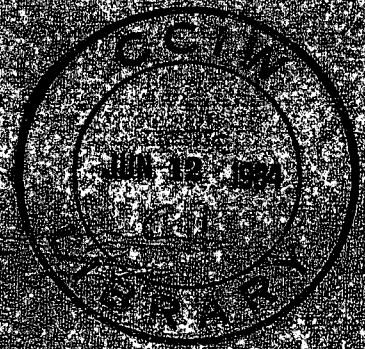


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Water Quality Sampling Methods  
at Niagara on the Lake

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Direction  
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## 1. INTRODUCTION

### 1.1 Background

Changes in the chemical characteristics of the Great Lakes have been caused primarily by the rapid increase in nutrient and material loadings since 1900 (Beeton - 1965). Therefore, the amount of material being discharged into the Great Lakes is vital information for the management of Great Lakes Water Quality. The Niagara River, the only outflow for Lake Erie, accounts for 50% of all incoming sediment materials to Lake Ontario (Kemp 1976) and could conceivably also be the largest single source of materials. The strategic location of this river provides an ideal situation to monitor the amount of material transported between Lake Erie and Lake Ontario.

In 1975, the Water Quality Branch - Ontario Region (WQB-OR) initiated a daily sampling program at Niagara on the Lake. The primary objectives of this program were:

- (i) to obtain annual estimates of Niagara River loading to Lake Ontario
- (ii) to develop sampling methodology for tributaries
- (iii) to establish long-term trends in various water quality parameters.

In 1976, the Surveillance Subcommittee of the Great Lakes Water Quality Board of the International Joint Commission (IJC) recommended that tributary loadings be part of an overall strategy in Great Lakes Surveillance (IJC 1976).

By 1978, increasing public concern had developed over the recurring detection of persistent, bioaccumulating, toxic substances, especially PCB's and mirex in the biota and bottom sediments of Lake Ontario. Levels of these compounds in the lake water are usually below or near the detection limits of the analytical methods. Therefore, WQB-OR decided to measure the levels of organic contaminants in the

suspended sediments of the Niagara River as a possible source of toxic organics to Lake Ontario. In 1978, a weekly sampling program was initiated using the already established sampling system and a Westfalia continuous flow separator for collecting suspended sediments.

The purpose of this report is to describe the program, the sampling system used and to document the changes which occurred to this project over the years.

## 1.2 Sampling Site

Five water quality surveys of the Lower Niagara River were conducted in 1974 to evaluate cross-stream variations. Three cross stream ranges of stations were sampled both upstream and downstream of the proposed sampling site at the Niagara on the Lake Water Treatment Plant (Figure 1). Results indicated that samples collected at Niagara on the Lake were representative of the water flowing into Lake Ontario. It was also found that there was no lateral or cross-sectional variation in the water chemistry at the mouth of the Niagara River due to the thorough mixing at Niagara Falls and in the whirlpool and the few known sources below the whirlpool (Chan 1977). This location was ideal because of its ease of accessibility, and readily available source of power. With the cooperation of the Regional Municipality of Niagara, the water intake shed of the Water Treatment Plant at Niagara on the Lake was chosen to house the sampler.

## 1.3 Chemical Constituents Analyzed

### 1.3.1 Water

Daily water samples are analyzed for the following parameters: pH, conductivity, turbidity, and nutrients. Weekly water samples are analysed for major ions, total trace metals, extractable trace metals and cyanide. A detailed listing of parameters measured is given in Table 1. Since 1980, weekly samples have been collected for the analysis of the PCB and organochlorine residues listed in Table 2.

### 1.3.2 Suspended Sediments

Suspended sediments have been collected on a weekly basis since 1979. These samples have been analyzed for a wide variety of organic contaminants including PCB's, organochlorine compounds, chlorobenzenes, pAH's, phthalates and particulate organic carbon and nitrogen (Table 2). Also total trace metals and acid extractable trace metals analysis have been completed on selected samples (Table 1).

## 2. SAMPLING SYSTEM

The sampling system consists of four components: intake line, pump, daily water sampler, and suspended sediments sampler (Figure 2). The intake line and the pump are submerged under water and the samplers are housed on the river bank.

### 2.1 Intake Line

The intake line (Figure 2), composed of a 1.9cm I.D. black, polyethylene tube was placed in the river, anchored to shore with a 0.6cm steel cable and weighted so as to settle onto the bottom of the river. This polyethylene tube was connected to an anchored spar buoy (Figure 2) which allowed the sample intake to float freely up from the river bottom. The intake line extended to a point approximately 30 m. from shore and was located in the main current of the Niagara River. This intake line extended up the spar buoy to a distance of about 6 m from the river bottom and 13 m below the river surface. The end of the intake line was then extended about 2 m from the spar buoy with a piece of polyethylene tube, plugged at the end. A series of 0.3cm holes was drilled from the end towards the spar buoy for a distance of about 1 m. The small holes act as a coarse filter, preventing fish and weeds from entering the intake pipe.

This system was required to collect samples in winter, therefore, the first 8 m of the intake tube from the sampling shed to the pump below the river surface was wrapped with a standard eavestrough heating cable.

Prior to 1980, the pump was activated every hour to keep the intake line from freezing and also to keep the intake line clean. In spite of these precautions, the intake line often was plugged with algae and weeds. In 1980, a 5.0cm, in-line, polyethylene Y-filter with a polyethylene screen of about 0.3cm pore size was installed immediately before the sampler. This filter was quite successful in reducing sampler failure due to plugging. It is cleaned once per week or as necessary.

## 2.2 Pump

Originally, in 1975, a submersible Little Giant, Model 3E - 12NR pump was used to collect daily water quality samples. It was located about 3m from shore on the river bottom. After analysis of suspended sediments was initiated in 1978, it became obvious that oil contamination was occurring. The oil seal on this pump was prone to wear, thus causing oil contamination on suspended sediment samples.

In June 1979, the Little Giant pump was replaced with a Moyno helico pump, Model 30101, Type FS. This pump, although reliable, economical and easy to service had difficulty in drawing water samples up from the river (about 10 feet head). Another difficulty encountered with this pump was in maintaining a constant prime.

Due to these difficulties, this pump was replaced with a March, Model 5CMD, magnetic drive submersible pump in July 1981. This pump eliminates the need for priming and, since it is a magnetic drive pump, the risk of sample contamination from lubricant leakage is eliminated.

### 3. SAMPLERS

#### 3.1 Daily Water Quality Sampler

An automatic daily sampler was designed and built by the Engineering Services Section of the National Water Research Institute. This sampler, (Figures 3 and 4) controlled by a series of timers (Figure 5) is designed to collect samples on either a daily or hourly basis depending on program objectives. The sampler holds 24 - 2L polyethylene bottles. The timer turns on the pump about one half hour before the sample is to be taken (for daily samples this was chosen as 11:00 AM) to flush the intake lines and pump. The timer activates the sampler arm for 4 sec to move it from drain to sampling mode. The sampler remains in sampling mode for about 4 minutes (enough time to allow the 2L bottle to flush and fill) and then moves to the drain mode ready for the next sampling cycle to begin.

In 1980, the sampler was slightly modified to contain only 12 sample bottles, since hourly sampling was no longer necessary. This modification decreased the possibility of contamination from sample to sample due to the closeness of the individual sampling inlets. Now the sampler has alternate drain and sampling inlets. Also to reduce the frequency of algae and weeds clogging the intake line the pump was activated only once per day at about 10:30 AM before sampling at 11:00 AM. This time was chosen because no diurnal variation was observed for water chemistry parameters in four, 24-hour surveys carried out at this location in 1974-75 (Chan 1978).



Further changes occurred in Nov 1981 when the entire sampling system was moved into a portable trailer at the site. The advantages of this trailer are that it is cleaner (reduced chance of contamination), warmer (reduce possibility of sampler and/or intake freezing) and it has an adequate 220 V power supply required for reliable operation of the Westfalia Separator.

### 3.2 Suspended Sediments Sampler (Westfalia Separator)

Using the intake line and pumps as previously described, suspended sediment sampling started in 1978. A Westfalia continuous flow separator (Figure 6), Model KA-02-06-075 with a four chamber all stainless steel bowl, identical to that used by (Thomas 1978), was used for collection of the suspended sediments. Recovery of suspended sediments as determined by pre and post filtration is 90-95% effective for this centrifuge at a flowrate of 6L/min. Particle size determination showed that as much as 70% of the total solids recovered were finer than 0.2 um (Allan 1979). Bowl speed when driven by a 1745 RPM motor is 9470 RPM (Centrico).

In comparison, during 1981 surveys of the Niagara River, particulate carbon and nitrogen samples were collected at two different stations with flowrates varying from 2-8L/min. These data (1) indicated recoveries of both particulate carbon and nitrogen from 79% at 8L/min to 89% at 2L/min. Using a flowrate of 6L/min the mean recovery of particulate nitrogen was 81% and the mean recovery of particulate carbon was 83% for the eleven samples analyzed.

The centrifuge, as received from Centrico, was equipped with a variable speed, belt driven drive train. In 1981 this motor was replaced with a direct drive, 1.5 HP, repulsion start-induction, BALDOR Model, NO. R-1392, 230V. single phase motor.

Previous to 1981, suspended sediment samples at Niagara on the Lake were collected for a period of about four hours on a weekly basis. With increasing requirements of sample material for analysis, storage

(1) K. Kuntz, WQB-OR unpublished data.

etc, sampling was increased to approximately 24 hours. Also in 1981 a Flow Technology Inc. flowmeter totalizer, Model SRT-1, with Omniflo Turbine Transducer was added to accurately measure the total flow through the centrifuge.

#### 4. SAMPLE HANDLING PROCEDURES

##### 4.1 Daily Water Samples

Samples are collected on a daily basis by the automatic sampling system described previously. Each week WQB personnel collect samples from the sampling site for analysis. While there, additional weekly samples such as trace metals, major ions, CN, Hg, pesticides, As, Se and radioactivity samples are collected as required in specially prewashed bottles as described in Table 3.

These samples are returned to the WQB-OR lab in Burlington. Daily nutrients and weekly samples such as trace metals are split, preserved, etc. as required (see Table 3 for details) and sent to the lab for analysis. Physical parameters such as pH, specific conductance and turbidity are also analysed upon returning to the lab. Detailed methods of analysis are described in the, W.Q.B. "Analytical Methods Manual" (Environment Canada 1979).

##### 4.2 Suspended Sediments

Since 1978, weekly suspended sediment samples have been collected for organic contaminants analysis. Once analyses for these samples were received, it became quite clear that some gross contamination by oils was occurring. Checks of our sample handling methodology revealed that one possible source of this contamination was the freeze drying process used to remove excess water from the suspended sediments.

Hence, pressure filtration, using a Sartorius Model SM 162-70, stainless steel, teflon coated pressure filter was substituted for freeze drying and sample contamination problems were eliminated. Samples, after collection from Niagara on the Lake, are removed from the stainless steel

centrifuge bowl by scraping and washing with distilled water. This solid-liquid slurry is then transferred to the pressure filter and filtered onto a 5 micron (pore size), 142 mm diameter, membrane filter paper (Millipore), using 50 p.s.i.g. pressure from a nitrogen cylinder as pressure source. The solid residue collected on the filter is then air dried in a desiccator at room temperature with Drierite ( $\text{CaSO}_4$ ) as drying agent. When dried, the samples are ground with mortar and pestle so that homogeneous samples are obtained. About 5 g of this sample is then submitted to the WQB - Organic Analysis Lab for analysis. These analyses are carried out according to methods described in the WQB - "Analytical Methods Manual" (Environment Canada 1979). Any remaining sample is stored dry, in the dark, at room temperature for future analysis.

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TABLE 1: Inorganic Compounds Analysed in Water and Suspended Sediment  
Samples at Niagara on the Lake

<u>Nutrients (Water)</u>	<u>Total Metals (Water)</u>
Total Phosphorus	Iron
Nitrate Nitrogen	Cadmium
Ammonia Nitrogen	Chromium
Total Kjeldahl Nitrogen	Copper
	Lead
<u>Major Ions (Water)</u>	Manganese
Calcium	Nickel
Magnesium	Zinc
Sulphate	Arsenic*
Chloride	Selenium*
Sodium	
Potassium	<u>Extractable Metals (Water)</u>
Total Alkalinity	Mercury*
	Aluminium
<u>Acid Extractable<sup>(1)</sup>Metals (Sediments)</u>	<u>Others (Water)</u>
Cadmium	Cyanide
Lead	Particulate Organic Carbon*
Cobalt	Particulate Nitrogen*
Copper	Radioactivity
Zinc	
Nickel	
Chromium	

(1) 0.5 N HCl digestion used

\* Analysis also done on suspended sediments

TABLE 2: Organic Compounds Analysed for in Suspended Sediments and Water  
at Niagara on the Lake

Chlorobenzenes (Sediments)

1,2 - Dichloro  
1,3 - Dichloro  
1,4 - Dichloro  
1,2,4 - Trichloro  
1,3,5 - Trichloro  
1,2,3 - Trichloro  
1,2,4,5 + 1,2,3, 5 Tetrachloro  
1,2,3,4 - Tetrachloro  
Pentachloro  
Hexachloro

Phthalates (Sediments)

Dimethyl  
Diethyl  
Di - n - Butyl  
Butyl - Benzyl  
Bis - 2 - Ethyl - Hexyl  
Di - n - Octyl

PAH's (Sediments)

Naphthalene  
Acenaphthylene  
Acenaphthene  
Fluorene  
Anthracene  
Phenanthrene  
Fluoranthene  
Pyrene  
Chrysene  
Benzo (a) Anthracene  
Benzo (a) Pyrene  
2 - Chloronaphthalene  
Dibenzanthracene

PCB and OC's (Water and Sediments)

PCB  
Aldrin  
Dieldrin  
Endrin  
 $\alpha$ -BHC  
 $\delta$ -BHC (Lindane)  
 $\alpha$ -Chlordane  
 $\gamma$ -Chlordane  
o,p-DDT  
p,p-DDT  
p,p-DDE  
p,p-TDE (DDD)  
Heptachlor  
Heptachlor Epoxide  
Hexachlorobenzene  
Mirex  
Methoxychlor  
 $\alpha$  - Endosulfan  
B - Endosulfan

TABLE 3: Summary of Bottle Cleaning Techniques and Preservatives for Water Quality Samples

<u>Parameter</u>	<u>Bottle Type</u>	<u>Preservative Used</u>	<u>Cleaning Techniques</u>
<u>Major Ions</u> (Ca, Mg, Na, K, SO <sub>4</sub> Cl, tot. Alk., SiO <sub>2</sub> , As, Se)	Polyethylene	none	Rinse once with high pressure tap water, then 10% HCl, then high pressure tap water, then twice with deionized water.
<u>Nutrients</u> (NO <sub>3</sub> , NH <sub>3</sub> , TKN,	Glass	none	Wash with 10% H <sub>2</sub> SO <sub>4</sub> , rinse with high pressure jet, rinse twice with deionized water.
<u>Total P</u>	Glass	1 mL 30% H <sub>2</sub> SO <sub>4</sub> / 100 mL sample	Same as for Nutrients above.
<u>Trace Metals</u>	Polyethylene	4 mL 50% HNO <sub>3</sub> /L	Wash with high pressure jet, 10% HNO <sub>3</sub> , high pressure jet, twice with deionized water (since 1979 bottles were soaked with deionized water spiked with 4 mL of 50% HNO <sub>3</sub> /L prior to use).
<u>Mercury</u>	Polyethylene	1 mL conc. H <sub>2</sub> SO <sub>4</sub> + 1 mL 5% k <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> (dithizone extracted) per 100 mL sample.	Wash with high pressure jet 10% H <sub>2</sub> SO <sub>4</sub> , high pressure jet and then twice with deionized water.
<u>Cyanide</u>	Polypropylene	1 mL 10% NaOH per 100 mL sample.	Same as for major ion bottles above.

TABLE 3: Summary of Bottle Cleaning Techniques and Preservatives for Water Quality Samples (Con't)

Parameter	Bottle Type	Preservative Used	Cleaning Techniques
<u>Organics</u>	Glass	none	Wash with soap and hot water, then rinse out soap with hot water and distilled water. Rinse two or three times with pesticide grade ethyl acetate and then with pesticide grade hexane. The bottle should then be drained and dried in oven at 130°C overnight. Clean bottles capped with solvent washed aluminum foil inside the plastic caps.



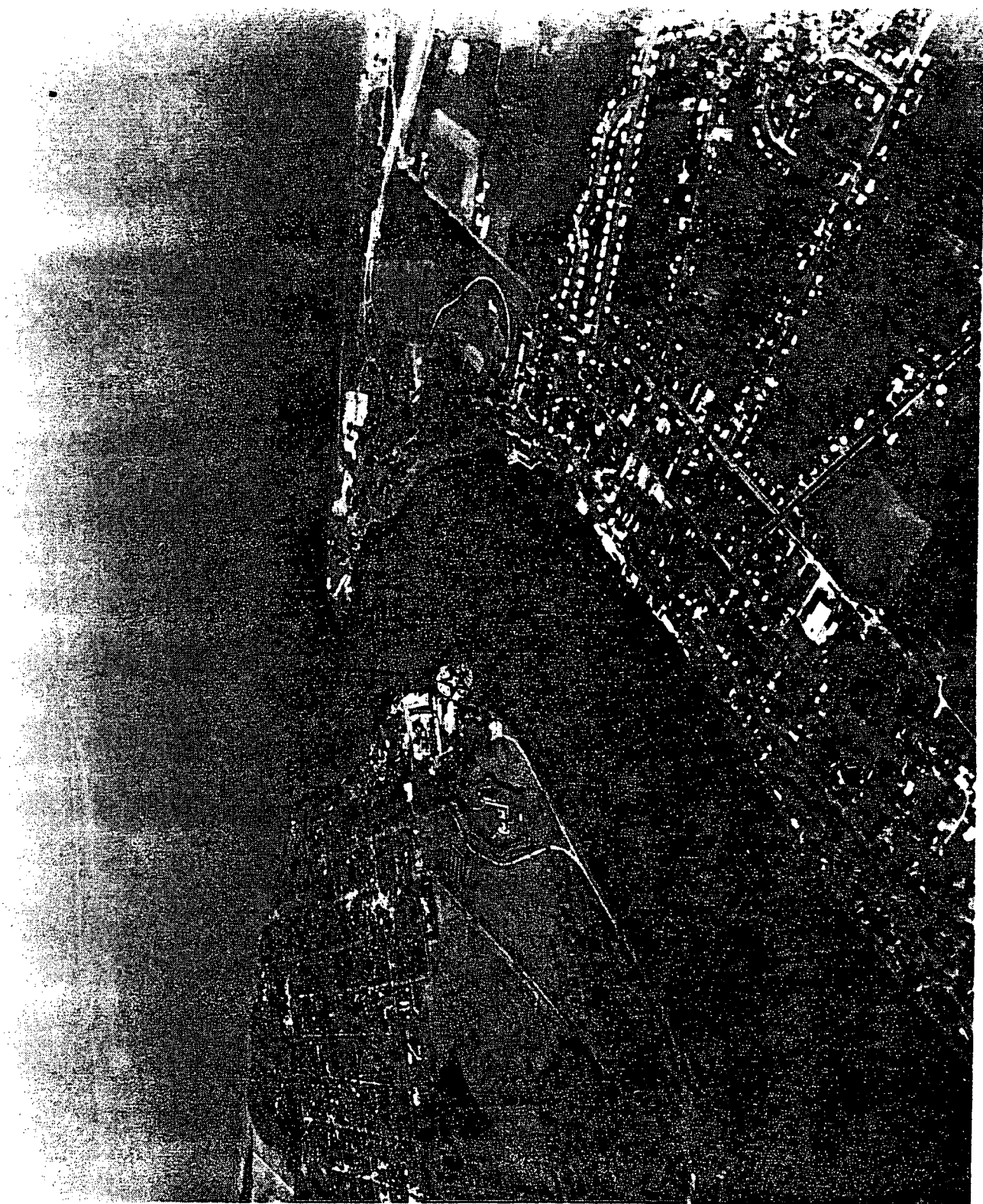
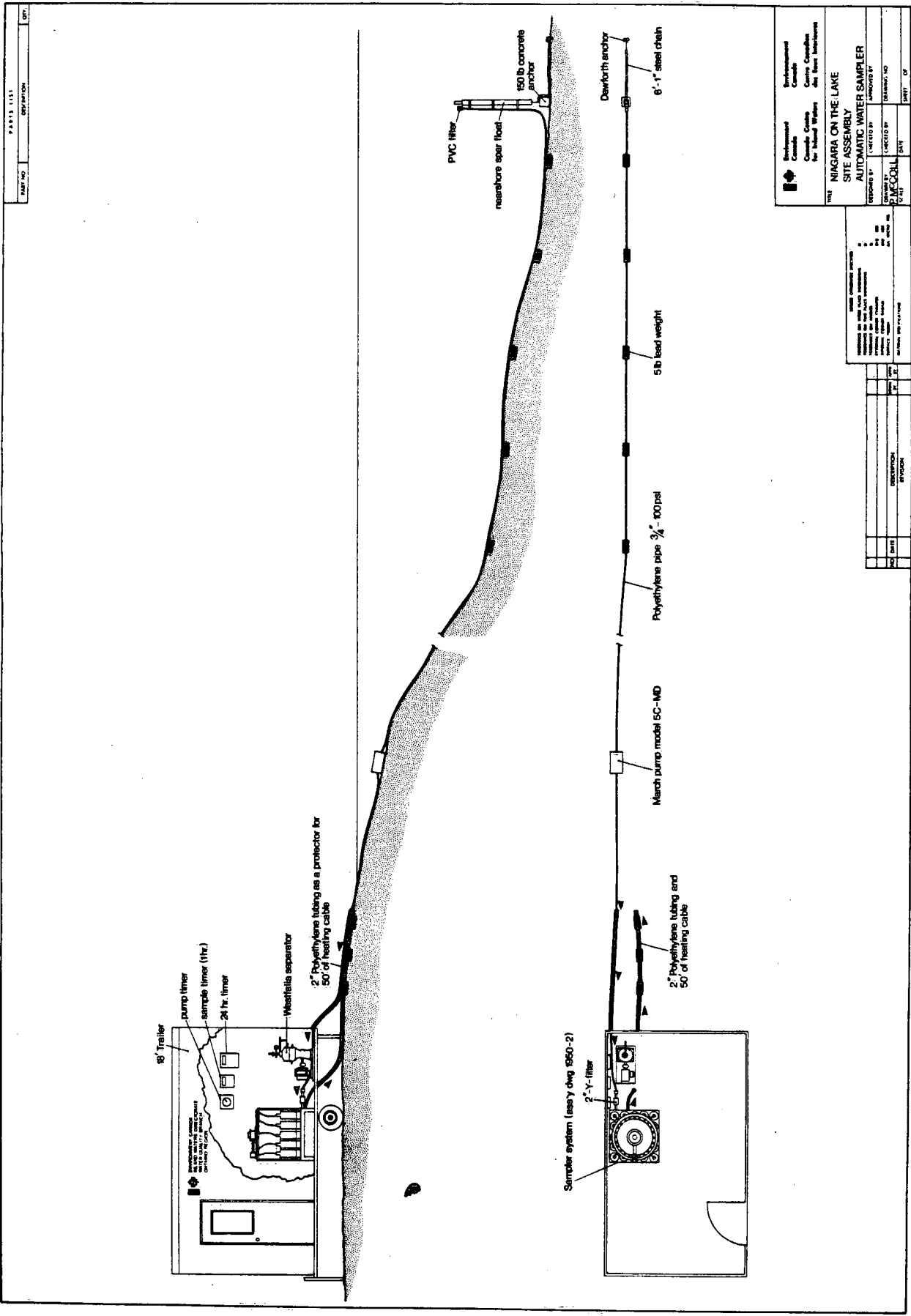


FIGURE 1 NIAGARA ON THE LAKE SAMPLING LOCATION ☆



PART NO.	DESCRIPTION	QTY.

Environment Canada	Environment Canada
Centre Canadien	Centre Canadien
pour l'écologie	for the Environment

<b>NIAGARA ON THE LAKE</b> <b>SITE ASSEMBLY</b> <b>AUTOMATIC WATER SAMPLER</b>	
DESIGNED BY	DATE
DRAWN BY	DATE
CHECKED BY	DATE
APPROVED BY	DATE

NO.	DATE	DESCRIPTION	BY/CHKD.

FIGURE 2 NIAGARA ON THE LAKE INTAKE ASSEMBLY

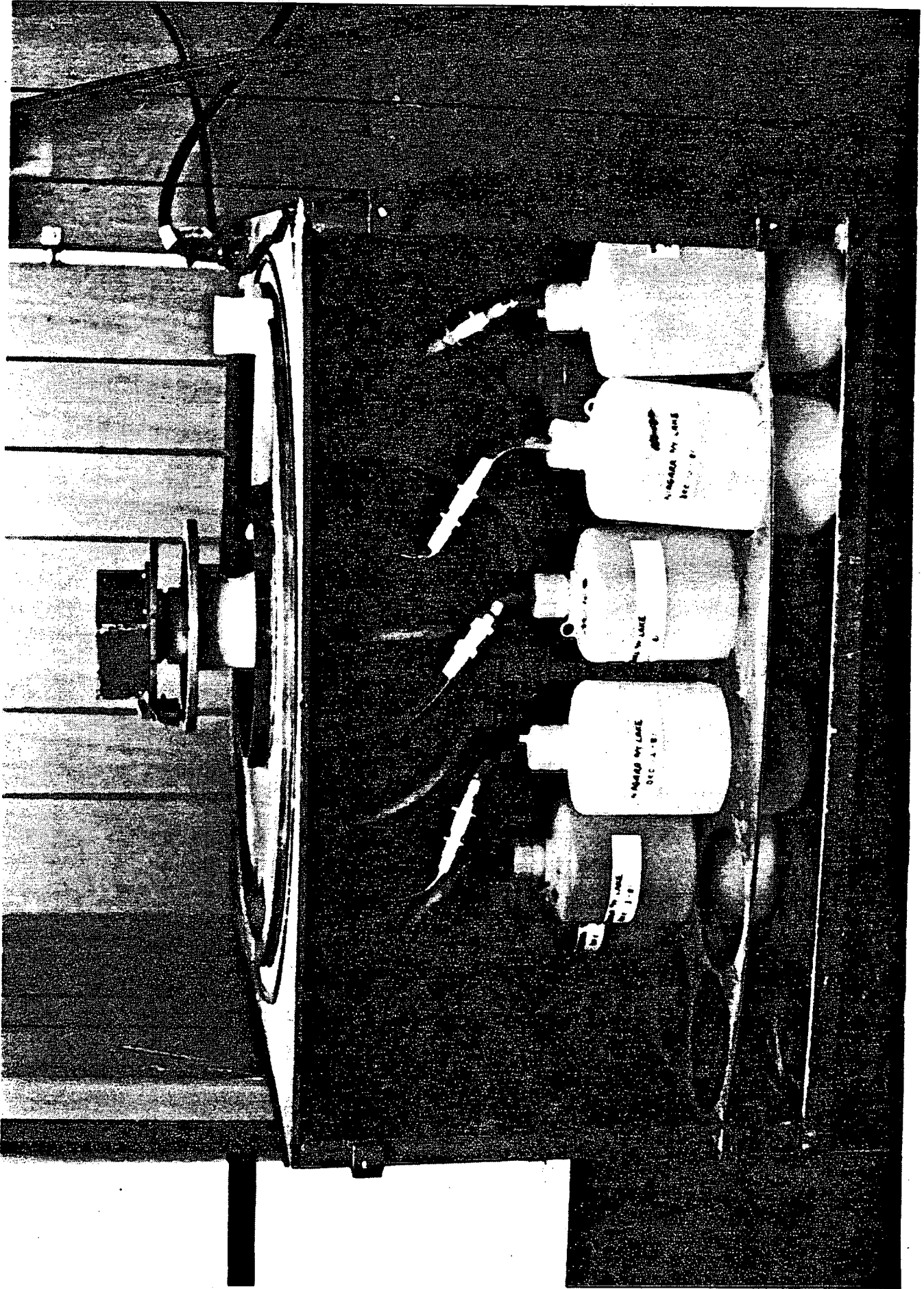


FIGURE 3 DAILY WATER QUALITY SAMPLER

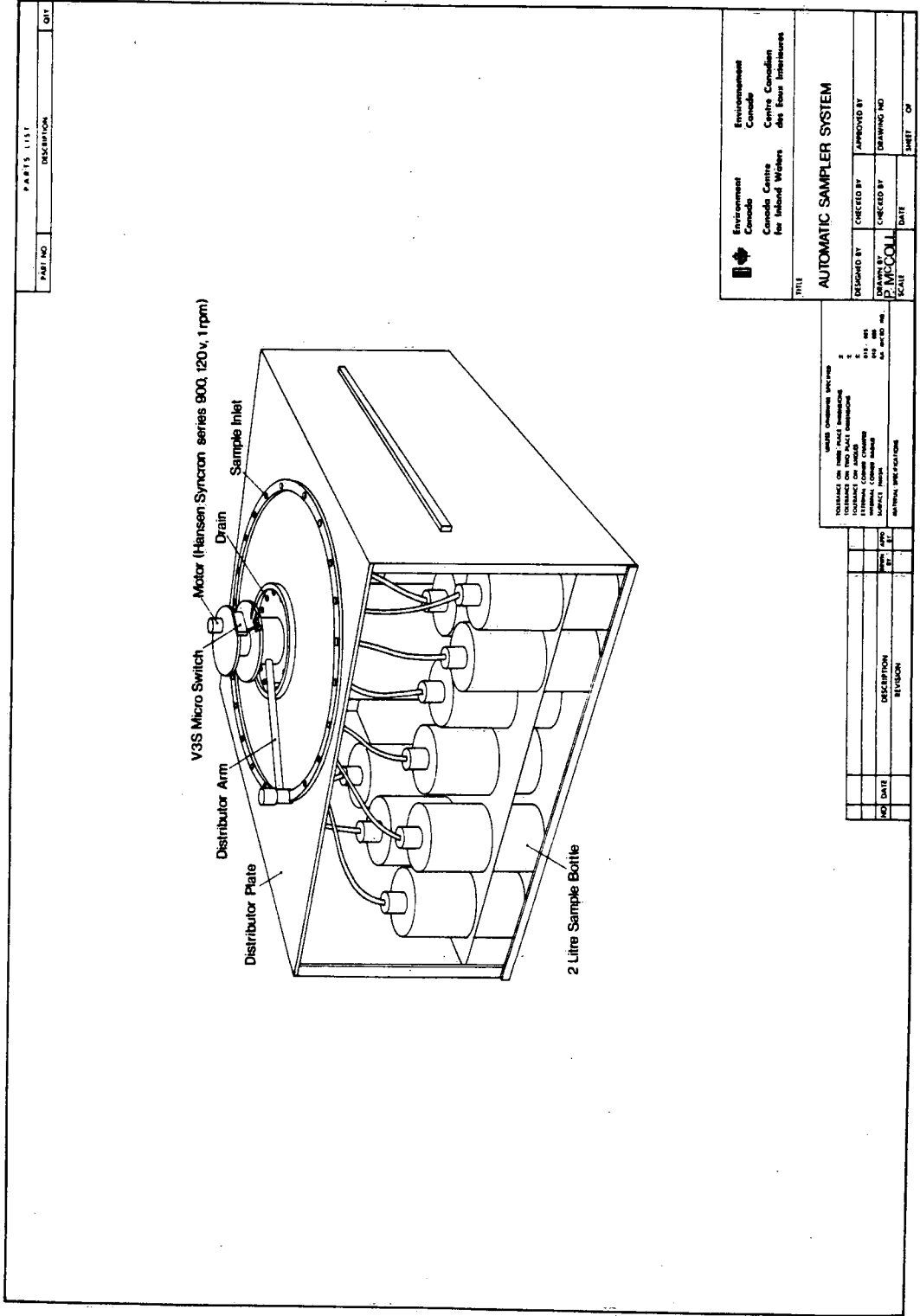


FIGURE 4 DAILY AUTOMATIC SAMPLER

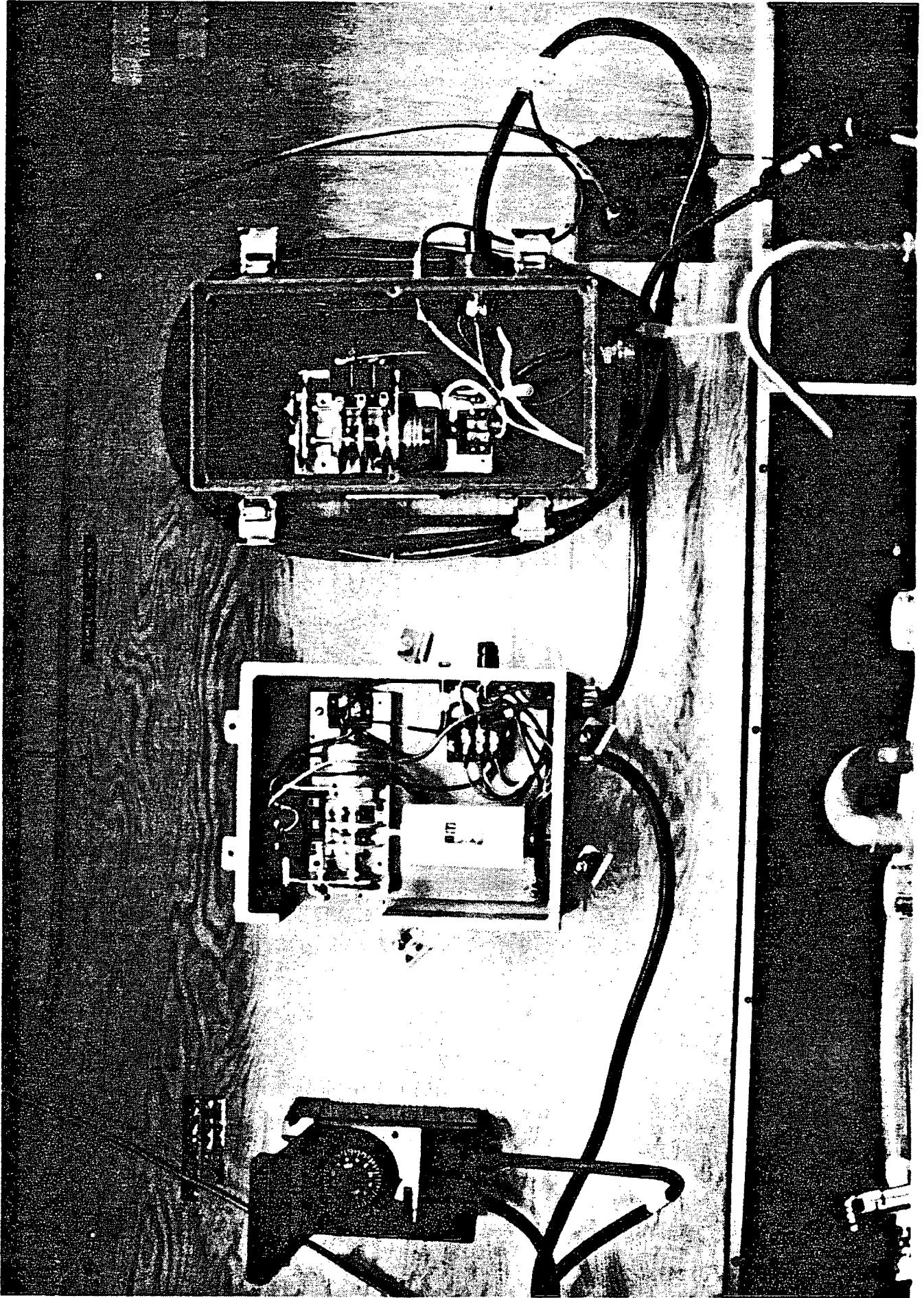


FIGURE 5 DAILY SAMPLE TIMERS

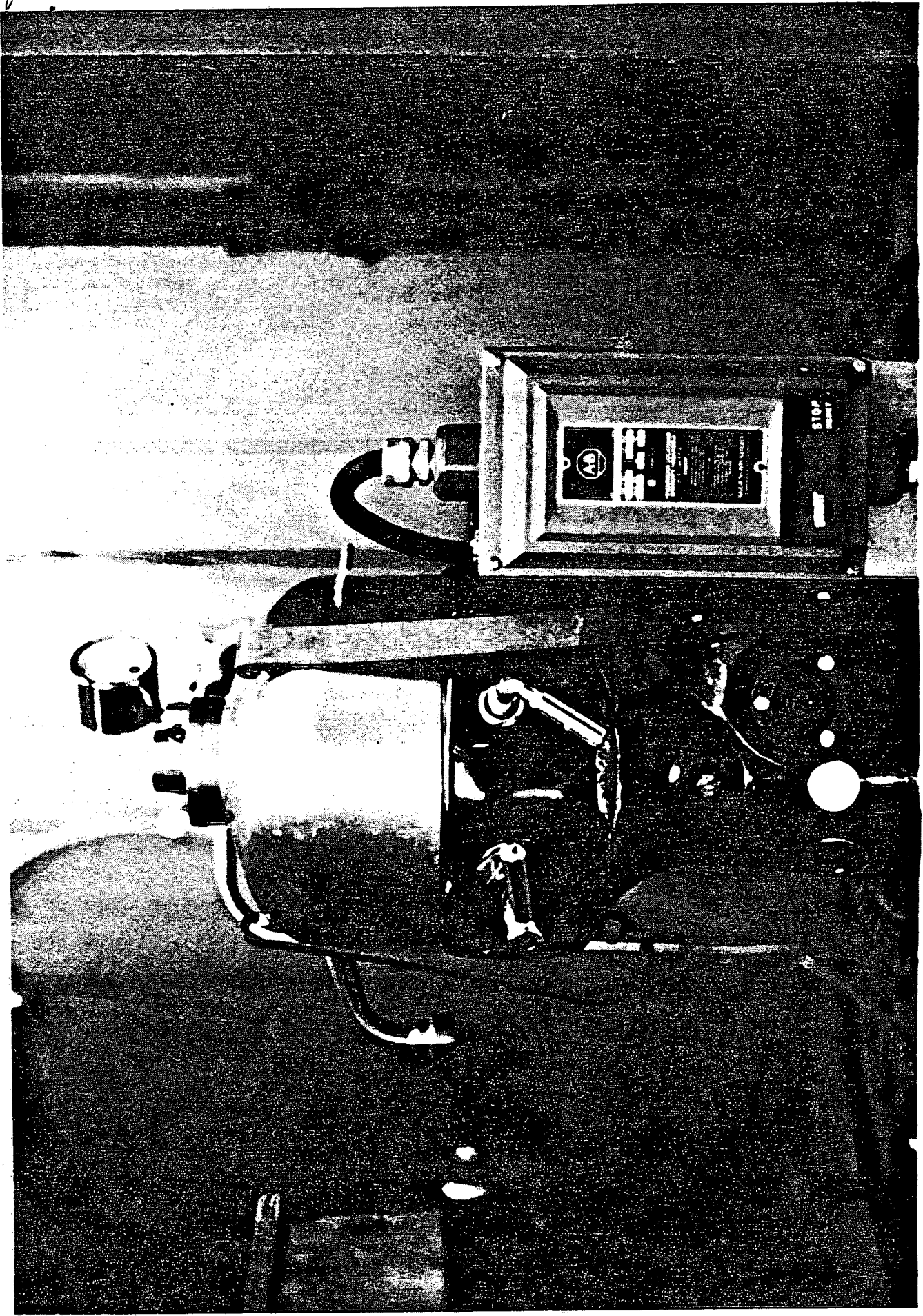


FIGURE 6 SUSPENDED SEDIMENTS SAMPLER (WESTFALIA SEPARATOR)

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