, and 4A. (Fig. 15).

The IR spectrum of sample 4A, from the site of previously stored unlabeled drums, indicates the presence of fatty acid (Fig. 16).

UV/vis spectra of seven of the dichloromethane extracts are presented in Fig. 17. The absorbances are expressed in absorbance units per mg (dry weight) per mL. The spectra of extracts from stations 5, 3A and 4A differ from the rest and those from 3A and 4A also present the extremes (note the multiplication factors). As mentioned before, sample 5 contains a relatively higher concentration of hydrocarbons. The shape of the spectra of samples 1, 1A, 2A, and 6 is similar and reflects their similar composition.

CONCLUSIONS

In conclusion, the soil around the generator building contains material that, depending on location, contains diesel fuel, a waste lube oil or a diester air-compressor oil product, consisting of some organic acids, esters and additives, such as phenols and industrial organophosphites. The red dye originates from the paint used on the door and steps of the light tower. Hydrocarbons, reported in 1998 at 0.4 mg kg^{-1}, are a relatively minor component on one side of the generator building (site 5, Map 1). More detailed attempts to characterize or identify the materials could be carried out, but only at a considerable expense.

The presented analytical data show that the structural features of organic compounds include hydroxy, carboxy and ester groups, and halogens do not appear to be present in more than a trace concentration. The absence of halogens and the presence of oxygen-containing groups are an indication that further decomposition of the organic compounds will take place in due course. The removal of the contaminated soil would just move the problem and carry an additional risk of spreading the contamination in the process. Consequently, a layer of topsoil and sod may be the most effective treatment of the vicinity of the generator building. The contaminated area between the generator building and the light tower (station 6) could be filled with clean soil to eliminate the 'dip', and also covered with a layer of topsoil and sod. The 'black goo' area should be excavated and the contaminated soil removed to a sanitary landfill. The whole site should be surveyed for the presence of any other such areas.

The cleanup recommended in the MGI report is based on incomplete chemical analytical data. This case also underlines the need for expert quality control, supported, if in doubt, by independent chemical analyses of contracted-out analyses.

ACKNOWLEDGMENTS

I thank Ms. Maria Buzeta for bringing this problem to my attention and for sample collection. Ms Marilynn Rudi edited and Ms. Brenda Best formatted the manuscript. Drs. Jocelyne Hellou and John Castell commented on the manuscript.

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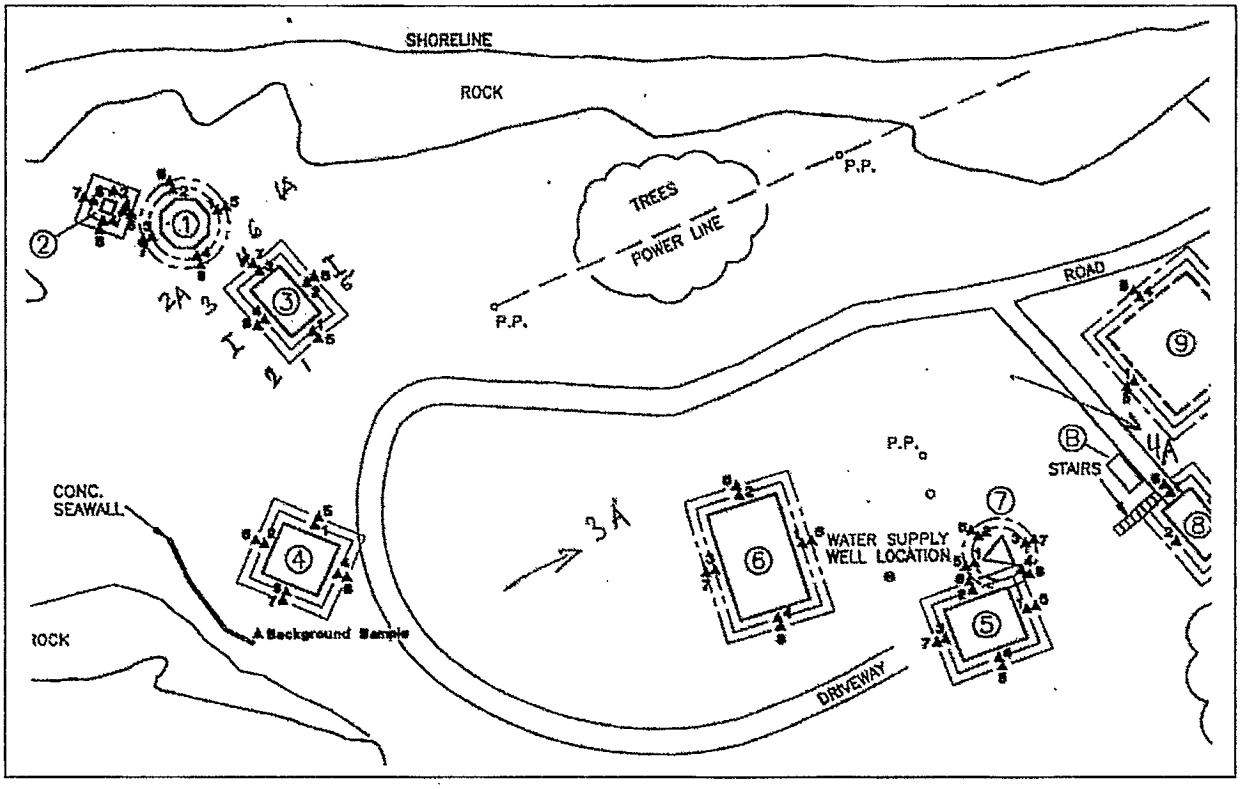

Map 1. Green's Point site. Objects: 1 - Light Tower, 2 - Fog Alarm Platform, 3 - Generator Building, 4 - Helicopter Pad, 5,6 - Dwellings, 7 - Radio Tower, 8 - Garage. B - stained soil and former location of unlabeled drums, location of sample 4A (adapted from MGI Limited 1998).
I - sites of the initial composite sample at the Generator Building, 1,2,3,4,5,6 - sites of subsequent sampling, 1A,2A,3A,4A - sites of additional expanded sampling.

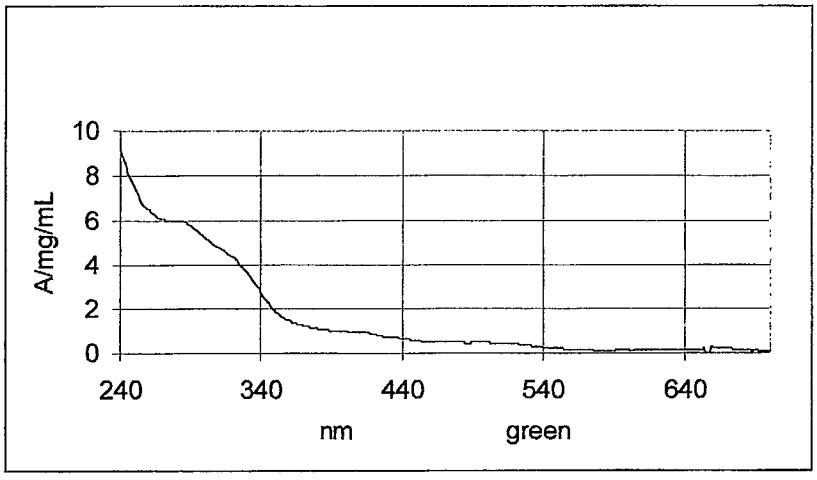

Fig. 1a. UV/visible spectrum of dichloromethane extract of the initial sample. X axis: wavelength in nm, Y axis, absorbance/(cm*mg mL^{-1}).

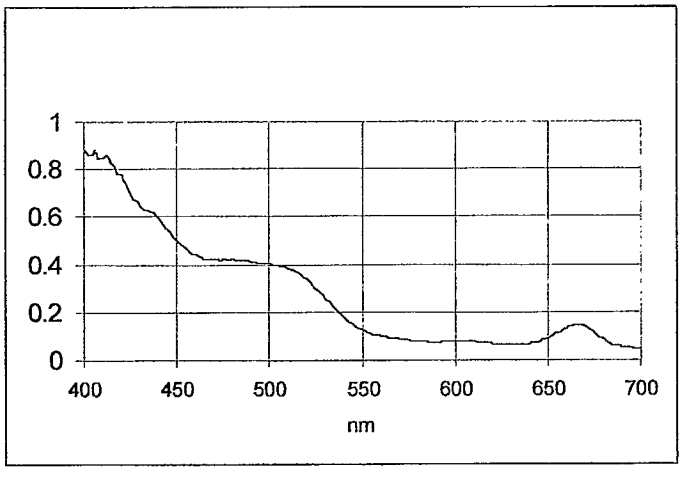

Fig. 1b. Visible spectrum of dichloromethane extract of the initial sample. X axis: wavelength in nm, Y axis, absorbance/(cm*mg mL^{-1}).

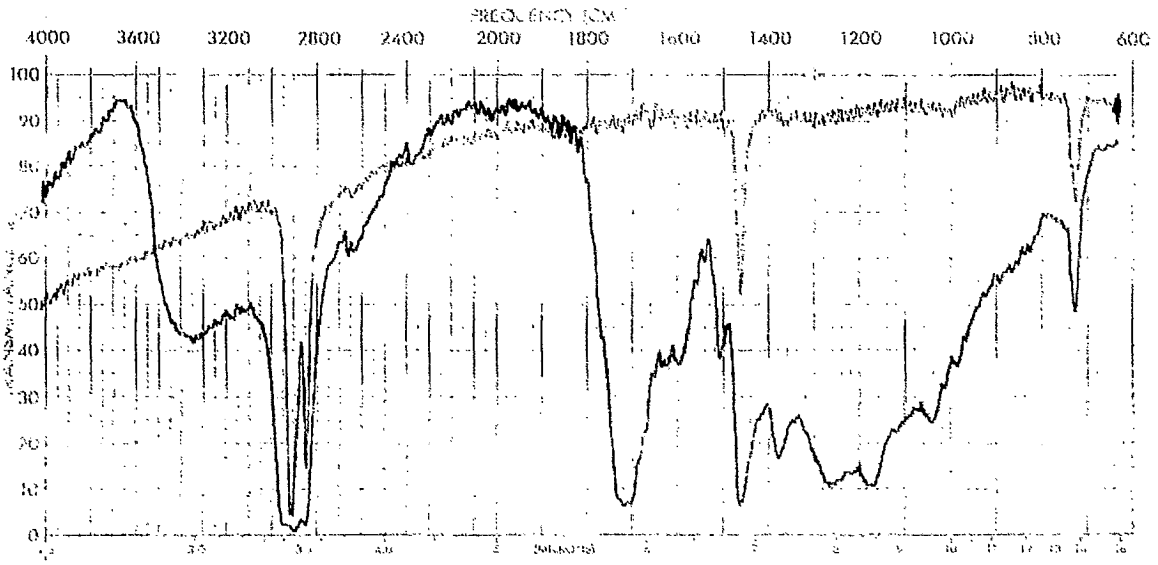

Fig. 2. Infrared (IR) spectrum of the dichloromethane extract in a 3M IR polyethylene card (blank is the upper spectrum).

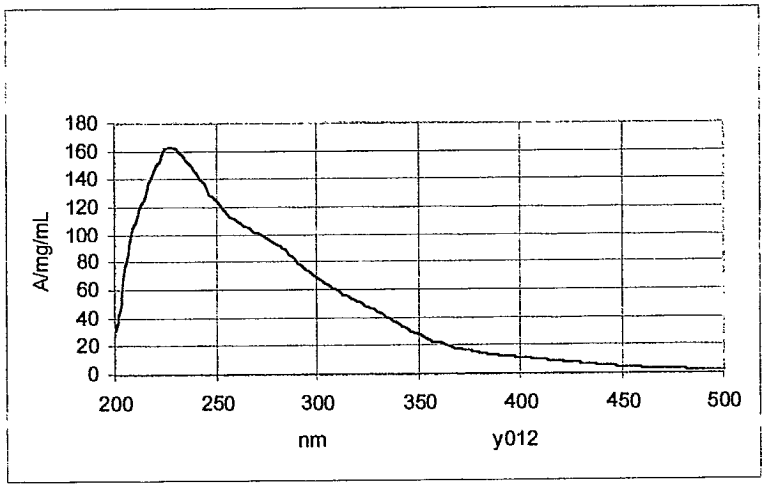

Fig. 3. UV/visible spectra of the methanol extract. X axis: wavelength in nm, Y axis, absorbance/(cm*mg mL^{-1}).

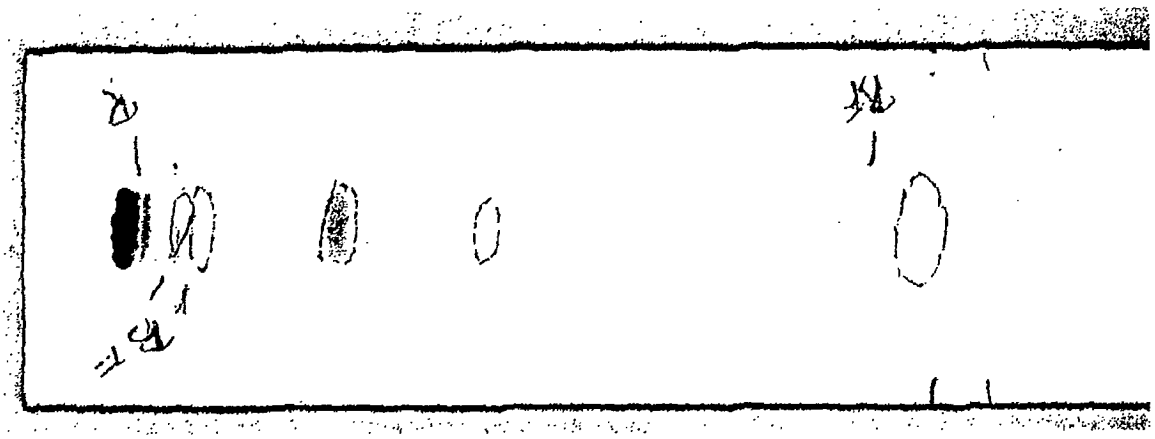

Fig. 4. Thin layer chromatogram (TLC) of the dichloromethane extract. Solvent: benzene.

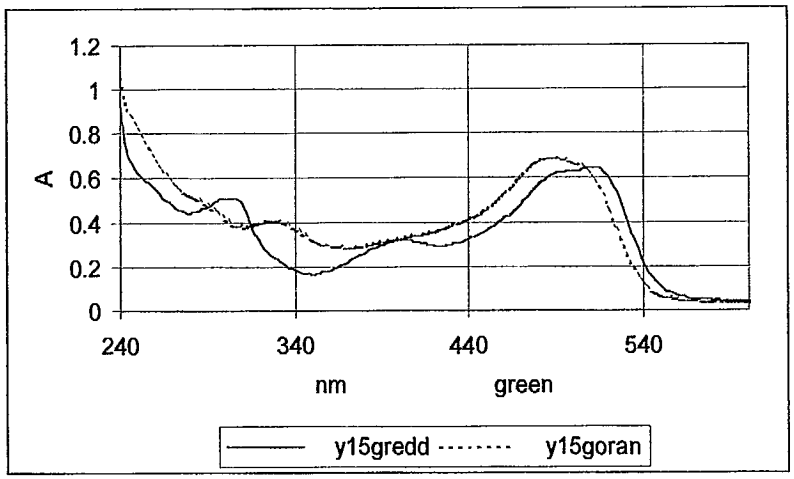

Fig.5 UV/vis spectra of dyes present in the dichloromethane extract. The absorption maxima are 514 nm, and 304 nm for the red dye, and 488 nm and 330 nm for the orange dye (dotted line).

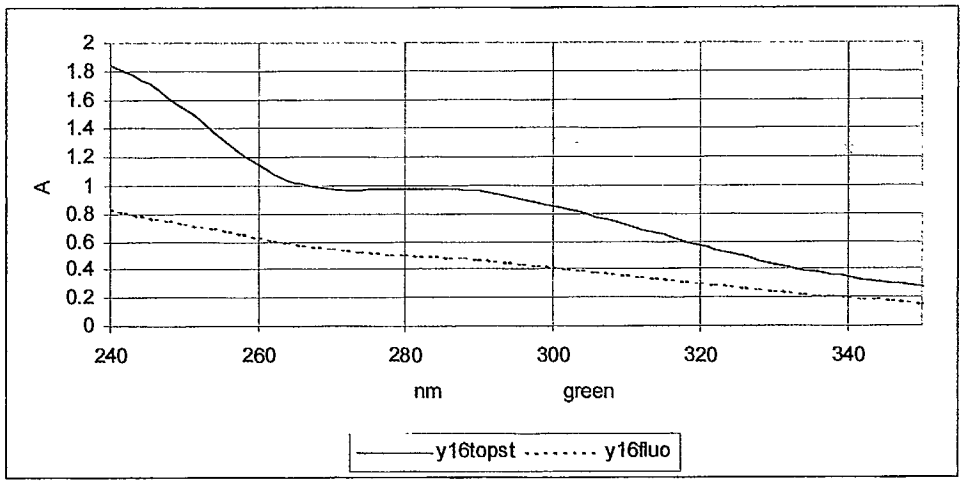

Fig. 6. UV spectra of two more polar zones from the dichloromethane extract. A narrow, fluorescent zone, dotted line, a more polar, 'brown' zone, solid line.

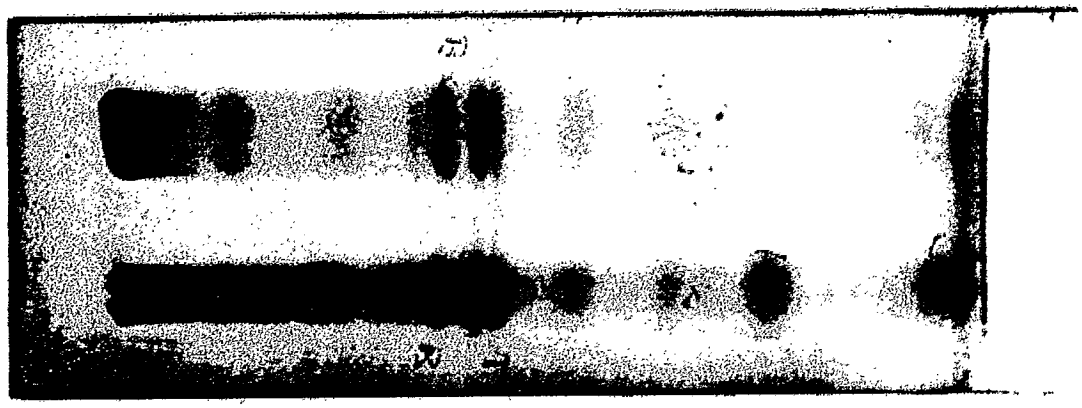

Fig. 7. More polar compounds in methanol (top) and dichloromethane extract (bottom).
Solvent: petroleum ether-diethyl ether-acetic acid (80:20:1). Detection: charring with sulfuric acid.

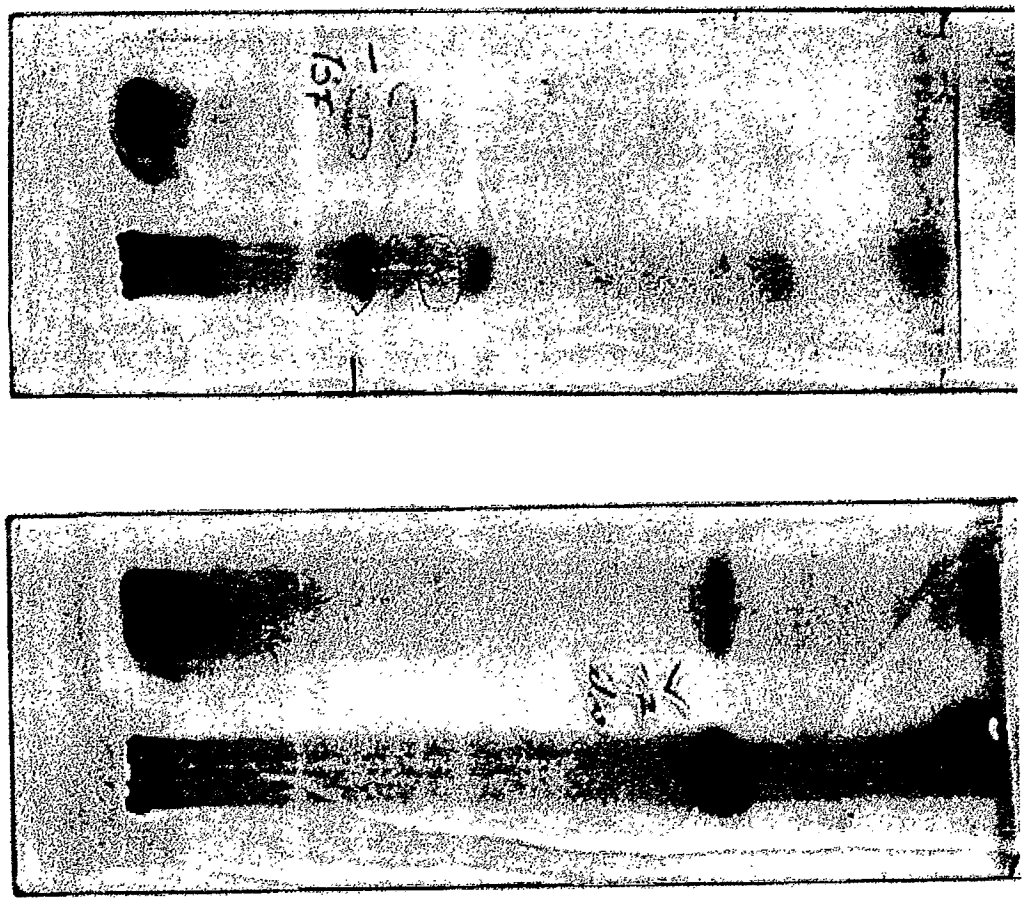

Fig. 8. TLC of methanol and dichloromethane extracts on silica, upper plate developed in petroleum ether-diethyl ether-acetic acid 80:20:1, lower plate in ethyl acetate. In both cases spots visualized by Fast Black K salt (dip in 0.5% aqueous solution, drying, and dip in 1N sodium hydroxide).

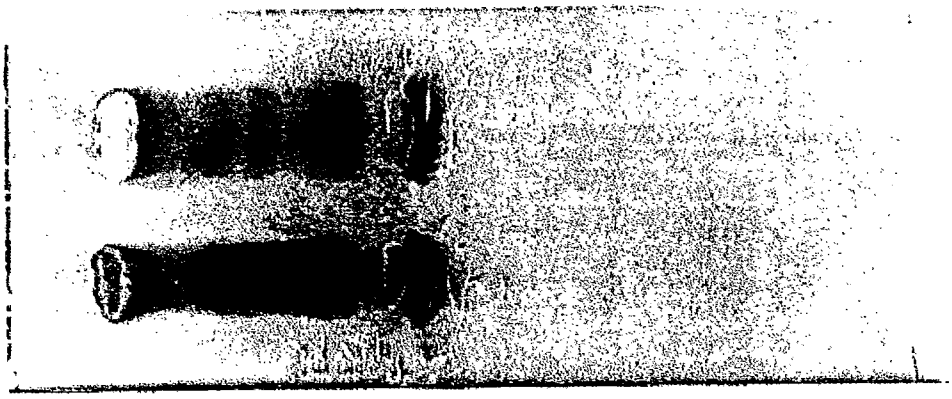

Fig. 9. TLC of methanol (upper) and dichloromethane extracts on silica, developed in petroleum ether- diethyl ether-acetic acid 80:20:1. Detection: silver nitrate.

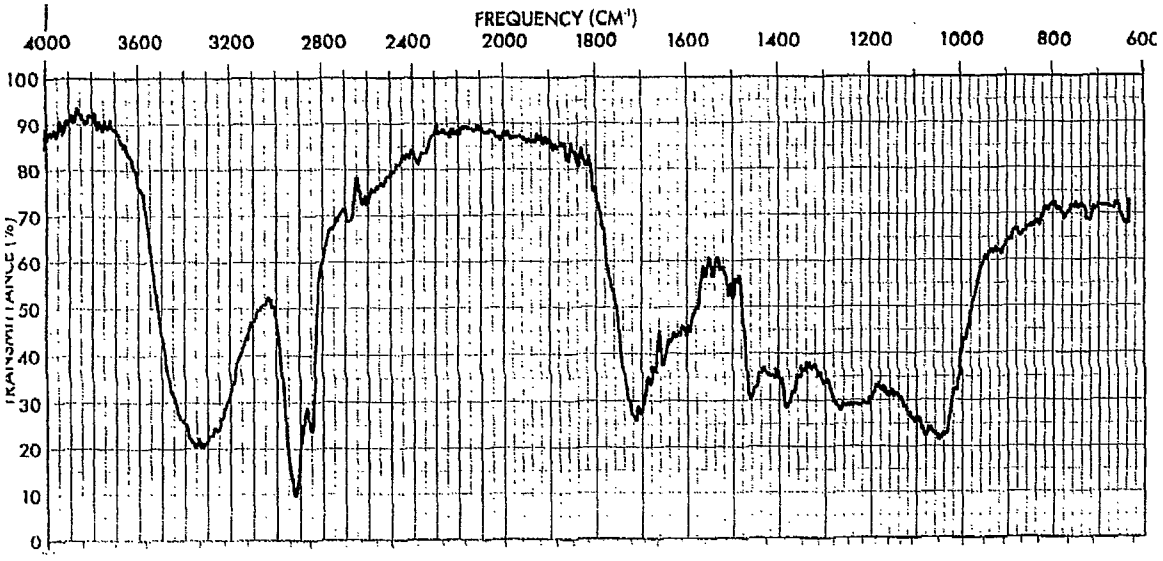

Fig. 10. Infrared spectrum of methanol extract in a potassium bromide pellet.

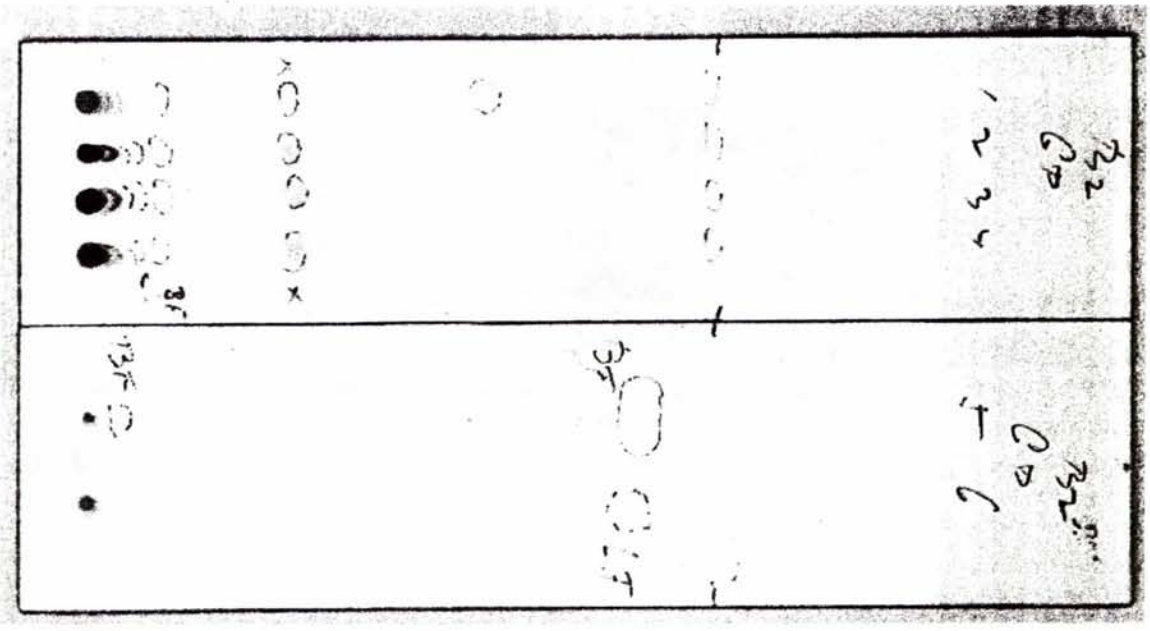

Fig. 11. TLC of dichloromethane extracts of samples taken around the generator building. Solvent: benzene, detection visual (dye), UV light. The samples 1-4 are similar, the samples 5 and 6 are different. See Map 1 for sampling locations.

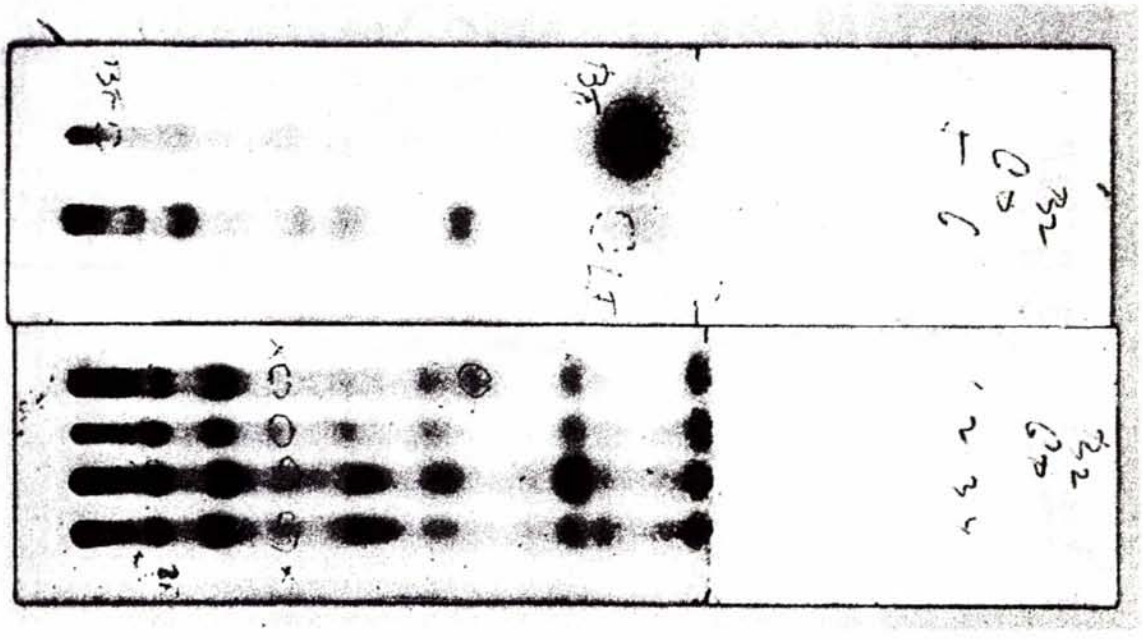

Fig. 12. TLC plates from Fig. 11 after charring with sulfuric acid.

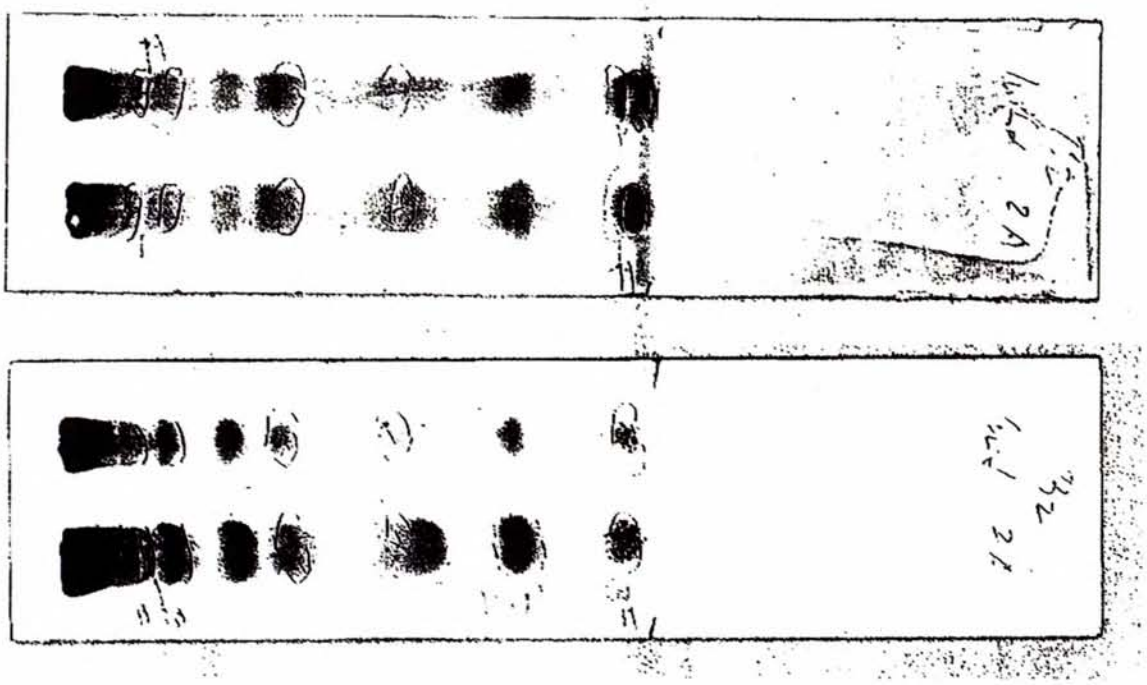

Fig. 13. TLC of dichloromethane extracts of the initial sample (upper track) and of sample 2A (lower track). Solvent: benzene, spots visualized by Fast Black K in the upper plate and by charring with sulfuric acid in the lower plate.

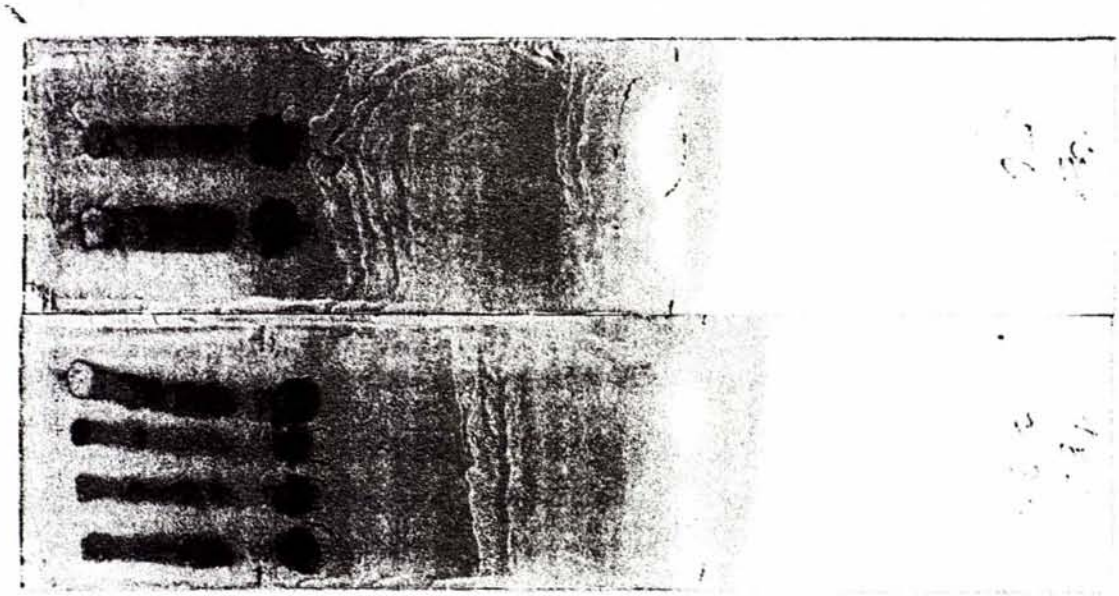

Fig. 14. TLC of dichloromethane extracts of samples taken around the generator building. Solvent: petroleum ether-diethyl ether- glacial acetic acid 80:20:1 detection silver nitrate. All samples are similar. See Map 1 for sampling locations.

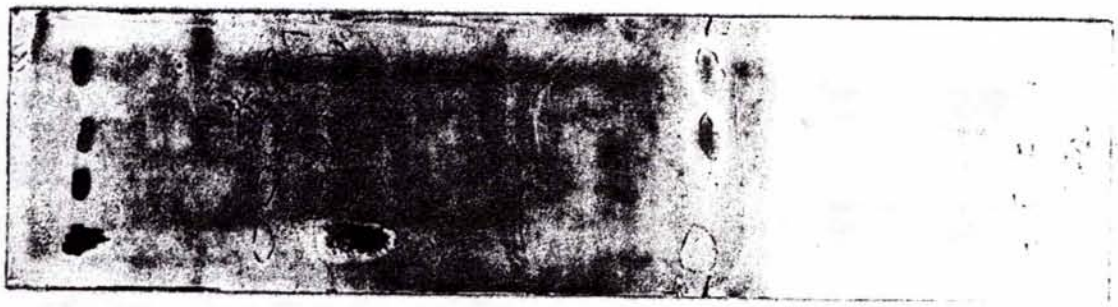

Fig. 15. TLC of dichloromethane extracts of samples 1A, 2A, 3A, and 4A. Plates are developed in petroleum ether-diethyl ether-glacial acetic acid 80:20:1 and compounds are visualized by reaction with silver nitrate. Compare with Fig. 9.

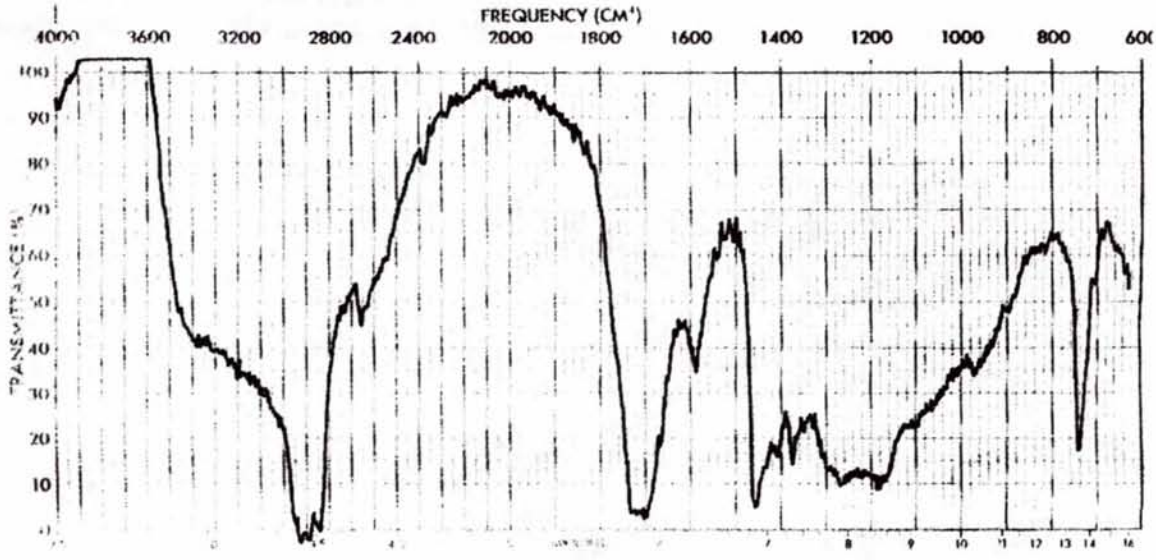

Fig. 16. IR spectrum of dichloromethane extract of sample 4A. Film on sodium chloride.

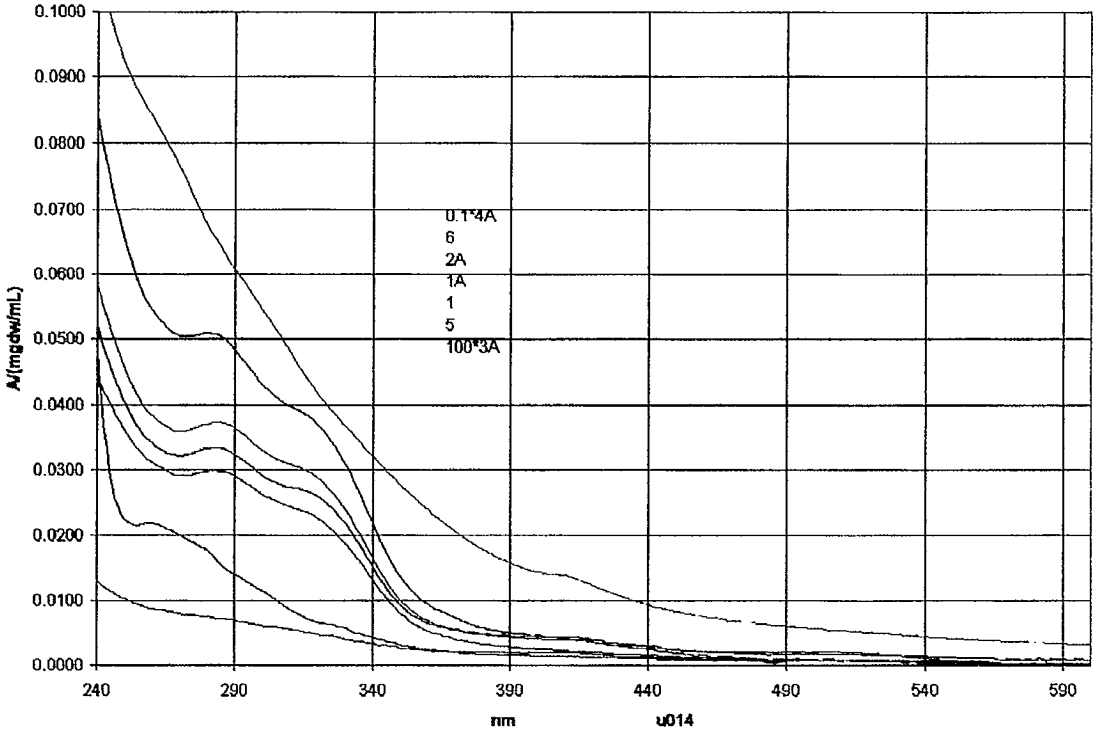

Fig. 17. UV/vis spectra of dichloromethane extracts. Absorbance in 1 cm cell of a solution corresponding to a sample concentration of 1 mg (dry weight)/mL. Spectra from top to bottom indicated in the figure. Note the multiplication coefficients for spectra of samples 3A and 4A.