NATIONAL BUREAU OF STANDARDS REPORT

7381

THE ATTACHMENT OF LOW-ENERGY ELECTRONS BY HALOGENATED HYDROCARBONS AND OTHER GASES

by

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1961

and

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

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The Attachment of Low-Energy Electrons by Halogenated Hydrocarbons and Other Gases

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ABSTRACT

A simple method for measuring the attachment of electrons to gas molecules is described. The method measures the total amount of attachment without differentiating between simple resonant capture and dissociative resonance attachment and yields no information on the energies of the electrons which are attached. The results of measurements on eleven gases are given.

1. Introduction

It has been proposed [1] that inhibition of flame reactions by halogenated hydrocarbons may be connected, in some obscure way, with dissociative resonance attachment of the electrons found in flames. The apparatus described was devised as a means of effecting a rough screening of compounds known to be flame inhibitors to find out if there are any such compounds which do <u>not</u> fall into the general class of electron attaching gases. Such a screening was thought to be desirable as a preliminary to the very difficult mass-spectrometric determination of the actural attachment process.

2. Apparatus

The apparatus is shown in Figure 1. It consisted of three sections of Pyrex tubing cemented coaxially to two pieces of 36 mesh bronze screen, each 7.5 cm square. A source of 10^4 alpha particles per second, consisting of polonium chloride on a platinum foil backing, was cemented into a small dimple in the center piece of glass tubing, midway between the two screens. The center section of the apparatus was enclosed in an electrostatic shield and the two screens connected to the shielded input connections of high impedence, feed-back, vacuum-tube, electrometer.

Operation of the detector unit is as follows: The 5 Mev alpha particles colliding with the gas molecules in the center section of tubing produce a plasma of positive ions and electrons. In the absence of gas flow, and assuming a uniform spacial distribution of alpha particles, the energies of both the positive ions and electrons decay rapidly to thermal energies, and the two screen electrodes behave as Langmuir probes, each assuming the same negative potential with respect to the plasma, as indicated by Langmuir probe theory. However, if there is a flow of gas down the tube in one direction (nitrogen was used in all the measurements reported here), positive ions will be dragged along by the gas molecules, while electrons will be relatively unaffected, with the result that the downstream electrode will be driven positive with respect to the upstream electrode. The resultant current is measured by the electrometer. If an electron capturing gas is added to the stream of nitrogen, electrons will be captured before reaching the upstream electrode, converted into negative ions and carried along downstream with the positive ions. Recombination of positive and negative ions in the gas stream and on the downstream electrode will further decrease the current through the electrometer. It should be noted that electrons may be captured at any stage of their energy decay. This method of measuring attachment makes no distinction between the various types of attachment.

3. Results

It was found that the apparatus was sensitive to the flow of nitrogen, as indicated by Figure 2. It was assumed that the reduction in current at higher rates of flow was the result of insufficient time of contact with the downstream electrode to allow collection of all the positive ions. The correctness of this assumption was substantiated by the insertion of an additional disk of screen into the downstream delivery tube where it was pushed into contact with the electrode. The plot of current vs. flow then showed a narrow, flat top as shown in Figure 3. In the actual determinations, the flow was maintained constant at 0.3 ℓ/min, rather than at 2 ℓ/min, which corresponded to the center of the flat part of Figure 3. This was a result of a compromise between the lower current obtained at low flow rates, the length of time required to saturate the system, and the small volume of the cylinder used to make up the gas mixtures.

The curves of Figures 2 and 3 show a residual current at zero nitrogen flow rate. This can be accounted for by the slightly non-symmetrical placement of the radioactive source.

Some trouble was encountered, initially, caused by the addition of too high a concentration of the attaching gas. There was a tendency for it to adsorb on surfaces and in the connecting tubing and, in some cases, it was extremely hard to eradicate. It was necessary to go to concentrations in the part-per-million range and, in addition, to substitute glass for the plastic and rubber tube connections.

The part-per-million gas concentrations were produced by making dilute mixtures in cylinders, using pressure measurements for the determination of concentrations, and then diluting further by means of a proportioning flow system using calibrated flow meters of appropriate ranges.

The results on the eleven gases are shown in Figure 4. In addition to gases known to be inhibitors, several others were included. Carbon tetrafluoride is ineffective as an inhibitor and has a small cross section for dissociative resonance capture only at relatively high electron energies[2]. It showed no attachment in the method described here. Methyl chloride does not attach electrons by the dissociative resonance process[3], but apparently does attach some to form the molecular ion (see Fig. 4). Oxygen[4] and sulfur hexafluoride [5] are known to capture electrons at low energies and are not inhibitors for flame reactions.

4. Conclusions

Because of the non-specific nature of the method, it is not expected that the gases would be placed in the same order as for their efficiencies as flame inhibitors, however, none of the gases which are known to be inhibitors failed to attach electrons.

[1] E. C. Creitz, J. Research NBS 65A, 389-96 (1961).

[2] V. H. Dibeler, R. M. Reese and F. L. Mohler, J. Research NBS 57, 113-18 (1956).

[3] V. H. Dibeler, R. M. Reese, J. Research NBS 54, 127-34 (1955).

[4] D. S. Burch, S. J. Smith, and L. M. Branscomb, Phys. Rev. 112, 171-5 (1958).

[5] W. M. Hickam and R. E. Fox, J. Chem. Phys. 25, 642-7 (1956).

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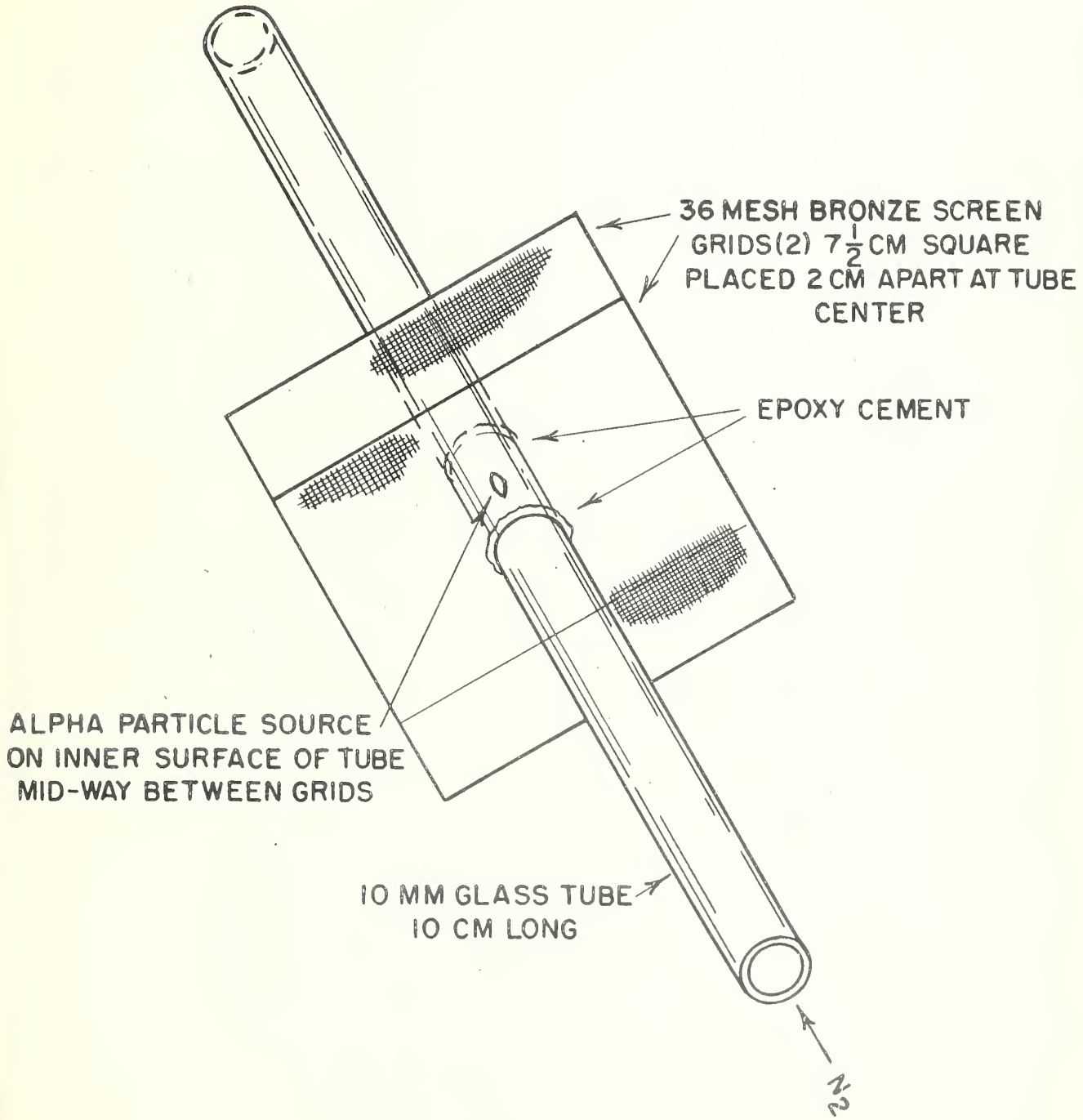
36 MESH BRONZE SCREEN
GRIDS(2) 7 1/2 CM SQUARE
PLACED 2 CM APART AT TUBE
CENTER
EPOXY CEMENT
ALPHA PARTICLE SOURCE
ON INNER SURFACE OF TUBE
MID-WAY BETWEEN GRIDS
10 MM GLASS TUBE
10 CM LONG
N-24

FIGURE 1

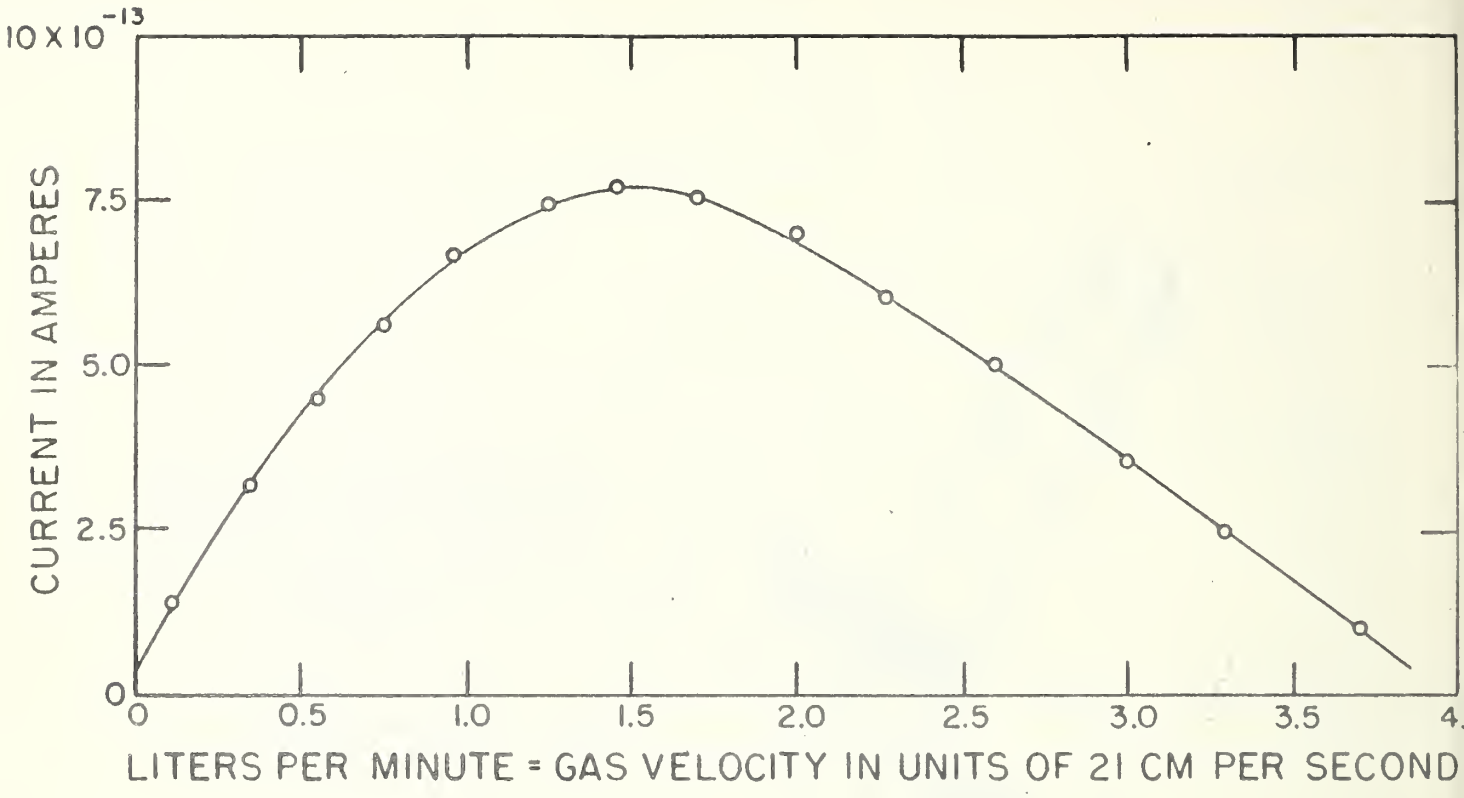

FIGURE 2

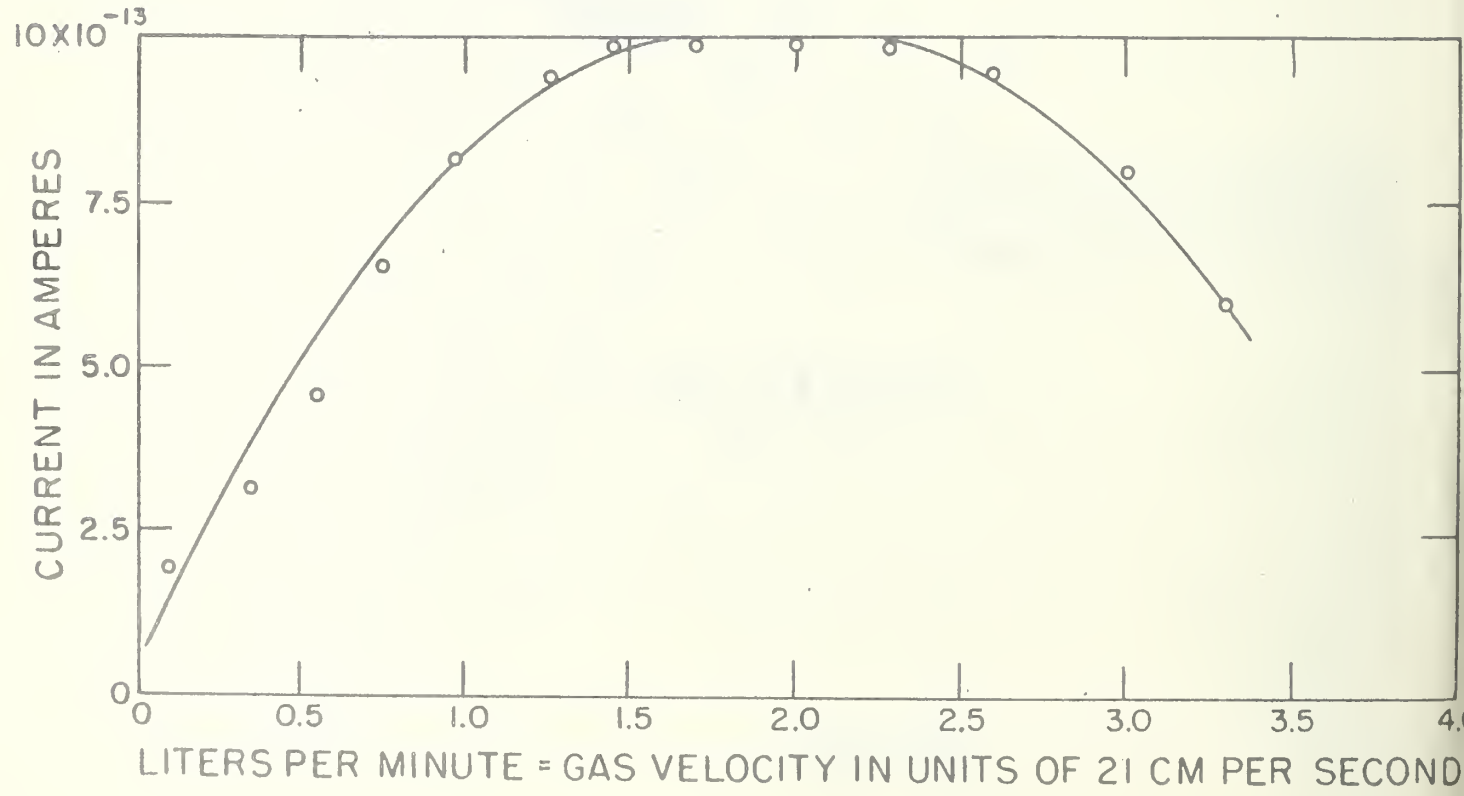

FIGURE 3

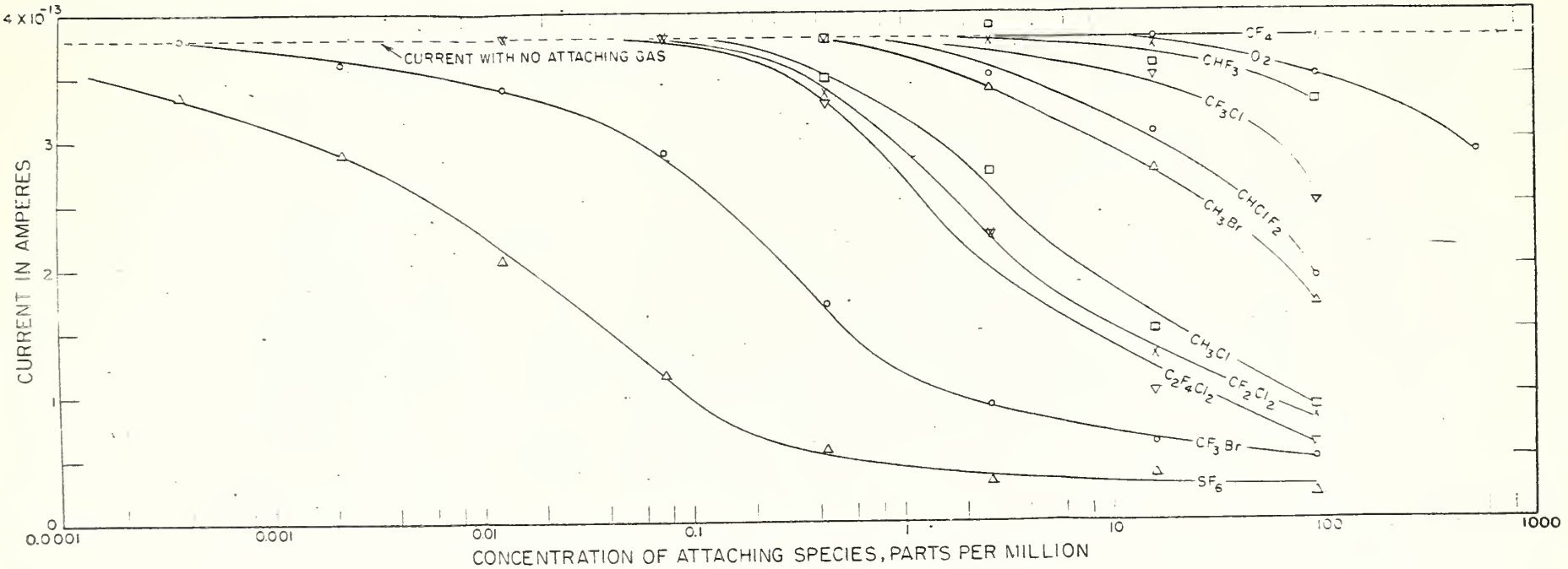
4 X 10⁻¹³
CURRENT WITH NO ATTACHING GAS
CF4
O2
CHF3
CF3Cl
CHClF2
CH3Br
CH3Cl
C2F4Cl2
CF2Cl2
CF3Br
SF6
CURRENT IN AMPERES
0
1
2
3
0.0001
0.001
0.01
0.1
1
10
100
1000
CONCENTRATION OF ATTACHING SPECIES, PARTS PER MILLION

FIGURE 4

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Luther H. Hodges, *Secretary*

NATIONAL BUREAU OF STANDARDS
A. V. Astin, *Director*

THE NATIONAL BUREAU OF STANDARDS

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WASHINGTON, D.C.

Electricity. Resistance and Reactance. Electrochemistry. Electrical Instruments. Magnetic Measurements. Dielectrics.

Metrology. Photometry and Colorimetry. Refractometry. Photographic Research. Length. Engineering Metrology. Mass and Scale. Volumetry and Densimetry.

Heat. Temperature Physics. Heat Measurements. Cryogenic Physics. Equation of State. Statistical Physics.

Radiation Physics. X-ray. Radioactivity. Radiation Theory. High Energy Radiation. Radiological Equipment. Nucleonic Instrumentation. Neutron Physics.

Analytical and Inorganic Chemistry. Pure Substances. Spectrochemistry. Solution Chemistry. Standard Reference Materials. Applied Analytical Research.

Mechanics. Sound. Pressure and Vacuum. Fluid Mechanics. Engineering Mechanics. Rheology. Combustion Controls.

Organic and Fibrous Materials. Rubber. Textiles. Paper. Leather. Testing and Specifications. Polymer Structure. Plastics. Dental Research.

Metallurgy. Thermal Metallurgy. Chemical Metallurgy. Mechanical Metallurgy. Corrosion. Metal Physics. Electrolysis and Metal Deposition.

Mineral Products. Engineering Ceramics. Glass. Refractories. Enameled Metals. Crystal Growth. Physical Properties. Constitution and Microstructure.

Building Research. Structural Engineering. Fire Research. Mechanical Systems. Organic Building Materials. Codes and Safety Standards. Heat Transfer. Inorganic Building Materials.

Applied Mathematics. Numerical Analysis. Computation. Statistical Engineering. Mathematical Physics. Operations Research.

Data Processing Systems. Components and Techniques. Digital Circuitry. Digital Systems. Analog Systems. Applications Engineering.

Atomic Physics. Spectroscopy. Infrared Spectroscopy. Solid State Physics. Electron Physics. Atomic Physics.

Instrumentation. Engineering Electronics. Electron Devices. Electronic Instrumentation. Mechanical Instruments. Basic Instrumentation.

Physical Chemistry. Thermochemistry. Surface Chemistry. Organic Chemistry. Molecular Spectroscopy. Molecular Kinetics. Mass Spectrometry.

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BOULDER, COLO.

Cryogenic Engineering. Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Cryogenic Technical Services.

Ionosphere Research and Propagation. Low Frequency and Very Low Frequency Research. Ionosphere Research. Prediction Services. Sun-Earth Relationships. Field Engineering. Radio Warning Services.

Radio Propagation Engineering. Data Reduction Instrumentation. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Propagation-Terrain Effects. Radio-Meteorology. Lower Atmosphere Physics.

Radio Standards. High Frequency Electrical Standards. Radio Broadcast Service. Radio and Microwave Materials. Atomic Frequency and Time Interval Standards. Electronic Calibration Center. Millimeter-Wave Research. Microwave Circuit Standards.

Radio Systems. High Frequency and Very High Frequency Research. Modulation Research. Antenna Research. Navigation Systems.

Upper Atmosphere and Space Physics. Upper Atmosphere and Plasma Physics. Ionosphere and Exosphere Scatter. Airglow and Aurora. Ionospheric Radio Astronomy.


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