CHAPTER 1
INTRODUCTION

1. Classification of Analytical Methods
2. Types of Instrumental Methods
4. Calibration of Instrumental Methods
5. Selecting an Analytical Method
Reading Assignment

• Chapter 1: pp. 1-24
A. Classification of Analytical Methods

A.1. Classical Methods

Classical methods/ wet chemical methods/ earliest methods of analysis; relied mainly on chemical properties of analytes.

Analytes are treated with reagents to form products that could be identified. Gravimetric and titrimetric methods were used for quantitative analysis.

Examples:

- Formation of precipitate and measurement of mass
- Oxidation of analyte and detection of end via the change of color of the analyte.
- Neutralization of analyte and detection of end point using acid-base indicator.
- Complexation of analyte and use of metallochromic indicators to detect end point.

Separation of analyte from matrix was achieved using precipitation, extraction and distillation.
A.2. Instrumental Methods

- Instrumental methods largely rely on physical properties of analyte, thus generally are not destructive.
- They are not necessarily more sensitive.

- Separation methods
  - Chromatographic
  - Electrophoretic

- Methods for the qualitative and quantitative analysis of analytes
B. Classification of Instrumental Methods based on Properties

TABLE 1-1 Chemical and Physical Properties Used in Instrumental Methods

<table>
<thead>
<tr>
<th>Characteristic Properties</th>
<th>Instrumental Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emission of radiation</td>
<td>Emission spectroscopy (X-ray, UV, visible, electron, Auger); fluorescence, phosphorescence, and luminescence (X-ray, UV, and visible)</td>
</tr>
<tr>
<td>Absorption of radiation</td>
<td>Spectrophotometry and photometry (X-ray, UV, visible, IR); photoacoustic spectroscopy; nuclear magnetic resonance and electron spin resonance spectroscopy</td>
</tr>
<tr>
<td>Scattering of radiation</td>
<td>Turbidimetry; nephelometry; Raman spectroscopy</td>
</tr>
<tr>
<td>Refraction of radiation</td>
<td>Refractometry; interferometry</td>
</tr>
<tr>
<td>Diffraction of radiation</td>
<td>X-ray and electron diffraction methods</td>
</tr>
<tr>
<td>Rotation of radiation</td>
<td>Polarimetry; optical rotary dispersion; circular dichroism</td>
</tr>
<tr>
<td>Electrical potential</td>
<td>Potentiometry; chronopotentiometry</td>
</tr>
<tr>
<td>Electrical charge</td>
<td>Coulometry</td>
</tr>
<tr>
<td>Electrical current</td>
<td>Amperometry; polarography</td>
</tr>
<tr>
<td>Electrical resistance</td>
<td>Conductometry</td>
</tr>
<tr>
<td>Mass</td>
<td>Gravimetry (quartz crystal microbalance)</td>
</tr>
<tr>
<td>Mass-to-charge ratio</td>
<td>Mass spectrometry</td>
</tr>
<tr>
<td>Rate of reaction</td>
<td>Kinetic methods</td>
</tr>
<tr>
<td>Thermal characteristics</td>
<td>Thermal gravimetry and titrimetry; differential scanning calorimetry; differential thermal analyses; thermal conductometric methods</td>
</tr>
<tr>
<td>Radioactivity</td>
<td>Activation and isotope dilution methods</td>
</tr>
</tbody>
</table>
C. Measurement Process and Domains

Stimulus \rightarrow \text{System under study} \rightarrow \text{Response}

Energy source \hspace{1cm} \text{Analytical information}
An instrument is a communication device between the system under study and the investigator.

**Instrument converts**

| Information contained in Chemical and physical Characteristics | Information for human interpretation in terms of property of interest and manipulation |
| Non electrical Domain | Transduction Processing | Non electrical Domain |
| Electrical Domain |
Understanding the Measurement Process

• **Examples:**
  – Property of interest: hydrogen ion activity
  – stimulus: sample/glass electrode
  – Potentiometer measures difference in potential
  – Difference in potential is converted to pH
  – pH = \(-\log a_H.\)
Understanding the Measurement Process

Signal generator (glass electrode)

↓

Signal transduction (information encoding) (diff. in $a_{H^+}$ to potential diff.)

↓

Signal modification (information decoding) (voltage to pH)

↓

Signal display

Information is encoded, processed, transferred, decoded and displayed.

Steps in the measurements involve transformation and processing of the signal between the different data domains.
## Instrument Components

### TABLE 1-2 Some Examples of Instrument Components

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Energy Source (stimulus)</th>
<th>Analytical Information</th>
<th>Information Sorter</th>
<th>Input Transducer</th>
<th>Data Domain of Transduced Information</th>
<th>Signal Processor/Readout</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photometer</td>
<td>Tungsten lamp</td>
<td>Attenuated light beam</td>
<td>Filter</td>
<td>Photodiode</td>
<td>Electrical current</td>
<td>Amplifier, digitizer, LED display</td>
</tr>
<tr>
<td>Atomic emission spectrometer</td>
<td>Inductively coupled plasma</td>
<td>UV or visible radiation</td>
<td>Monochromator</td>
<td>Photomultiplier tube</td>
<td>Electrical current</td>
<td>Amplifier, digitizer, digital display</td>
</tr>
<tr>
<td>Coulometer</td>
<td>Direct-current source</td>
<td>Charge required to reduce or oxidize analyte</td>
<td>Cell potential</td>
<td>Electrodes</td>
<td>Time</td>
<td>Amplifier, digital timer</td>
</tr>
<tr>
<td>pH meter</td>
<td>Sample/glass electrode</td>
<td>Hydrogen ion activity</td>
<td>Glass electrode</td>
<td>Glass-calomel electrodes</td>
<td>Electrical voltage</td>
<td>Amplifier, digitizer, digital display</td>
</tr>
<tr>
<td>Mass spectrometer</td>
<td>Ion source</td>
<td>Mass-to-charge ratio</td>
<td>Mass analyzer</td>
<td>Electron multiplier</td>
<td>Electrical current</td>
<td>Amplifier, digitizer, computer system</td>
</tr>
<tr>
<td>Gas chromatograph with flame ionization</td>
<td>Flame</td>
<td>Ion concentration vs. time</td>
<td>Chromatographic column</td>
<td>Biased electrodes</td>
<td>Electrical current</td>
<td>Electrometer, digitizer, computer system</td>
</tr>
</tbody>
</table>
Data Domains: 
*Representation and Transformation of Information*

• Types of Data Domains
  – Non-electrical domains
  – Electrical domains

• Measurements start in the non-electrical domain (chemical and physical) and end in a non-electrical domain (number, scale position, image on screen).
Information flow → Source intensity → Fluorescence intensity of analyte → Electrical current $I$ → Voltage $V$ → Number

Governed by → Laws of chemistry and physics → Transducer transfer function → Ohm's law $V = IR$ → Meter transfer function
Interdomain Conversions

(a) Phototransducer

Energy source

Laser

Tonic water (analyte)

Optical filter

Resistor

Digital voltmeter

(b) Information flow

Source intensity

Fluorescence intensity of analyte

Electrical current $I$

Voltage $V$

Number

(c) Governed by

Laws of chemistry and physics

Transducer transfer function

Ohm’s law $V = IR$

Meter transfer function

Input transducer

Output transducer
Three modes of information encoding in the electrical data domain
Analog Domain

- Information is encoded as the magnitude of current, voltage, charge or power.
- In analog domains information encoded is continuous in amplitude and time.
- Amplitude is related to property of interest.
Time Domain

- Information is encoded in the form of a time dependent fluctuation of a signal.
- Frequency of fluctuation is related to property of interest
- e.g: in photon counting the rate of arrival of photon at the detector is related to intensity.
Digital Domain

• Information is encoded in the form of a number.
• Devices used (LED, toggle switch, logic circuit) display two states only behavior (on or off).
  – Lights (on/off)
  – Logic levels (HI/LO) (1/0)
• Fundamental unit of information in digital domain
  – Bit = each piece of Hi-LO info.
  – 4 bits = 1 byte
(a) Count

(b) Binary (serial)

(c) Binary (parallel)

Time interval

$2^2$ $2^1$ $2^0$

$n = 4 + 1 = 5$

$n = 4 + 1 = 5$
Conversion of information between data domains

- *Input Transducer* - converts information in non-electrical domains to information in electrical domains
  - e.g. Electronic photodetectors convert radiant power into a current or voltage
- *Transfer function of the transducer* - relates the electrical output to the input.
  - Voltage or current to radiant power or intensity.
- *Output Transducer* - converts information in electrical domain to information in non-electrical domain (Voltmeters, computer screens, ADC)
- *Readout device* - Transducer that converts information in the electrical domain to information that can be interpreted by an analyst.
Detectors, Transducers, Sensors

- *Detector* - mechanical, electrical or chemical device that identifies, records, or indicates a change in one of the variables in its environment.

- Detection system: entire assemblies that indicate of record physical or chemical quantities.

- Transducer: device that converts information between nonelectrical and electrical domains

- *Sensor* - analytical devices that are capable of monitoring specific chemical species continuously and reversibly. transducer + chemically selective recognition phase.
Molecular recognition phase

- Enzymes
- Antibodies
- Receptors
- Polymers
- Organelles
- Microbes
- Cells
- Tissues

Chemical, mass, light, heat, sound, pressure, electrical signal

Transducer

- Electrode
- Semiconductor
- QCM device
- Phototransducer
- Sound transducer
- Thermistor

Electrical output
C. Computers and Computerized Instruments

Microprocessors and Microcomputers

• A microprocessor
  – large scale integrated circuit
  – hundreds of thousands and even millions of transistors, resistors and diodes and other circuit elements
  – miniaturized to fit on a single silicon chip with dimensions of a few millimeters on a side.
  – often serves as the arithmetic and logic component, called the central processing unit (CPU), of a microcomputer.
• Microprocessors are widely used for the control of the operation of analytical instruments.

• Microcomputers
  – one or more microprocessors combined with other circuit components that provide memory, timing, input, and output functions.
Use of microcomputers in analytical instrumentation

- Control of the instrument
- Processing data
- Storing data
- Displaying data
- Transferring data
Operational Modes of Computerized Instruments

OFF-LINE
Data collected by analyst and subsequently transferred to computer for data processing.

- Computer and mass storage
- Analyst
- Analytical Instrument
ON-LINE

Computer communicates directly with analytical instrumentation via an electronic interface.

Signal from instrument is shaped, digitized and stored. (Computer is still a distinct entity for mass storage of data and instructions for processing. Off line processing is also possible with this arrangement)
IN-LINE

Most modern instruments are configured with the computer in-line whereby the computer or microprocessor is imbedded in the instrument. Operator communicates with and directs instrument operation via the computer.
In line

- Operator does not necessarily program the computer

- Primary software is usually provided with commercial instruments with a programming language so that the users may program optional modes of data acquisition and manipulation.

- In in-line and on-line operations, the data are often transferred to the computer in real time, i.e. as the data is being generated by the instrument.

- Real-time processing involves data treatment performed simultaneously with data acquisition.
Why connect a computer to an analytical instrument?

• partial or complete automation of measurements
• more data can be accumulated for short period, which leads to increased precision.
• faster and better control over experimental variables than a human operator leading to more precise and accurate data.
• Computational and data handling capabilities. E.g FT calculation, signal averaging, correlation techniques.

The Chemist and the instrument

• An instrument is a collection of functional modules.
• Understand function of components, integrated circuits, computers.
• Know how to connect them.
• This understanding helps in diagnosing system malfunctions and in the efficient/ clever application of instrumental systems to solve chemical problems.
D. Calibration of Instrumental Methods

- **Calibration:**
  - Standards are used to verify the relationship between the analytical response (signal) and the analyte concentration.
  - Determines proper operation of the instrument.
- **Standardization:**
  - Establishes the relationship between signal and analyte concentration.
  - Determines $m$, the sensitivity of the method.
• **External-standard Calibration**
  – An external standard is prepared separately from the sample.
  – Suitable in the absence of interference and other matrix effects
  – **Determination of an unknown concentration**
    - Least square method
    - Review on page 12 and appendix (1 p.986)
    - Correction p.12 $s_x$ not $s_y$
Regression analysis

\[ y = mx + b \]

\[ C_x = \frac{\bar{y}_c - b}{m} \]

\[ s_c = \frac{s_x}{b_1 \sqrt{\frac{1}{M} + \frac{1}{N} + \frac{(\bar{y}_c - \bar{y})^2}{m^2 \sum (x_i - \bar{x})^2}}} \]

\[ \mu_c = c \pm t s_c \]

- \( M \) number of replicate measurements on sample
- \( N \) number of standards used to generate the calibration curve
- **Confidence interval for the analyte's concentration**
- \( t \) for (n-2) degrees of freedom
Standard-Addition Methods

• Useful for complex samples with important matrix effects
• Sample is spiked with standard
• Standard addition methods
  – Add increasing known amount of standard to the sample and perform measurement after each addition.
  – Make several samples of same volume containing same amount (volume, $V_x$) of unknown with known increasing amount (volume, $V_s$) of standards
Standard addition method

\[
\begin{align*}
\text{Total concentration of analyte} & \quad C_a = \frac{V_a}{V_t} \\
\text{Add } V_y \text{ of } C_a & \quad \text{Dilute to } V_t \\
\text{Total concentration of analyte} & \quad C_{a'} = \frac{V_a}{V_t} + C_b \left( \frac{V_y}{V_t} \right)
\end{align*}
\]

\[
(\text{Abs}) = m(V_a) + b
\]

\[
\begin{align*}
m &= 0.03820 \\
(\text{Abs})_0 &= -6.31 \text{ mL (calculated or extrapolated)} \\
b &= 0.2412
\end{align*}
\]
\[ S = \frac{kC_s V_s}{V_t} + \frac{kC_x V_x}{V_t} \]

\[ S = mV_s + b \]

slope = \( m = \frac{kC_s}{V_t} \)

\( y - \text{int ercept} = b = \frac{kC_x V_x}{V_t} \)

\[ \frac{b}{m} = \frac{kV_x C_x / V_t}{kC_s / V_t} = \frac{V_x C_x}{C_s} \]

\[ C_x = \frac{bC_s}{mV_x} \]
\[ S = \frac{kC_s (V_s)_0}{V_t} + \frac{kC_x V_x}{V_t} = 0 \]

\[ C_x = -\frac{(V_s)_0 C_s}{V_x} \]
<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
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<tbody>
<tr>
<td>1</td>
<td><strong>Determination of Fe in Natural Water by Colorimetry with Multiple Additions</strong></td>
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<td>2</td>
<td>Concentration of standard, $c_s$</td>
<td>11.10 ppm</td>
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<tr>
<td>3</td>
<td>Volume of unknown used, $V_u$</td>
<td>10.00 mL</td>
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<td><strong>Volume of standard added</strong></td>
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<td>10</td>
<td><strong>Regression Equation</strong></td>
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<td>11</td>
<td><strong>Error Analysis</strong></td>
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<td>12</td>
<td>Standard error in $y$</td>
<td>0.004858</td>
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<tr>
<td>13</td>
<td>$\bar{y}$</td>
<td>5</td>
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<td>14</td>
<td>Standard deviation in volume</td>
<td>0.143011</td>
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<td>15</td>
<td>Standard deviation in $c$</td>
<td>0.16</td>
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</tbody>
</table>

**Equation:**

$$y = 0.0302x + 0.2412$$

$$R^2 = 0.9998$$

![Graph showing the relationship between volume of standard solution and emission signal.](image)
Internal Standard Method

• Internal Standard: substance added in constant amount to all samples, blanks, and calibration standards
• Could be a constituent of samples
  – Large amount
  – Its concentration does not change
• Compensates for:
  – Random and systematic errors
  – Instrumental and method fluctuations
  – Uncontrollable variations that occur from sample to sample
• Can compensate for matrix effects if the Signal of the IS is affected in a manner similar to the signal of the sample for analysis
• How is data analyzed?
<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Method of internal standards for flame spectrometry</td>
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<tr>
<td>2</td>
<td>1000 ppm Li added as internal standard</td>
<td></td>
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<tr>
<td>3</td>
<td>Na conc., ppm</td>
<td>( I_{\text{SN}} )</td>
<td>( I_L )</td>
<td>( I_{\text{SN}}/I_L )</td>
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<tr>
<td>4</td>
<td>0.50</td>
<td>0.11</td>
<td>86</td>
<td>0.001276</td>
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<td>9</td>
<td>Unknown</td>
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<td>Regression equation</td>
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<td>Slope</td>
<td>0.012975</td>
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<td>12</td>
<td>Intercept</td>
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<td>Concentration of unknown</td>
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<td>14</td>
<td>Error Analysis</td>
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<tr>
<td>15</td>
<td>Standard error in ( y )</td>
<td>0.000356</td>
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<tr>
<td>16</td>
<td>( N )</td>
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<tr>
<td>17</td>
<td>( S_{xy} )</td>
<td>71.148</td>
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<tr>
<td>18</td>
<td>( y ) bar (average ratio)</td>
<td>0.043363</td>
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<tr>
<td>19</td>
<td>( M )</td>
<td>4</td>
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<td>Standard deviation in ( c )</td>
<td>0.046923</td>
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<tr>
<td>21</td>
<td>Documentation</td>
<td></td>
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<tr>
<td>22</td>
<td>Cell D4=IF4/C4</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>23</td>
<td>Cell B11=SLOPE(D4:D8, A4:A8)</td>
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<tr>
<td>24</td>
<td>Cell B12=INTERCEPT(D4:D8, A4:A8)</td>
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<tr>
<td>25</td>
<td>Cell B13=(O9-B12)/B11</td>
<td></td>
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<tr>
<td>26</td>
<td>Cell B16=STDEVX(D4:D8, A4:A8)</td>
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<tr>
<td>27</td>
<td>Cell B16=COUNT(A4:A8)</td>
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<tr>
<td>28</td>
<td>Cell B17=DEVSQ(A4:A8)</td>
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<tr>
<td>29</td>
<td>Cell B18=AVERAGE(D4:D8)</td>
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<td></td>
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</tr>
<tr>
<td>30</td>
<td>Cell B19=( \text{intercept no. of replicates} )</td>
<td></td>
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<tr>
<td>31</td>
<td>Cell B20=B15<em>B11</em>SQRRT((B19+B16+(O9-B18)^2)/(B11^2)*(B17))</td>
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</tbody>
</table>

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E. Selecting an Analytical Method

• Define the Problem

  – Detection method
    • Physical and chemical properties
  – Accuracy
  – Amount of sample available
  – Concentration range of the analyte
  – Interferents
• **Performance characteristics of methods**

Performance characteristics expressed numerically are referred to as **Figures of Merit**

**TABLE 1-3 Numerical Criteria for Selecting Analytical Methods**

<table>
<thead>
<tr>
<th>Criterion</th>
<th>Figure of Merit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Precision</td>
<td>Absolute standard deviation, relative standard deviation, coefficient of variation, variance</td>
</tr>
<tr>
<td>2. Bias</td>
<td>Absolute systematic error, relative systematic error</td>
</tr>
<tr>
<td>3. Sensitivity</td>
<td>Calibration sensitivity, analytical sensitivity</td>
</tr>
<tr>
<td>4. Detection limit</td>
<td>Blank plus three times standard deviation of the blank</td>
</tr>
<tr>
<td>5. Dynamic range</td>
<td>Concentration limit of quantitation (LOQ) to concentration limit of linearity (LOL)</td>
</tr>
<tr>
<td>6. Selectivity</td>
<td>Coefficient of selectivity</td>
</tr>
<tr>
<td>Terms</td>
<td>Definition*</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------------------------------------------</td>
</tr>
<tr>
<td>Absolute standard deviation, $s$</td>
<td>$s = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N - 1}}$</td>
</tr>
<tr>
<td>Relative standard deviation (RSD)</td>
<td>RSD = $\frac{s}{\bar{x}}$</td>
</tr>
<tr>
<td>Standard error of the mean, $s_m$</td>
<td>$s_m = s/\sqrt{N}$</td>
</tr>
<tr>
<td>Coefficient of variation (CV)</td>
<td>CV = $\frac{s}{\bar{x}} \times 100%$</td>
</tr>
<tr>
<td>Variance</td>
<td>$s^2$</td>
</tr>
<tr>
<td>TABLE 1-4 Other Characteristics to Be Considered in Method Choice</td>
<td></td>
</tr>
<tr>
<td>---------------------------------------------------------------</td>
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</tbody>
</table>