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HÄLSINGEGATAN 43
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CHLORINATED HYDROCARBONS IN THE ATMOSPHERE

Anders Laveskog, Anne Lindskog

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1. SUMMARY

In 1969 periodic sampling of chlorinated hydrocarbons in airborne fallout was started in Sweden.

In addition to this fallout investigation, air sampling is being carried out at 10 stations in Sweden, and the contents of DDT and PCB are determined.

The results from the fallout sampling indicated a general occurrence of PCB and DDT in air, and it was clear that the origin and general routes of transport of PCB to the environment ought to be investigated.

For this purpose we have developed a method for sampling and determining chlorinated hydrocarbons in combustion gases.

The particles are trapped on glass wool supported on a glass filter, while the substances occurring in the gaseous state are absorbed on Apiezon M on Chromosorb W contained in a glass column. After extraction of the glass wool and elution of the column followed by clean-up, the samples are analysed by GLC using an electron-capture detector.

To date, measurements have been performed of the PCB content in gases emitted by municipal incinerators and by different plants for combustion of sewage sludge, waste-oil and scrap cables.

2. BACKGROUND

The occurrence of chlorinated hydrocarbons in the environment today is well documented, and it has been suggested that an atmospheric transport is the most probable. The mechanism for this atmospheric transport, however, is not yet fully understood.

In Sweden, periodic sampling of chlorinated hydrocarbons in airborne fallout was started in 1969 by Södergren. (1) In 1972, a sampling network of eight stations was organized by Ekstedt and Odén in order to study the content of chlorinated hydrocarbons in the lower atmosphere. (2) A method for measuring PCB in combustion gas was developed, also used for the sampling of airborne fallout. (2, 3, 4, 5)

2.1 Airborne fallout

The technique, developed by Södergren in 1968, is as follows. (6)

The fallout is trapped on a 200 μm nylon net (30 x 30 cm) which, in a standardized procedure, is impregnated with a thin film of silicone oil (SE 30). Such impregnated nets are exposed in open places for 2 to 3 months and, after the collection, extracted with n-hexane in a soxhlet apparatus for 2 x 24 hours. The solution is purified by treatment with concentrated sulfuric acid and analyzed by means of GLC and GLC/MS. The method does not distinguish between fallout with rain and direct particulate fallout, nor is there any estimate of the distribution of particles in the air.

In 1971 seven sampling stations were established in southern Sweden. Five of them were situated in agricultural districts, one in the city of Lund and one in

the city of Malmö close to a municipal-refuse disposal plant. The nets were exposed for 3 months and the amounts of PCB (Clophen A50) and Σ DDT (pp'-DDT+pp'-DDE) were determined. Higher levels of PCB were recorded in the western part of the region; the distribution of Σ DDT was more uniform.

For one year (October 1972 to October 1973) airborne fallout was collected at 15 places throughout Sweden.

(7) The highest levels of PCB were recorded in the southern and southwestern parts of Sweden, and stations situated in coastal areas showed consistently high levels. Compared to earlier studies, the actual amount of PCB in the airborne fallout in southern Sweden had declined. For Σ DDT (p,p'-DDE+p,p'-DDD+o,p'- and p,p'-DDT) no distinct distributional pattern was revealed.

On the basis of his investigations of airborne fallout in Sweden and other countries, the author concluded the following (7):

Σ DDT was more uniformly distributed than PCB. In spite of the DDT restrictions in Sweden, DDT was still present in airborne fallout and no clear indication of decreasing levels could be seen. The author found it impossible as yet to determine whether the DDT originates in Sweden or is transported from places far away.

PCB was frequently present in the lower atmosphere in industrialized areas. The distributional pattern within Sweden indicates that local sources are of greater importance for the pollution than long-range transport. The author suggests that municipal incineration may be one local source.

This theory is supported by the fact that no (or only small amounts of) PCB is found in airborne fallout in

Iceland (8), Africa or Sri Lanka. (7)

2.2 Content in the lower atmosphere

Ekstedt and Odén started their investigations of the atmospheric content of DDT and PCB in 1972. (2) In 1974 the sampling network included 12 stations in Sweden. (9)

The air sampling equipment consists of a filter impregnated with a glycerol-water mixture (1:1), a filter holder, and a pump with a capacity of $2.3 \text{ m}^3/\text{h}$. The filters are extracted with acetone in an ultrasonic bath for 15 minutes, and, after addition of hexane, the extraction is continued for another 15 minutes. The hexane phase is separated by addition of 0.9% NaCl solution, transferred, and then purified with fuming sulfuric acid. With an air sample volume of about 100 m^3 , the detection limit for DDT is 0.02 ng/m^3 and for PCB 0.8 ng/m^3 . (2)

During the period, from October 1972 to October 1973, a total of 200 samples were collected on seven different occasions. DDT (DDE, DDD, DDT) was found in all samples but one, but PCB was detected in only 38 samples of 200.

The content of p,p'-DDT in the lower atmosphere shows a seasonal variation with a minimum value during the winter ($0.05\text{-}0.10 \text{ ng/m}^3$) and a maximum value during the summer ($0.35\text{-}0.45 \text{ ng/m}^3$).

In addition, the investigation indicated a latitudinal gradient in the distribution.

The authors conclude that two different systems for the atmospheric transport of DDT seem to exist and that the

polar region appears to be a source area during the winter. In addition to the global transport of DDT adsorbed on particles, the presence of DDT in the lower atmosphere in Sweden is due to evaporation from areas earlier treated with DDT elsewhere.

The PCB content in the lower atmosphere shows no seasonal variation, although this may be due to the limited number of samples containing detectable amounts. The authors assume that the high levels of PCB occurring occasionally result from emissions from local sources.

3. EMISSION OF PCB

When the results of the fallout sampling in southern Sweden indicated a general occurrence of PCB in the lower atmosphere (1), it was clear that the origin and general routes of transport of PCB to the environment, should be investigated.

For this purpose, we have developed a method for sampling and determining chlorinated hydrocarbons, primarily PCB, in combustion gases. (3, 4, 5) The sampling technique makes it possible to distinguish between gaseous PCB and PCB adsorbed on particles.

3.1 Sampling equipment

The sampling equipment is made of glass (Pyrex) with standard fittings and consists of the following parts. Fig. 1 and 2.

Probe. The inner diameter is adapted to the flow rate in the flue to achieve an almost isokinetic sampling. The probe is heated with electrical heating tape during the sampling to prevent condensation and occlusion.

Precipitator. A short glass column with a glass filter disc (porosity 2) filled to half its height with glass wool (acid washed and treated with TMCS). The precipitator is shaped to fit a soxhlet extractor and thus replaces the extraction thimble. The precipitator is also heated during the sampling.

Condenser

A 200 mm standard condenser is used to chill the gas before it enters the concentration column.

Concentration column. A short glass column with a glass filter disc (porosity 0) and a Teflon stopcock. The inner diameter is 10 or 20 mm. The column is filled to a height of 25 mm with Chromosorb W (60-80 mesh, acid washed and TMCS treated) and coated with a stationary phase, Apiezon M. The amount of Apiezon has been varied between 25 and 40%. The condensed water is collected in a flask following the column. (In a few cases, this flask was replaced by a washing flask with ethanol, where any PCB, possibly not retained by the Apiezon could be trapped).

The necessary flow rate of about $0.2 \text{ m}^3/\text{h}$ through the two columns is effected by a vacuum pump. The gas volume passing is measured by a gas meter.

3.2 Analytical method

3.2.1 Extraction of PCB adsorbed on particles

The collected particles are extracted with 40 ml of chloroform in a soxhlet equipment for 24 hours. After extraction the chloroform is evaporated. To avoid loss of PCB, a few drops of Apiezon M in hexane are added to

the extract. After evaporation, the extract is redissolved in 15 ml of hexane and evaporated once more.

3.2.2 Cleanup of the extract

The extract is transferred to a Florisil column with a maximum of 3 ml of hexane in small portions. The column is eluted with hexane to 10 ml. The eluate is collected in a graduated centrifuge tube and concentrated to 1 ml; 1 ml of fuming sulfuric acid (7% sulfur trioxide) is added, and the tube is placed in an ultrasonic bath for 5 minutes. After centrifugation, the tube is dipped into a carbon dioxide bath. (10) When the sulfuric acid has frozen, the hexane phase is decanted, and the frozen acid is washed with a few drops of hexane. Sometimes, an extra cleanup on a Florisil column is necessary, after the acid treatment. Before the injection into the GC, the volume is adjusted to 1 ml.

3.2.3 Eluation of PCB from the concentration column

The column is eluted with 40 ml of absolute ethanol. The eluate is collected in a conical beaker (125 ml) and evaporated to 2 ml. The concentrated eluate is then decanted into a measuring flask (100 ml) and the beaker is washed with 2 ml of hexane, which is added to the eluate. The flask is now cautiously filled with distilled water and the hexane phase is transferred to a Florisil column with anhydrous sodium sulfate for cleanup. Another 2 ml of hexane is added to the measuring flask, and the flask is turned up and down about five times. This second hexane portion is added to the Florisil column when the liquid level has fallen to the top of the bed. The cleanup is then completed as described above.

3.3 Instrumentation and conditions

A special made chromatograph fitted with Varian tritium electron capture detector and electrometer was used. Lately this GC has been exchanged and we now use a Hewlett-Packard 5713A with ^{63}Ni ECD.

Injector temperature, 230°C
Detector temperature, 220°C
Column temperature, $180-185^{\circ}\text{C}$
Gas flow (nitrogen), 25 ml/min

GLC-columns, made of pyrex glass with an i.d. of 1.8 mm, silanised.

1.5% OV 1 on Chromosorb W (80-100 mesh), 70 cm
1.5% OV 101 on Chromosorb W (80-100 mesh), 70 cm
2% XF-1150 on Chromosorb W (80-100 mesh), 70 cm
1.5% SP 2401 on Supelcoport (80-100 mesh), 145 cm

The columns were interchangeable with a LKB 9000 combined gaschromatograph-massspectrometer and used in MID analyses.

GLC-columns for HP 57.3 A, made of pyrex glass with an i.d. of 1.8 mm, silanised.

8% QF 1 + 4% SF 96 (67:33) on Chromosorb W (100-120 mesh), 160 cm
3% SP 2300 on Varaport 30 (100-120 mesh), 140 cm

3.4 Determination of absorption and desorption efficiency

A series of experiments has been performed to determine the efficiency of the sampling method, as well as the methods for extraction, elution, and clean-up.

3.4.1 Activated charcoal

Adsorption on activated charcoal is a common procedure in the sampling of volatile substances. It has also been used in determinations of chlorinated hydrocarbons in water. (11) The charcoal is desorbed with chloroform. (11. 12)

Our tests were made with columns (the same as the concentration column) with a 4 mm layer of activated charcoal between glass wool wads. 2 μg PCB in 40 μl n-hexane was injected into the charcoal, and air was sucked through the column for 3 minutes.

As we knew that chloroform interferes in GC-EC analysis, we tried both elution with n-hexane, and soxhlet extraction in 24 h with n-hexane. None of the methods gave a satisfactory result. With soxhlet extraction in 24 h with chloroform the desorption efficiency was 100%. (3)

3.4.2 Concentration column

2 μg of PCB in 40 μl of n-hexane was injected into concentration columns. The columns were eluted with abs. ethanol and the eluates were treated as described above. The recoveries varied between 82% and 90%.

In order to check the capacity of the Apiezon to retain the applied substance, 0.25 m^3 and 0.50 m^3 of gas from the combustion of light fuel oil was sucked through the pretreated columns. (The combustion gas was proved to

be free from PCB.) The recoveries varied this time between 83% and 91%. (3)

In two complementary recovery experiments outside of the laboratory, two sampling equipments were connected in parallel to one probe, inserted into the flue of a municipal incinerator. The tests were carried out in two ways:

- 1) 500 ng PCB in n-hexane was injected into one of the Apiezon columns.
- 2) One of the precipitators was filled up to the 10 mm level with activated charcoal, into which 500 ng PCB in n-hexane had been injected.

The recovery from the column was 87% and from the activated charcoal 98%, after subtraction of the PCB added from the incinerator gas.

The efficiency of the Apiezon to retain gaseous PCB was also investigated. For this purpose two concentration columns were connected in a series with a precipitator on top. PCB was applied on a glass wool wad in the precipitator and gasified at the same time as air was sucked through the columns. The two columns were eluted separately and the analyses showed that more than 99% of the PCB was retained by the upper column.

The combustion gas from an incinerator always contains some quantity of water, mostly acid. For that reason, it remained to be proved if the Apiezon column could absorb PCB from water. Water solutions of PCB (Clophen A 60), with 500 ng and 5 µg in 100 ml water and approx. 1% hexane and 0.5% abs. ethanol were prepared. In some tests the solution was made slightly acid (10^{-3} - 10^{-4} M HCl) to resemble the condensed water formed by incinera-

tion of waste containing PVC.

The water solution was kept in a special funnel with Teflon stopcock (Rotaflo) allowing small drops to fall into the concentration column at the same time as air was sucked through the column. It has been reported (13) that PCB in water is adsorbed to glass surfaces. Similar results were obtained in our own experiments. After each experiment the funnel was therefore rinsed with hexane and the adsorbed amount of PCB was estimated. In this way it was possible to calculate the amount of PCB that actually passed through the column.

The recovery was 80% for the neutral water solution and 95% for the acid solution. Thus, the Apiezon column could well be used in sampling, even when water is present in the gas. (4)

3.5 Sources of emission

3.5.1 Municipal incineration

When the aforementioned method for determining PCB in flue gases became available in 1972, a series of measurements was started.

Incineration of municipal refuse was already suggested as one possible source (1). Industrial use of PCB in the manufacture of capacitors and transformers might be another.

In 1972 and 1973, measurements were carried out in nine different municipal incinerators for household wastes, hospital wastes, and sewage sludge. In some cases, incineration of waste oil was included.

The results and type of waste and equipment are given in table 1.

The total emission of PCB in Sweden from municipal incinerators can be estimated to be less than 10 kg/year, 75% of which is particle bound. Dehydration of sewage sludge by means of incinerator gases may cause an emission of PCB of the same magnitude.

Compared with an estimated fallout in southern Sweden, based on figures published by Södergren (1), these two sources of emission account for 1 to 2%.

3.5.2 Industrial use

One transformer factory was investigated. In the air evacuated from the autoclaves, the PCB content (Ascarell 3, about 30% chlorine) was about 2.5 mg/m^3 . Inside the factory, levels of 0.1 mg PCB/m^3 were measured about 5 m from the autoclaves.

3.5.3 Burning of waste oil

Analyses of waste oil have revealed the occasional occurrence of PCB. Last year, a series of measurements was carried out in different plants where waste oil is burned.

The waste oil is dewatered and centrifugated or filtered before use.

In three of the plants, waste oil from filling stations is used as heating oil. The amounts used range from 2 to about 300 m^3 /year. The amount of PCB in the flue gas was less than 200 ng/m^3 .

Sometimes, waste oil is used as support fuel in incinerators for household wastes and sewage sludge or in bark burners.

Analysis of the flue gas indicates that the emission of PCB does not depend on whether waste oil is used. There are greater differences between different plants incinerating only household wastes than between those using waste oil and those not.

In no case in 1974 did the PCB emission from the investigated plants of this kind exceed $1 \mu\text{g}/\text{m}^3$ flue gas.

These sample tests indicate that even rather inefficient burning of pretreated waste oil does not give rise to significant emission of PCB; that is, of the same magnitude as emissions from municipal incinerators.

3.5.4 Burning of scrap cables

PCB has been used as plasticizers and as oil in insulating paper in cables. Plants where cables are burned at low temperature to recover copper and lead could consequently be possible sources of PCB emission.

To date, three plants have been investigated.

In plant A, a total of 5,000 tons of cables are treated each year. Half of this amount is decomposed mechanically; the other half is burned. This means that 12 to 13 tons are burned every 24 hours.

The flue gas analysed contained about $400 \text{ ng PCB}/\text{m}^3$, as Aroclor 1254.

Plant B is equipped with three furnaces having after-combustion chambers and multicyclone filters. The flue gas is washed with recirculating lye. This lye was not exchanged between the test occasions (9 months a part). The capacity of this plant is 10 tons of cables per shift.

The amount of PCB in the flue gas ranged between 10 and 330 $\mu\text{g}/\text{m}^3$ on the first test occasion and between 35 and 80 $\mu\text{g}/\text{m}^3$ on the second.

The distribution between gaseous and particle bonded PCB constitutes the greatest discrepancy in this investigation. On the first occasion, 58 to 97% of the PCB was particle bonded, whereas on the second occasion, only 0.2% was particle bonded.

The annual PCB emission can be estimated to be 2.7 kg.

By means of a GLC-MS analysis of a flue gas sample, the following substances were identified:

- PCB with 4 to 8 chlorine atoms
- Polychlorinated naphthalenes with 3 to 5 chlorine atoms
- Hexachlorobenzene (HCB)

On the second occasion, samples of the recirculating lye were analysed. The solution contained about 0.2 μg PCB/l, and the particles filtered off contained 2.0 μg PCB/g, as Aroclor 1254. With a particle content of 2.4%, the total amount of PCB was about 5 $\mu\text{g}/\text{l}$, or 5 ppm.

The investigation of plant C included not only analysis of the flue gas but also of airborne fallout, vegetation (spruce needles), and voles from the neighbourhood.

The plant is equipped with 2 + 8 furnaces and an after-combustion chamber with heating oil as fuel.

The gas chromatograms from the flue gas samples are very complex, and the identifications of PCB and HCB were carried out by means of GLC-MS with MID technique. This technique was also used for the quantification of

deca-, nona- and octachlorobiphenyls, which were present in an amount of 2 to 35 $\mu\text{g}/\text{m}^3$ flue gas.

To calculate the total amount of PCB, it was necessary to use a perchlorination method. (14) Compared with Arochlor 1254, the total amount of PCB in the flue gas was about 80 $\mu\text{g}/\text{m}^3$, of which 88% was particle bonded.

No paper-insulated cable was burned during the sampling periods.

The yearly emission can be estimated to be 2 kg.

During the period from September 10th to October 9th 1974, airborne-fallout sampling was carried out in nine places around the plant. The sampling equipment consisted of the already described concentration column (i.d. 20 mm) and precipitator now completed with a glass funnel. The fallout area is 0.0314 m^2 .

During the sampling period, the precipitation was 85.8 mm, which means that a rainwater volume of 2.7 l is filtered through the column.

The PCB content (Arochlor 1254) in the fallout ranged between 5 and 103 $\mu\text{g}/\text{m}^2$ /month. No DDT was detected, although HCB was identified in some of the samples.

Fifty-five voles from the area were trapped between September 10th and 12th, 1974. Extraction, cleanup, and analyses were carried out as described by Jensen et al., 1972. (15) One gram of hindleg muscle tissue was used.

These analyses are not yet completed, and the gas chromatograms are rather complex, with peaks overlapping the PCB peaks. Where PCB has been identifiable, it has proved to be Arochlor 1254 in amounts of 1 to 11 ppm (fat-weight bases).

HCB has been identified by means of GLC-MS in amounts of 0.3 to 6.8 ppm (11 voles).

4. CONCLUSIONS

The measurements performed permit the following conclusions to be drawn:

The presence of PCB in airborne fallout indicates that emission of PCB still exists, in spite of the restrictions.

The fact that the concentration of PCB in biological samples seems to be increasing supports this conclusion.

The measurements performed so far have not revealed the main sources of PCB emission.

The presence of decachlorobiphenyl (not present in technical PCB) in the flue gas from incineration of scrap cables indicates that chlorination may occur during the burning.

Dr. Anders Laveskog, National Swedish Environment
Protection Board, P.O. Box, S-171 20 SOLNA, Sweden.

Anne Lindskog, M.Sc., Swedish Water and Air Pollution
Research Laboratory, Box 5207, S-402 24 GOTHENBURG,
Sweden.

PCB content in gases from incinerators

Type of wastes	Year	Particle bound	ng PCB/m ³ gas Gaseous	Total	Remarks	
I	1972	37- 78	28- 203	79- 259	(1)	
	1973	n.d.	10- 353	10- 353		
	1972	77-1614	31- 343	108-1901	(2)	
	1973	25- 47	10- 27	25- 74		
	1973	50- 173	10- 80	73- 173	(1)	
	1973	25- 130	32- 591	-	(2)	
	II	1972	243- 716	2200-6900	2440-7600	
		1973	29- 498	1578-3457	1600-3900	
1973		121-3131	134-1326	1341-3265	(3)	
III	1973	35- 95	22- 400	60- 495	(3)	

I Household wastes

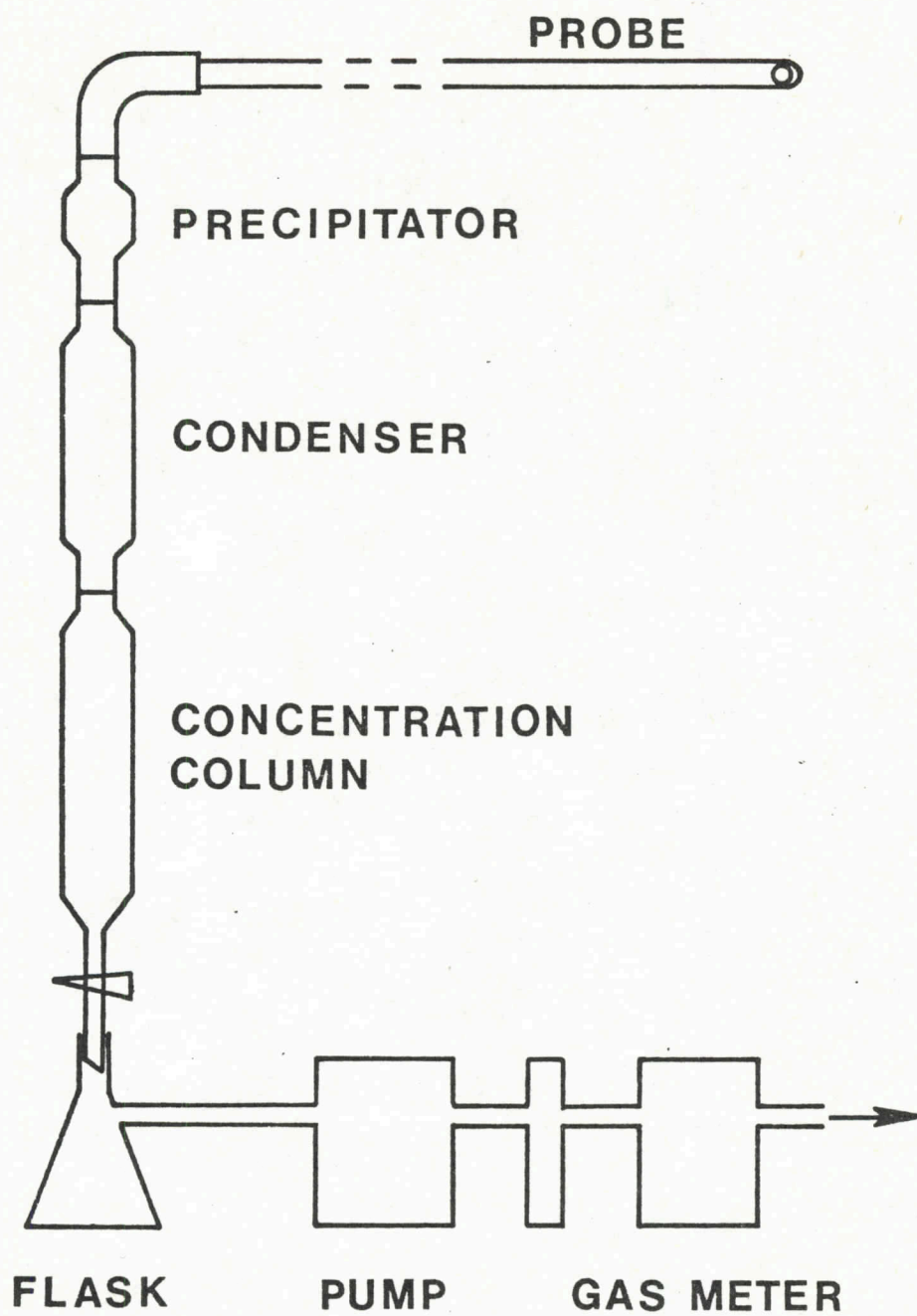
II Drying of sewage sludge with gases from burning of household wastes

III Sewage sludge + oil waste

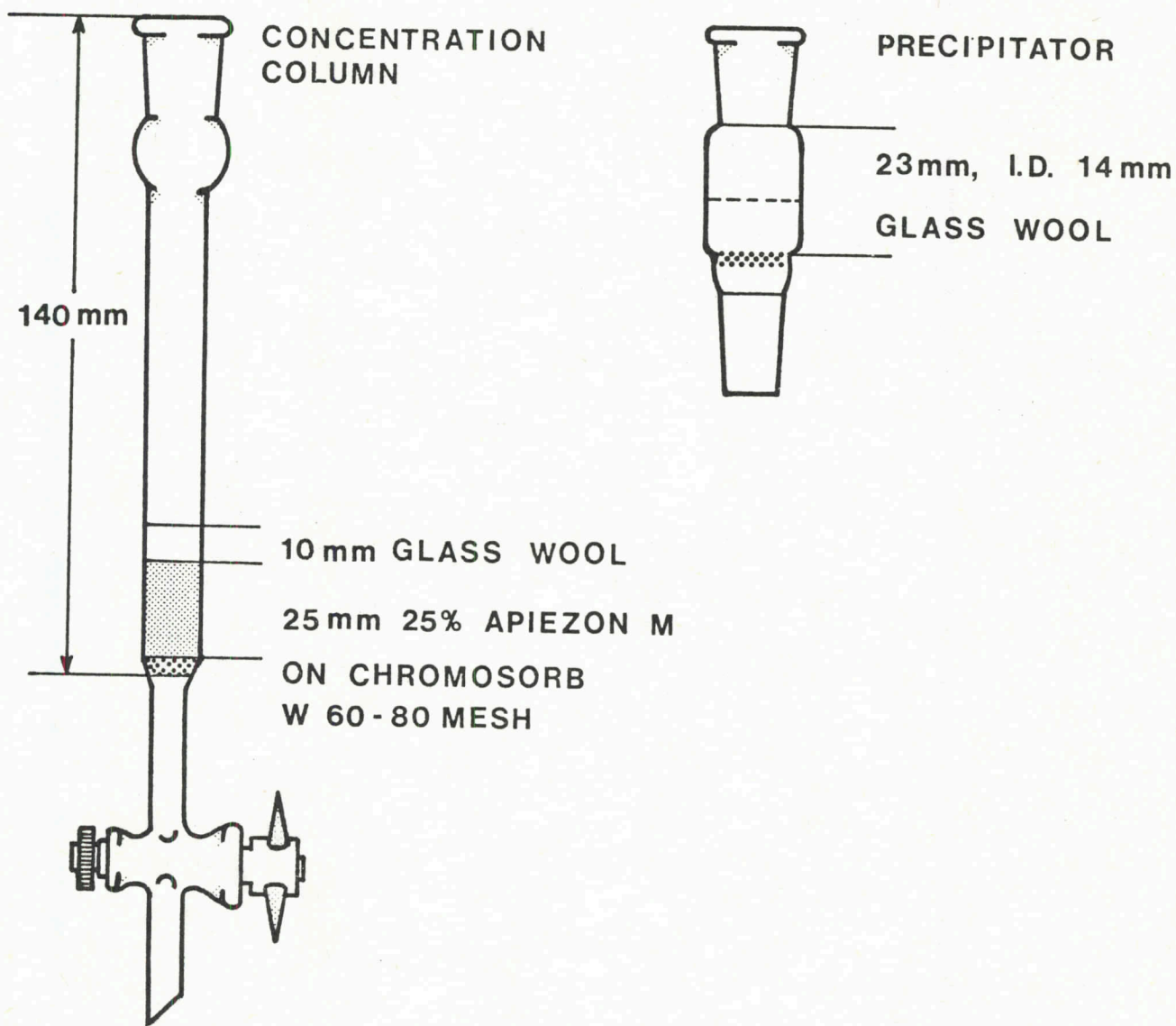
(1) Plant equipped with multicyclon filter

(2) Plant equipped with electro filter

(3) Plant equipped with water scrubber



FIGUR 1 SAMPLING EQUIPMENT



FIGUR 2

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