A SENSITIVE FLUORESCENT INDICATOR FOR IDENTIFYING
AND DETERMINING THE CONCENTRATION OF THE
ALUMINUM ION IN MINERALS AND SOILS

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Since the chemical and physical properties of a soil characterize
the way in which a soil can be used, elemental analysis is resorted
to in order to determine a few of these properties. It is also known
that the clay fraction controls most of the important properties of
a soil. These clay minerals are principally secondary, hydrated
crystalline ferro-aluminum silicates.9, 10

The "aluminon" (ammonium salt of aurin tricarboxylic acid)
method for aluminum determination as standardized by Smith et
al8 has been a popular method used in soil chemical analysis. Inter-
ferences by cations and anions are extensive with the aluminum-
aluminon complex. Jackson6 lists these interferences and gives the
precautionary procedures which should be followed to minimize or
to eliminate the effects of these diverse ions.

Feigl5 lists several reagents which yield reactions with the alu-
minum ion. All of these reagents, 8-hydroxyquinoline and its deriva-
tives; dithiozox; dithiocarbamate; thiourea; EDTA; morin; aliza-
rine and others, have a common feature, namely, that they all are
chelating agents. Our investigation for another complexing agent
which would react in a characteristic manner with the aluminum
ion, led us to study the properties of PAN [1-(2-pyridylazo)-2-
naphthol].

PAN as an analytical reagent has had a rather brief history.
It was first used by Liu9 as a chelating agent for the heavy metals.
Cheng and Bray2 published the characteristics of PAN and several
of its complexes, Flaschka et al4 investigated the use of PAN as an
indicator in EDTA titrations. PAN is a brilliant orange compound
whose melting point is 126–7°C. It is insoluble in water but is read-
ily soluble in organic solvents, such as: alcohols, ketones, benzene,
and carbon tetrachloride. The metallo-complexes formed by PAN
show solubilities similar to that of PAN. Betteridge et al4 reported
that the pKₐ of PAN is 12.3, indicating the PAN is a weak acid.

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PAN belongs to the category of aryl azo dyes, the structures of the complexes formed by divalent and trivalent metal ions with PAN show the tridentate character of this reagent as a chelating agent, figure 1. The color of the metallo-PAN chelates is generally red; however, the color may vary from yellow-orange to pink depending upon the solvent used to dissolve the chelate precipitate, Table 1. The aluminum-PAN mixtures exhibit several properties not shared by the other metallo-PAN chelates. First, as previously noted by Cheng and Bray\(^2\), no reaction is detectable between PAN and the aluminum ion in an aqueous solution. Secondly, a reddish solution results when aluminum and PAN are brought together in an ethanol or an acetone solution. This solution exhibits the property of fluorescence when exposed to ultraviolet radiation. None of the other metallo-PAN complexes reported, thus far, exhibits a similar property.

Holzbecher\(^5\) reported a large number of aromatic compounds which formed fluorescent complexes exclusively with the aluminum ion. He observed that each of these reagents had a phenolic hydroxyl group either ortho or para to its aluminum complexing group. As seen in figure 1, PAN possesses a phenolic hydroxyl group ortho to its complexing group which is the azo group in the structure. No other element in the qualitative Group III elements, other than aluminum, has exhibited this property of fluorescence with PAN. This property of fluorescence of the aluminum-PAN complex in ethanol when irradiated with ultra-violet radiation was the basis of our investigation of using this phenomenon for the determination of the aluminum ion.

Since aluminum in clays and in mineral colloids occurs primarily as the secondary hydrated ferro-aluminum silicate, any of the standard analytical methods for the separation of the aluminum ion from the other ions associated with it in the complex may be used. The precipitate of aluminum hydroxide must be freed of iron and chromium (III) hydroxides, because iron and chromium (III) ions form chelates with PAN which tend to quench the fluorescence of the aluminum-PAN-complex. The purified aluminum hydroxide is dissolved in \(3\ M\ \text{HNO}_3\) and the resulting solution is evaporated just to dryness. The hydrated aluminum nitrate is permitted to cool. A qualitative estimation of the concentration of aluminum ion present is conducted by dissolving one of the replicate runs in 2 ml. of 95% ethanol. To this solution, 2 drops of 0.1% (W/V) ethanolic solution of PAN is added. This alcoholic solution of Al-PAN complex is checked for fluorescence with an ultraviolet source such as 15T8-BLB black light fluorescent tube. With experience one can estimate the Al\(^{3+}\) ion concentration to as low as
### Table 1. Colors of Metal-Pan Complexes Under Ultra-Violet Light

<table>
<thead>
<tr>
<th>Complex</th>
<th>ETOH</th>
<th>MEOH</th>
<th>PROH</th>
<th>BUOH</th>
<th>AMOH</th>
<th>HEXOH</th>
<th>ACETONE</th>
<th>ET₂O</th>
<th>C₆H₆</th>
<th>CCl₄</th>
<th>CHCl₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-PAN</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>B</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Fe-PAN</td>
<td>BR</td>
<td>BR</td>
<td>BR</td>
<td>BR</td>
<td>BR</td>
<td>BR</td>
<td>BR</td>
<td>BR</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Mn-PAN</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Ni-PAN</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>R</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Zn-PAN</td>
<td>R</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Co-PAN</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
<tr>
<td>Al-PAN</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>Y</td>
<td>Y</td>
<td>Y</td>
</tr>
</tbody>
</table>

B = Blue  
BR = Brown  
P = Pink  
PU = Purple  
O = Orange  
L = Lavender  
R = Red  
G = Green  
Y = Yellow
Figure 1.
DEVICE FOR OBSERVING FLUORESCENCE

$10^{-3}\ M$. For quantitative determinations, the desiccated aluminum nitrate unknown should be volumetrically diluted with 95% ethanol. An aliquot containing about $10^{-3}\ M$ of $\text{Al}^{3+}$ ion is pipetted into a 50 ml. volumetric flask. One ml. of a $5 \times 10^{-3}\ M$ ethanolic solution of PAN is added and this combination is volumetrically diluted to 50 ml. with 95% ethanol. The fluorescence is compared in a photofluorometer against standard solutions made by volumetrically diluting one ml. of $5 \times 10^{-3}\ M$ of ethanolic PAN and increments of 1 to 4 ml. of $10^{-3}\ M\ \text{Al(NO}_3\text{)}_3 \cdot 9\ \text{H}_2\text{O}$ to 50 ml. with 95% ethanol. The procedure was used to obtain a calibration curve in the range of $3 \times 10^{-2}$ to $12 \times 10^{-2}$ mg. of aluminum per 50 ml. of solution using a Coleman Photofluorometer (Model 12-B with filters No. 12–222 and 14–212). The Al:PAN ratio does not need to be constant in the standard solution because only the complex fluoresces and not the excess PAN, Standard techniques for fluorescent analysis are followed. These fluorescent techniques should be of sufficient sensitivity to determine aluminum accumulation levels in leaf tissue, seedlings, etc. Excellent results were obtained in the detection of $10^{-6}$ grams of $\text{Al}^{3+}$ per ml and acceptable results with $27 \times 10^{-9}$ grams of $\text{Al}^{3+}$ per ml.
REFERENCES

3. FEIGL, F. Chemistry of Specific, Selective and Sensitive Reactions, 1954.