NBSIR 77-1227 (NBS)

Thermometry in the Control of Water Quality

Sharrill D. Wood

Temperature Section
Heat Division
National Bureau of Standards
Washington, D.C. 20234

February 1977

Issued: May 1977
Final Report

U. S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

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THERMOMETRY IN THE CONTROL OF WATER QUALITY

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THERMOMETRY IN THE CONTROL OF WATER QUALITY

Introduction

Despite the immensity of the water resources of the earth, it is obvious that the present level of human activity can significantly modify the quality of the water. Because most of the changes are detrimental, either directly to health, or indirectly to food supply, e.g., fisheries, recreation, etc., the uses of water must be regulated. The need for societal response is greatest in the industrialized nations, where the effect of large scale manufacturing and the unusually lethal quality of some of the output are the most threatening. Most typically, the quality of water is adversely affected, i.e., "polluted", by the introduction of undesirable chemicals and bacteria, but because of the effect on biological processes, it may also be adversely affected by the introduction of heat. It should be recognized, on the other hand, that some chemical or temperature modifications of water resources might be beneficial.

The scope of this document is limited to assessing national needs for thermometry in the testing and control of water quality, and the means by which the National Bureau of Standards could contribute more effectively in that area by research, calibration, voluntary standards participation and educational activities. Practically, this reduces to a consideration of the needed accuracies of temperature measurements for chemical analysis and thermal monitoring of water quality, and the NBS role to assure measurement reliability.

Water pollution is addressed by over 200 different regulations at the state level as well as by many federal laws. Many of these laws require some level of monitoring[1]. The most sweeping of these laws is PL 92-500, the Federal Water Pollution Control Act, which established water quality criteria and limits for pollutants in effluents. It requires that all industries, governmental agencies, and individuals that discharge effluents into navigable waters must monitor their own effluents for chemical and bacterial contaminants. In addition, the steam electric generating[2], cement[3], and sugar processing[4] industries are required to monitor (and control) their effluent temperatures[1]. State and local regulatory agencies also monitor water effluents to see that discharges conform to permitted limits.

One approximately complete record of the number of temperature measurements made each year as part of the monitoring effort is contained in STORET, the EPA file of water pollution data. From 1968 to 1973, there was an average of 167,000 temperature entries per year - 7% of the total 2.5×10^6 entries. Agencies of the Federal Government generated 70% of the data in STORET (EPA-25%, USGS-36%, others-9%). Furthermore, because of incomplete reporting, these 117,000 entries represent less than the actual number of Federal Government temperature measurements[1]. Some idea of the number of new private (industrial) temperature measurements expected in the near future can be developed from the fact that there are at least 65,000 discharge permits either approved or under consideration by EPA[1]. If 10% of these permits require measuring one temperature each week, some 340,000 temperature measurements per year will have to be made. Actually, power plants often measure temperature at several points, either daily or by averaging continuous readings periodically, so it is possible that many more than 340,000 new temperature readings will be made by industry each year.

An estimate of the large number of temperature measurements involved in water quality control can be attempted by considering the relative levels of instrumentation for pollution monitoring and the growth in monitoring activities. As shown in Fig. 1, the relative numbers of analytical instruments required in the "non-government" sectors dwarfs the government needs by 30-fold, and waste water analysis constitutes about half the total effort. In a dollar sense, the growth taking place can be inferred from the fact that the states alone had committed $14,000,000 for surveillance in 1972 and these costs are predicted to reach $60,000,000 by 1980. All of these data indicate that the number of temperature measurements for pollution monitoring can be expected to surpass an annual rate of 10,000,000 by 1980[1].

Temperature Measurements for Water Analysis

The commitment of national resources to water analysis is large and will grow and become more sophisticated as new technology is developed. The volume of tests that are temperature sensitive can be expected to increase in step with the growth in the level of water quality monitoring but with an additional (but unpredictable) increment as better reliability is sought.

At present, there are many water analysis tests that are sensitive to temperature. Tests utilizing or measuring reaction rates depend upon the temperature as do tests of several physical properties, and tests for bacteria require temperature control. Table 1 is a partial listing of temperature sensitive tests which appear in *Standard Methods - Water and Wastewater*, a collection of recommended analytical procedures, which is published jointly by the American Public Health Association, the American Water Works Association, and the Water Pollution Control Federation[5].

In many tests, no standard temperature is required and temperature sensitivity is taken into account by running standard samples concurrently with the sample under study. There are many tests in which the compound of interest is either precipitated (for which temperature is essentially unimportant) or analyzed spectrophotometrically (in which case the temperature need only be controlled within a few degrees for accuracies of a few percent). In fact, the presently attained accuracy does not limit the accuracy of most analytical tests, where temperature control within 0.2 to 0.5 °C is usually considered adequate.

The greatest need for accuracy occurs in analytical tests involving live organisms. The most rigid specifications in analytical tests are for fecal coliforms (44.5 ±0.2 °C) and they require that the thermometers be checked against thermometers calibrated by NBS.

Ordinarily there is less need for accuracy in the analytical laboratory than for stability during testing. Good temperature control over long periods of time for biological tests and over shorter periods of time for chemical tests produces better precision with more meaningful inter-laboratory comparisons. When standards and blanks are run and calibration and testing are done all at the same temperature, inter-laboratory comparisons are possible and thereby much of the need for accurate temperature measurements is eliminated.

While the existing analytical thermometers and the general state of thermometry appear to be adequate, two problems are apparent. Accuracy and precision are often not differentiated in the literature or by the people contacted during this study. More importantly, too many researchers apparently do not question the accuracy of their thermometers. While the temperature and fecal coliform sections of *Standard Methods - Water and Wastewater* discuss thermometer calibrations, there was no mention of such a necessity anywhere else in the book. The general feeling seems to be that thermometry is so well under control for the needed level of precision and accuracy that no special precautions are necessary for adequately accurate temperature measurements.

Temperature Measurement of Thermal Pollution

For the thermal pollution aspect of the study we tried to determine the types of temperature measurements that are made and the accuracies that are required. As mentioned earlier, the steam electric generating, cement, and sugar industries are required to monitor the temperature of their effluents. Other temperature measurements needed to monitor potential thermal pollution include thermal plume tracing, and those for reservoir management, and marine biological research.

Steam Electric Generating Utilities

Of the three industries cited above, this study deals only with the steam electric generating industry because it is the major producer of waste hot water and is growing rapidly. EPA estimates that the steam electric power generating capacity of the U. S. will quadruple between 1970 and 1990. However, this estimate could be reduced somewhat by the long-term effects of the "energy crisis". The growth in the use of water is shown in Fig. 2. In 1960, 37% of the 3.7×10^{14} liters of water withdrawn from waterways in the United States and Puerto Rico was used by the power industry (1.38×10^{14} ℓ). By 1970, the power industry was using 3.35×10^{14} ℓ of water, 46% of the total[6].

What happens to this water as it passes through a power plant? A typical, conventional steam electric plant must discharge approximately 5400 J h^{-1} per watt of generating capacity[7]. There are more than 1100 steam electric plants in existence today[8] generating more than 4×10^{10} W. It is estimated that in 1970, steam electric generating plants in the U. S. discharged more than 1.2×10^{15} J h^{-1} of waste heat[7]. Although not all of this heat was discharged directly into our waterways, in 1970 approximately 75% of the plants used once-through cooling so that nearly 10^{15} J h^{-1} of waste heat was dissipated in our streams, rivers, and lakes[9]. This much heat necessarily will have some long-term, currently unknown, effect on the environment.

Power plants monitor not only the temperature of their effluents but of their intake water and the temperature gradients across their condensers. Thermocouples and resistance thermometers are used, as are liquid-in-glass thermometers. The thermometer and its instrumentation are chosen according to the required frequency and convenience of reading, the desired accuracy and the need to minimize costs. The indications of thermocouples and resistance thermometers can be continuously recorded and so these are convenient to use in an effluent stream or at a pump. Liquid-in-glass and resistance thermometers are used where periodic reading is permissible (input lines for example). The reliability of the results is also limited by the choice of sensor location, but these thermometers, if used with reasonable care, are capable of measuring temperatures with inaccuracies not exceeding $\pm\frac{1}{4}$ or $\pm\frac{1}{2}$ °C.

It is difficult to assess the role of operator technique as a source of measurement error in power plant thermometry. There appears to be wide understanding about how heat flow affects thermometer readings, so that care is generally taken to place thermometers so as to obtain the temperature at the point of interest (inlet, outlet, condenser, etc.). The picture is not so bright concerning accuracy, however. It is true that a number of people who were contacted during this study have some means of checking the accuracy, at least to the extent of seeing that two thermometers in the same location agree, and some people have relatively sophisticated internal calibration routines. On the other hand, while EPA's Environmental Monitoring and Support Laboratory in Cincinnati recommends that field thermometers be checked against either NBS calibrated thermometers or secondary fixed points[10], personnel in the NBS liquid-in-glass and thermocouple calibration laboratories report that in spite of the expanding requirements to measure the temperature of their effluents, thermometers are not sent for calibration from power plants in appreciable numbers. Clearly, thermometers used in the field are not always checked directly or indirectly against NBS calibrated thermometers.

In general, the potentially attainable accuracies of available thermometers do not impose severe limitations on the accuracy of field work. In their paper on "Continuous Water Quality Measurement; Present Status and Future Trends", Suffet and Radzuil remark that "Temperature is the most reliable sensor, conductivity second"[11]. The limitations in the reliability of thermometry result not from limitations in the sensors *per se* but in their choice and applications and from the unreliability of recording instruments. For example, prior to 1968, the Federal Water Pollution Control Administration lost 16% of its temperature data for 629 consecutive days for the following reasons:[7]

Cause of Loss	Sensor	Recorder	Other	Total
% of Data	0	7	9	16

There is definitely a need to improve the design of thermometer instrumentation and the quality of recorders to make them more rugged and more reliable.

Opinions vary as to whether the most severe limitations on thermometry are due to operator error or equipment. Dr. Marvin Skougstad, a hydrologist in the Water Resources Division of the USGS, stated in correspondence with him that failure to attain an inaccuracy of less than ±0.5 °C was usually the result of poor technique or error by the operator[12]. On the other hand, Dr. Dwight Ballinger, Director of the Environmental Monitoring and Support Laboratories (EPA) in Cincinnati expressed the opinion that the limitations were generally due to the available equipment[10]. However, Dr. Ballinger wrote about errors of several degrees, which implies inaccuracy since most field thermometers are capable of higher precision. Both of these opinions imply that quality control, operator training, and probe design are important areas for consideration by NBS.

Thermal Plume Monitoring

A second method of observing thermal pollution, thermal plume monitoring, was briefly reviewed. This is an area in which the inaccuracy of the thermometers may limit the usefulness of the results. Precision water-monitoring thermometry equipment is available; oceanographers have been tracking ocean currents for many years using very precise temperature measurements. In order to track a current well, the inaccuracy of the measurements should not exceed ±0.01 °C. Oceanographers have developed sophisticated, expensive probes which are accurate but power plant personnel and researchers have expressed a need for small inexpensive probes that are accurate to float down rivers or in lakes and transmit position and temperature to a receiver on shore. The probes now used in monitoring power plant effluents (thermocouples, liquid-in-glass, and resistance thermometers) will not do this, either because of their inherent nature (liquid-in-glass) or because sophisticated auxiliary equipment is needed.

Reservoir Management

In a large reservoir there is usually a vertical thermal gradient so that the temperature of water released downstream will vary considerably depending upon the depth from which the water is taken. The Army Corps of Engineers continuously measure the temperature of its reservoir outfalls in order to regulate discharge temperatures. The allowable error in their temperature measurements is ±½ to ±1 °C and their sensors are reliable within that imprecision, The major thermometric problem which they have identified is system reliability[13].

Biological Research

Biological research is growing rapidly; its results are used by public officials, and voluntary standards groups to set water quality standards. The accuracy of temperature measurements is very important to this work because water temperature has far-reaching effects on water dwelling organisms. Raising or lowering the temperature of a body of water changes both the metabolism of the resident organisms and the amount of oxygen available to them. In addition, many species of fish need seasonal temperature changes to trigger their spawning or hatching cycles, which may be disrupted by the addition of heated water. A change in the water temperature may change the diseases with which organisms must cope or it may alter species distributions, to the extent of permitting toxic algae or trash fish to flourish. On the other hand, raising the mean water temperature of a particular lake or stream may encourage a commercially valuable organism. For these reasons, it was felt important to look at the research data which lead to an evaluation of water quality. None of the biological literature reviewed for this study cited temperature measurements with an imprecision of less than 0.1 °C[14,15]. This is considered adequate at present, because fish do not respond significantly to change of less than 0.1 °C. Often more important than how much the temperature changes is how fast it changes, but in real systems time constants are large, and rapid fluctuations are not generally a problem over large areas. If the temperature varies beyond a certain range, marine and fresh water organisms will die; however, these limits are often many degrees wide so neither the accuracy nor the precision of biological research thermometry presently appears to be a problem here.

Standards Committees

The last area covered by this study is the work of standards committees dealing with thermometry in water analysis. The following is a list of committees whose work encompasses water pollution and the names of members who were contacted during the course of this study.

ASTM D-19 (Water)

Marvin Skougstad, Chairman
Dwight Ballinger

ASTM D19.03 (Sampling of Water and Water Formed Deposits, and Surveillance of Water)

Robert Booth

ASTM D19.01.04.02 (Native Aquatic Bacteria Subsection of the Section on Microbiology)

Rita Colwell, Co-Chairperson

ASTM D19.07 (Methods of Testing Water-Formed Deposits and the Properties of Water)

Jay Carver

*Water Pollution Control Federation Committee on Standard Methods of Sewage and Industrial Waste Analysis

Marvin Skougstad
Dwight Ballinger

*American Water Works Committee on Standard Methods for the Examination of Water, Sewage, and Industrial Wastes

Marvin Skougstad
Dwight Ballinger

*American Public Health Association Subcommittee on Standard Methods for the Examination of Water and Sewage of the Co-ordinating Committee on Laboratory Methods

ANSI Committee on Calibration of Measurement Systems (Pressure, Temperature, and Flow)

Paul Lederer, Technical Advisor

Those committees which are starred contribute to *Standard Methods - Water and Wastewater.* ASTM Committee D19.07, Methods of Testing Water-Formed Deposits and Properties of Water, has written "Proposed Methods for Determining the Temperature of Water"[16]. Jay Carver, its principal author, remarked that although there has not been a vacuum in the usage and appreciation of thermometers, there has been one in the attention to thermometry problems[17]. This document is to be a "how-to" report and is comprehensive and well written. This, and the USGS publication (see below), appear to be two important "standards" publications which discuss thermometry in terms of water pollution measurements. Otherwise, there is little attention to thermometry in the standards committees whose work bears on water pollution at this time. Many are aware that there are thermometry problems to be addressed but other tasks have taken a higher priority.

Conclusions and Recommendations

The major deficiencies in thermal pollution thermometry appear to lie in the areas of system reliability and of operator training. Because of the harsh nature of field conditions and the need for systems which do not require frequent maintenance, the amount of data obtained and the reliability of the system depend on the system engineering. Good quality control when combined with sound engineering and careful training of personnel in the proper use of equipment will do much to improve the state of thermometry in thermal pollution monitoring. With the noticeable exception of thermal plume monitoring, existing sensors can meet many of the present requirements. More rugged and specialized sensors will be needed for some of the field work. There are already many specialized sensor designs with no one design in demand above all others. The U. S. Public Health Service formerly maintained the Robert A. Taft Sanitary Engineering Center in Ohio which served as a design shop. While this service is no longer offered, there is still a substantial need for it[18]. The National Bureau of Standards can offer valuable technical advice but cannot, with its limited resources, undertake to do the work. It might be accomplished effectively by EPA working with industry.

Improving quality control is a major problem and should be attacked. The NBS might make four contributions here. First, it could increase the variety of thermometers calibrated and issue more publications concerned with the philosophical and technical aspects of calibration and reliability assessment. One means of attaining wider distribution is for these publications to appear in trade journals as well as the regular NBS formats. The ASTM has taken a step by establishing its Proposed Methods for Determining the Temperature of Water. The USGS has also been active in educating the public about thermometry with its publication of "Water Temperature—Influential Factors, Field Measurements, and Data Presentation"[19]. This is an excellent comprehensive publication for personnel engaged in field work.

The second and third possible contributions are perhaps the most useful approaches to improving quality control. The Precision Measurement Seminars currently offered in thermometry by NBS could be expanded in two directions. They could be tailored to specific industries or groups of related industries and they might be offered at various locations throughout the country, either by travelling instructors or by film or videotape. This would enable us to reach a large audience with information directed to its needs. In addition, a Measurement Assurance Program (MAP) could be initiated with EPA for either analytical laboratory or power plant personnel in an effort to more completely assess the state of thermometry. If interest and needs warrant, NBS could then maintain a continuing large-scale MAP. Each of these activities could demonstrate large improvements in measurement reliability for the industries involved in water temperature monitoring.

Lastly, the NBS staff might become more active in water pollution standards committees. While the Temperature Section staff are active on many standards committees, they are not very active in those committees with interest outside of thermometry *per se*. More committee work would involve an additional commitment of staff resources but it would create a channel through which we can "advertise" our services and monitor the state of water pollution thermometry.

Some of the recommendations contained herein could be generalized to include other industries with related problems for a greater impact. Involvement with standards committees and with the EPA would appear to require the least commitment of NBS resources and would be perhaps the most productive channel until firmer needs are felt by the NBS in water pollution thermometry.

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R. Thomas, Blue Plains Sewage Treatment Plant.

S. Wasik, Thermochemical Measurements and Standards Section, NBS.

TABLE I

Clean Water

Test	Accuracy or Stability	Temperature	Remarks
Aluminum, Eriochrome Cyanine R Method		N.G.	
Boron, Curcumin Method	A	55 ±2 °C	Water bath used to control drying time and temperature
CO_2	A	±0.5 °C	Nomogram used has 1 °C intervals
Chlorinated Hydrocarbons, Gas Chromatogram Method	A	N.G.	Column temperature controlled with oven
Chlorine, Leuco Crystal Violet Method	S	$T \leq 40$ °C	
Chlorine Demand	A	N.G.	Hold temperature of sample to temperature of water being studied
$C\ell O_2$ Amperometric Method	S	N.G.	Use same temperature throughout test
Iodine, Photometric Method	A	30 ±0.5 °C	Water bath used
Odor	A	40,60 ±1 °C	Temperature influences threshold of odor
pH, Glass Electrode Method	A	25 °C	pH varies with sample temperature
Potassium, Colorimetric Method	S		
Residue	A	104,180 ±1 °C	Temperature at which sample is dried is important
$CaCO_3$	S		Varies with temperature as pH varies
Specific conductance	A	25 °C	Results vary 2%/°C
Sulfate, Turbidimetric Method	A	Ambient ±5 °C	

TABLE I (continued)

Test	Accuracy or Stability	Temperature	Remarks
Taste	A	40 °C	Sample should be neither hot nor cold
Vanadium, Gallic Acid Method	A	25 ±0.5 °C	Water bath used
		Polluted Water	
BOD	S	N.G.	
Chlorine, Orthotolidine Method	A		Color development depends on sample temperature
Chlorine Requirement	S		Must know temperature when sample is in chlorinated
Nitrate, Storage	S	$\geq$ 0 °C	
Nitrate, Zinc Reduction Method	S	N.G.	
Nitrate, Brucine Method	S		Control temperature of sample while heat is liberated
Odor	A	40 °C	See clean water entry above
Dissolved Oxygen, Membrane Method	A		Membranes have large temperature coefficients
Phenols, Storage	S	5-10 °C	
Phenols, Gas Chromatogram Method	A	210 ±0.2 °C	Temperature of Column controlled by oven
Residue	A	103 °C	See clean water entry above
Sulfide, Titrimetric Method	S	25 ±5 °C	
Toxicity to Fish	A	15,25 ±2 °C	Temperature chosen according to species of fish

TABLE I (continued)

Test	Accuracy or Stability	Temperature	Remarks
Coliforms Total Count	A	T ±0.5 °C	
Standard Plate Count	A	20,35 ±0.5 °C	
Standard Total Most Probable Number Test	A	35 ±0.5 °C	
Fecal Coliforms EC Medium	A	44.5 ±0.2 °C	
Coliforms, Boric Acid Lactose Bath Method	A	43.0 ±0.2 °C	

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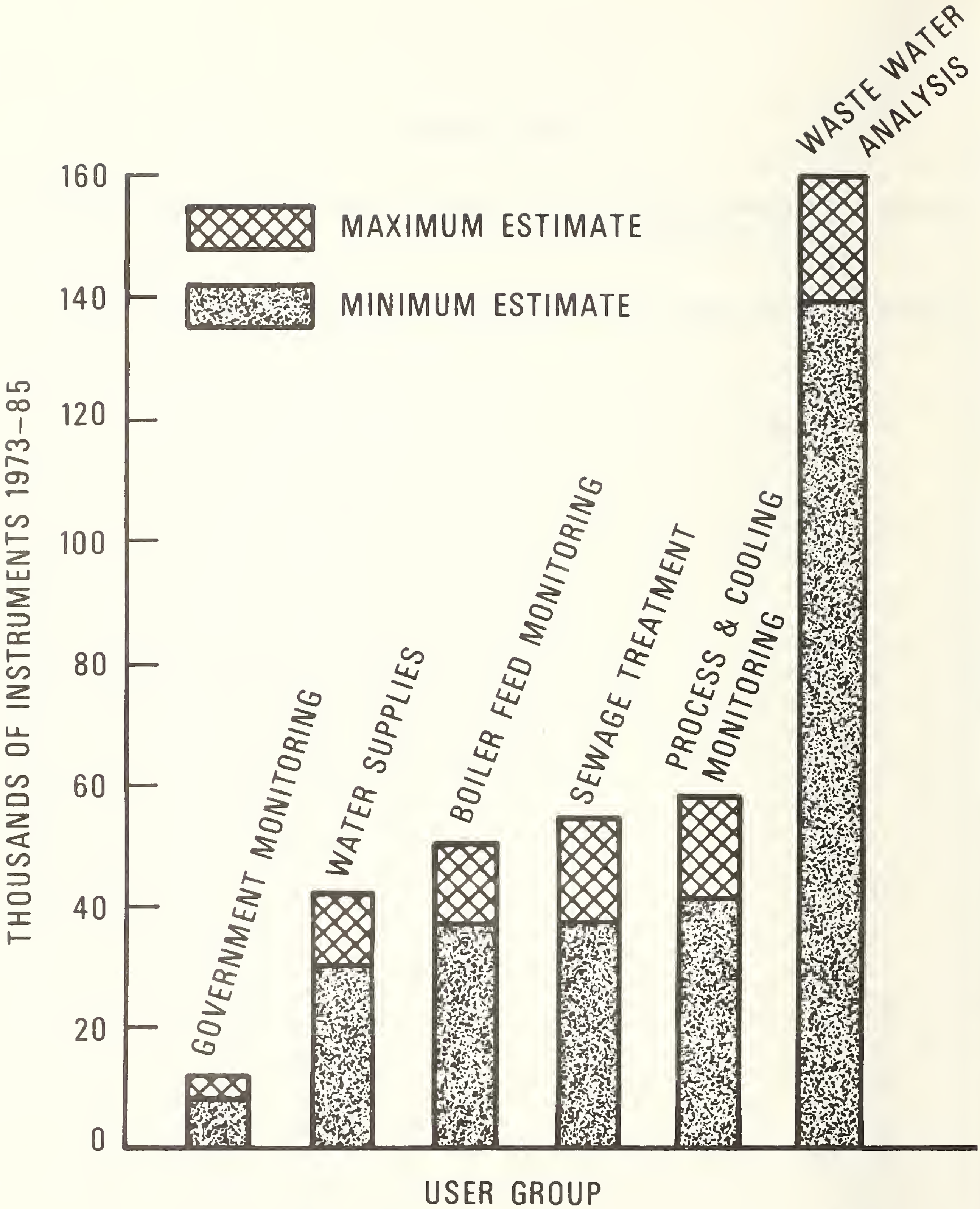
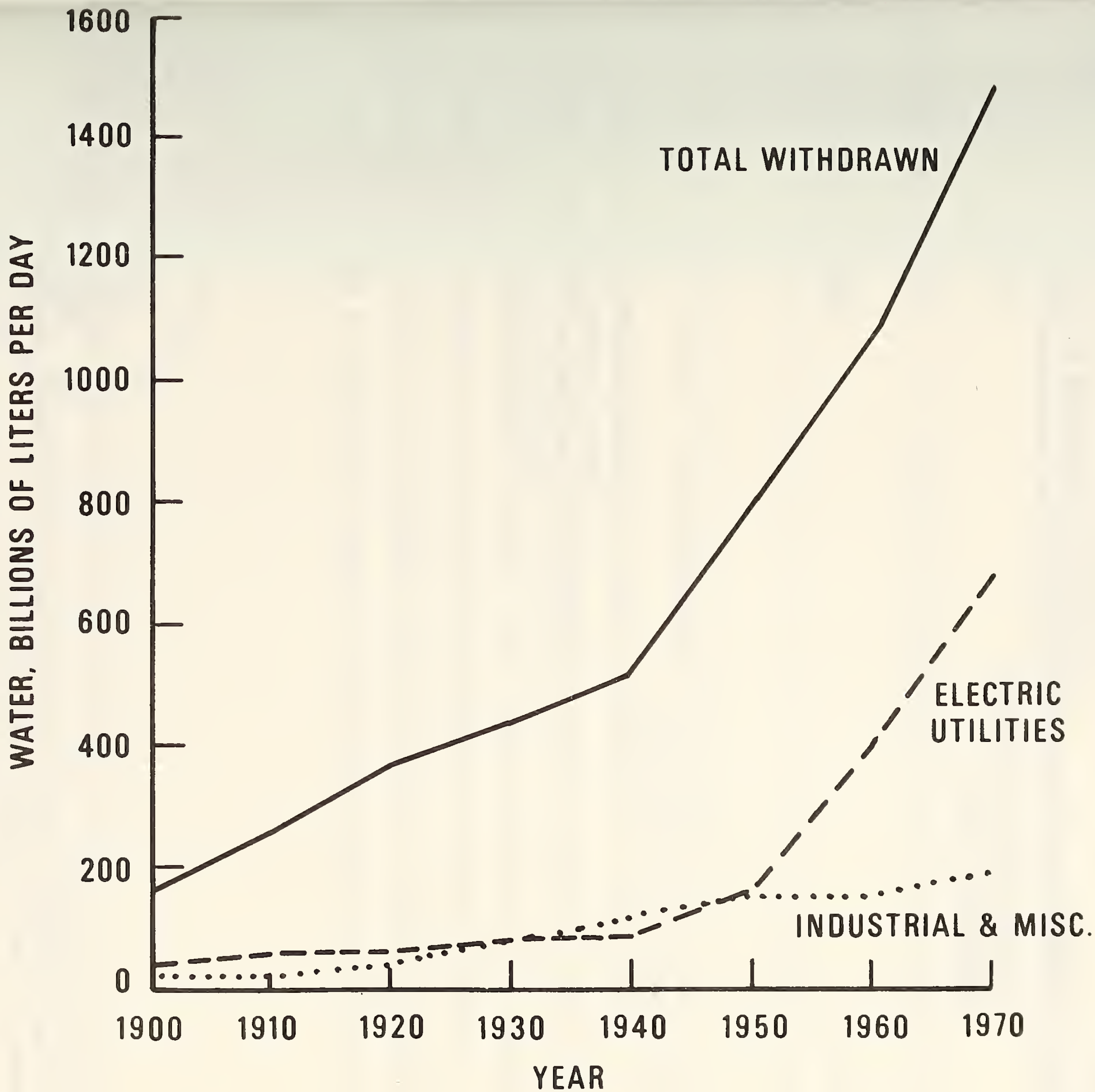
FIGURE CAPTIONS

Figure 1 Estimated needs for water quality instrumentation for the period 1973 to 1985[1].

Figure 2 Water usage by selected groups for the period 1900 to 1970[6].



THOUSANDS OF INSTRUMENTS 1973–85
0
20
40
60
80
100
120
140
160
MAXIMUM ESTIMATE
MINIMUM ESTIMATE
GOVERNMENT MONITORING
WATER SUPPLIES
BOILER FEED MONITORING
SEWAGE TREATMENT
PROCESS & COOLING MONITORING
WASTE WATER ANALYSIS
USER GROUP



TOTAL WITHDRAWN
ELECTRIC UTILITIES
INDUSTRIAL & MISC.
WATER, BILLIONS OF LITERS PER DAY
1600
1400
1200
1000
800
600
400
200
0
1900
1910
1920
1930
1940
1950
1960
1970
YEAR

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15. SUPPLEMENTARY NOTES

16. ABSTRACT *(A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)*

A limited study of thermometry in water pollution was made which focused on water analysis, thermal pollution, and the work of standards committees. It was concluded that the current needs in this field can be addressed most efficiently by the National Bureau of Standards with educational and calibration activities. Suggestions are made concerning possible contributions by NBS with an emphasis on those activities having large impacts for small investments of NBS resources.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)*

Pollution; standards committees; temperature measurements; thermal pollution; thermometry; water analysis; water pollution.

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