Analysis of yttrium and scandium content in industrial phosphoric acid using wavelength dispersive X-ray fluorescence spectrometry (WDXRF)

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Abstract: The wavelength-dispersive X-ray fluorescence spectrometry (WDXRF) method for determining yttrium and scandium in industrial phosphoric acid passes all validation tests and can be used for these elements. The proposed method's procedure is simple, fast and does not require reagents for preparation and with low operating costs. The yttrium and scandium concentrations in Tunisian phosphoric acid are in the order of 60 ppm for yttrium with a coefficient of variation of 1.09 % and about 15 ppm for scandium with a coefficient of variation of 1.33 %.

Key words: yttrium, scandium, optimization, validation, wavelength-dispersive X-ray fluorescence spectrometry

1. Introduction

The chemical treatment of phosphate rock with sulfuric acid is used to produce phosphoric acid; this process is characterized by the following overall reaction of :[1,2]

$$Ca_{10}(PO_4)_6F_2 + 10\ H_2SO_4 + 20\ H_2O$$
$$\rightarrow 10\ (CaSO_4 \cdot 2\ H_2O) + 2\ HF + 6\ H_3PO_4 \quad (1)$$
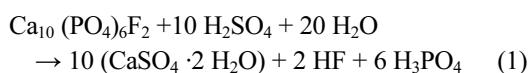
Industrial Phosphoric acid is one of the most important chemical products; it is used in the production of phosphate fertilizers such as TSP: $Ca(H_2PO_4)_2$ and DAP: $(NH_4)_2HPO_4$, feed livestock ($CaHPO_4 \cdot 2H_2O$), and phosphate sequestration (sodium hexametaphosphate).

The sulfuric attack dissolved practically all of the soil's contaminants at the same time as apatite. Heavy metals, radionuclides, and other natural elements are among them.[3] Some of these impurities, such as Yttrium, Scandium and lanthanides, can be recycled and recovered.

The unique physical and chemical properties of rare earth elements (REEs), scandium, and yttrium enable their use in a variety of scientific and engineering fields. Rare earth elements (REEs) such as scandium, yttrium, and lanthanides play an important role in the global economy. Rare earth-based materials are used in the electronic industry, steel industry, household batteries, fluorescent lamps, permanent magnets, and lasers for surgical and nuclear technologies.[4,5]

The global consumption of REE exceeded 100,000 t in 2011.[4,6] Some rare earth elements are more important

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for industrial applications than others, and their supply may be threatened in the coming decades. Nd, Eu, Tb, Dy, and Y in particular are expected to become highly strategic future metals.[7,8] For example, global demand for Nd and Dy is expected to increase by 700 % and 2600 %, respectively, over the next 25 years.[4]

Scandium, yttrium, and their oxides are especially important in the production of optical glass, high-temperature ceramics, and superconductors. Furthermore, these metals have a wide range of applications in conventional fields such as metallurgy, such as the manufacturing of high-duty cast iron, low-alloy steels, and specific alloys.[9-11] Scandium is used for producing filters for generating quasi_monochromatic neutron beams, targets for neutron tubes and generators and sources of β particles.[12]

The efficiency of using pure REEs, including scandium and yttrium, is primarily determined by their impurity composition, which influences the material structure and properties. However, due to the similarity of physical and chemical properties of REEs, analyzing them is a complex problem, particularly when it comes to determining rare earth impurities (REIs). As a result, multielement selective and precise methods with high sensitivity must be used.Various methods are used to analyze REEs and their oxides, including atomic emission, neutron activation, photometric, polarographic, and others.[13-26] However, for pure REEs, the most universal and informative methods are inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). These methods have advantages such as low detection limits and a broad linear range of determined concentrations. However, a number of issues limit their use for analytically pure and high purity REEs and their oxides. Spectral foldings during atomic emission analysis of REEs with a multilinear spectrum are a serious problem that has received a lot of attention.[14-18] The attempt to use mathematical and software means for cross accounting for foldings, complex sample preparation, and analysis using the method of REEs separation (extraction, chromatography) did not allow for the development of unified

metrologically secure techniques.[17,18]

The matrix effect and spectral interferences are the primary limitations of the ICP-MS method.[19-24,27] The matrix element's content has a significant impact on the analytical signal, so the matrix element in the solution must be considered to obtain reliable quantitative results. The ICP-MS method's second limitation is related to spectral interferences. During the ICP-MS analysis of REEs, the element of the base forms oxide and hydroxide ions, which interfere with the determination of singly charged REIs. The interference effects are reduced by optimizing the mass spectrometer's operating parameters,[19] using a series of reference specimens analogous to the analyzed objects,[20,21] and alternative recording of the signal of doubly charged ions of the sought elements,[22] preliminary matrix separation,[23,24] etc. However, the majority of these procedures are labor intensive and time consuming, and the addition of the stage of chemical pretreatment results in the formation of additional sources of uncertainty.

As a result, it would be advantageous to have a simple, quick, and accurate method for determining yttrium and scandium in industrial phosphoric acid. Because of its acceptable precision and accuracy, as well as its lower cost when compared to the techniques mentioned above, X-ray fluorescence spectrometry (XRF) is always an acceptable technique. We propose using wavelength-dispersive X-ray fluorescence spectrometry (WDXRF) to analyze yttrium and scandium in industrial phosphoric acid with the use of the intensity of the line Kα.

The X-ray fluorescence method was used to detect traces of uranium and thorium in industrial phosphoric acid,[28,29] and the author determined values ranging from 0 to 100 ppm of uranium and 0 to 50 ppm of thorium.

2. Experimental

2.1. Materials
2.1.1. Spectrometer
For the determination of yttrium and Scandium, an X-ray fluorescence spectrometer (Magix 3 kW,

PW2403, PANalytical) was used; it is a sequential spectrometer with wavelength-dispersive with a channel of measure based on a single goniometer covering the entire range of measure. It has an X-ray tube that serves as the X-ray source, and the anode of the X-ray tube is made of rhodium.

2.1.2. Scintillation detector

It is made up of a sodium iodide crystal with homogeneous distribution of thallium atoms (NaI; Tl), a photocathode, and a tube photomultiplier. The X-ray is converted into light, which is then measured with a photomultiplier.

2.1.3. Gas flow detector

Gas flow detectors generally comprise a thin, insulated wire (for example; 50 µm diameter) mounted in the centre of a cylindrical metal housing. The wire is set to a positive voltage of 1500 – 2000V and acts as the anode, the housing acts as the cathode. The X-rays enter the detector through a thin window (generally a layer of polypropylene 1 to 6 µm thick).

2.2. Sample preparation

Without any prior preparation, industrial phosphoric acid samples are analyzed directly. The industrial phosphoric acid is placed in a cup (special sample holder for liquids) with a polymer film on the bottom and is exposed directly to incident X-rays from the X-ray tube. It comes down to an inverted optical in our case. The X-ray tube is situated under the sample. If the film breaks during the liquid analysis, it can cause damage to these components. As a result, a sufficiently resistant film must be used, as well as a compromise with X-ray absorption and the presence of additives in the film (which allow the film to be more resistant to some products). In the case of direct optical, this problem does not exist. We used a film for liquid analysis by XRF that does not absorb X-rays and has no effect or interference matrix that could influence

Table 1. Measurement conditions of yttrium and scandium

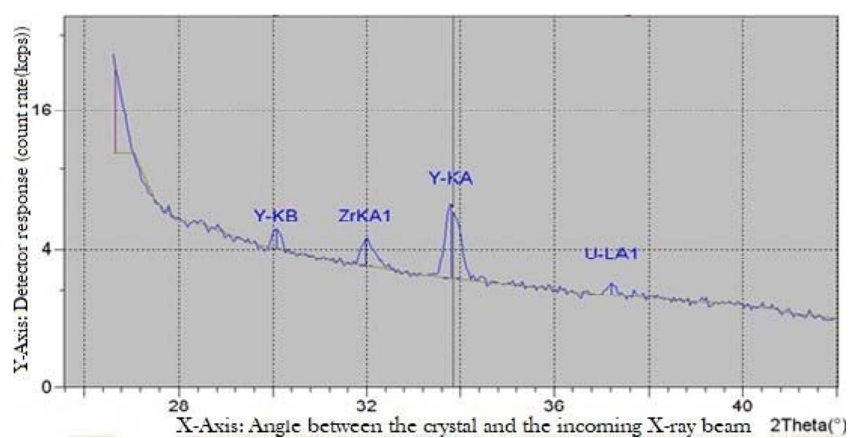| Measurement conditions	Yttrium	Scandium
Atmosphere	Helium (900 hPa pressure)	Helium (900 hPa pressure)
Power	40 kV, 30 mA	40 kV, 75 mA
Crystal	LiF220	LiF200
Collimator	150 microns	300 microns
Detector	Scintillation Detector	Gas Flow Detector
Lines	Y-Kα line of 14.964 keV	Sc-Kα line of 4.087 keV
Angle 2Theta (°)	33.826	97.728

Fig. 1. Detection of yttrium peak in industrial phosphoric acid using WDXRF.
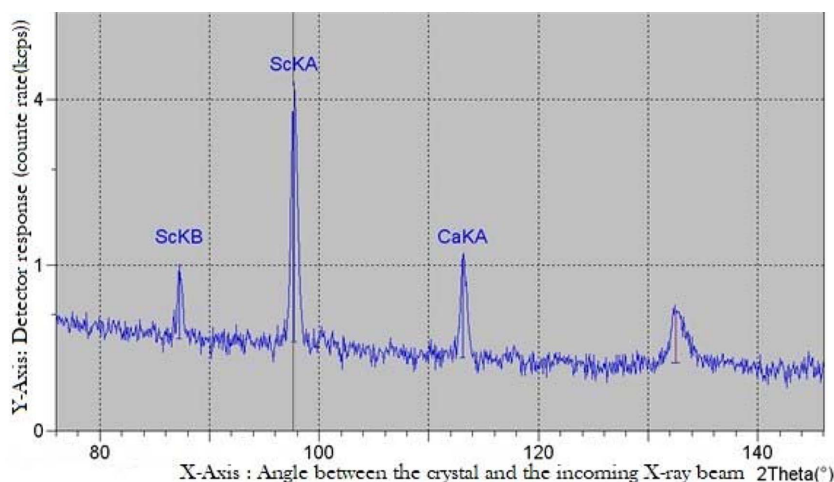
Fig. 2. Detection of scandium peak in industrial phosphoric acid using WDXRF.

our results for this problem. This is MYLAR® X-Ray film with a diameter of 63.5 mm. For the industrial phosphoric acid sample, we used a mass of 3 g with a precision of 0.1 mg. To avoid boiling in the vacuum, the analysis is performed under helium (900 hPa pressure).

2.3. Measurement conditions

Measurement conditions of yttrium and scandium in industrial phosphoric acid using WDXRF are summarized as follows in *Table* 1.

Figs. 1 and 2 shows the WDXRF analysis of yttrium and scandium in industrial phosphoric acid.

- The experimental angle of the line of Yttrium : Y-Kα (2θ°) [noted Y- KA] : 33,848°
- The experimental angle of the line of scandium : Sc-Kα (2θ°) [noted Sc- KA]: 97,623°

3. Validation

Linearity, detection limit and quantification limit, specificity, repeatability, reproducibility and accuracy were applied to validate the proposed method.[30]

3.1. Linearity

The linearity of an analytical procedure is its ability (within a given range) to obtain test results that are directly proportional to the concentration (amount) of analyte in the sample.

3.1.1. Limit of detection and quantification
1) Limit of detection (LD)

The detection limit of an individual analytical procedure is the lowest amount of analyte in a sample that can be detect but not necessarily quantitated as an exact value.

2) Limit of quantification (LQ)

The quantification limit of an individual procedure is the lowest amount of analyte in a sample that can be quantitatively determined with suitable precision and accuracy. The quantitation limit is a parameter of quantitative assays for low levels of compounds in sample matrices and is used particularly for the determination of impurities and/or degradation products.

3.2. The specificity

Specificity is the ability to asses unequivocally the analyte in the presence of components which may be expected to be present. Typically these might include impurities, degradants, matrix, etc.

3.3. The fidelity (repeatability and reproducibility)[31]
3.3.1. Repeatability

Repeatability expresses the precision under the same operating conditions over a short interval of time. Repeatability is also termed intra-assay precision.

3.3.2. Reproducibility

Reproducibility expresses the precision between laboratories (collaborative studies usually applied to standardization of methodology).

3.4. The accuracy

The accuracy of an analytical procedure expresses the closeness of agreement between the average value obtained from a large series of test results and an accepted reference value. This is sometimes termed trueness.[31]

4. Results and Discussion

4.1. Linearity and detection limit and quantification limit

We repeated the analysis (n = 6) at six concentration levels of 0, 25, 50, 100, 150, and 200 ppm for yttrium

Table 2. The measurements of linearity test for Yttrium

Concentration (ppm)	Repetition 1 (kcps)	Repetition 2 (kcps)	Repetition 3 (kcps)	Repetition 4 (kcps)	Repetition 5 (kcps)	Repetition 6 (kcps)
0	-0.0136	0.001	0.0002	-0.0105	-0.0001	0.0001
25	0.6282	0.5702	0.6374	0.5781	0.5898	0.6101
50	1.1909	1.1823	1.2098	1.2105	1.2301	1.1954
100	2.4133	2.3978	2.4001	2.4257	2.4082	2.4212
150	3.6396	3.6054	3.6445	3.6094	3.6131	3.6247
200	4.8783	4.8473	4.9097	4.8613	4.9046	4.8594

Table 3. The measurements of linearity test for Scandium

Concentration (ppm)	Repetition 1 (kcps)	Repetition 2 (kcps)	Repetition 3 (kcps)	Repetition 4 (kcps)	Repetition 5 (kcps)	Repetition 6 (kcps)
0	0.0001	0.0010	0.0002	0.0012	-0.0001	-0.0001
20	0.3372	0.3451	0.3502	0.3394	0.3421	0.3473
40	0.6757	0.6802	0.6826	0.6721	0.6654	0.6634
60	1.0135	1.0141	1.0150	1.0134	1.0130	1.0142
80	1.3586	1.3520	1.3401	1.3421	1.3433	1.3398
100	1.6981	1.7001	1.6924	1.6823	1.6923	1.6901

Table 4. The results of linearity test for Yttrium

Source of variation	Sum of squared deviations	Degree of freedom	Fisher (observed value)	Fisher (critical value)
Regression	105.579	1	F_l = 297561.63	F_l = 7.56
Error model	0.005	p-2 = 4	F_{nl} = 3.85	F_{nl} = 4.02
Experimental error	0.011	p (n-1) = 30		
Total	105.595	np-1 = 35		

Table 5. The results of linearity test for Scandium

Source of variation	Sum of squared deviations	Degree of freedom	Fisher (observed value)	Fisher (critical value)
Regression	11.952	1	F_l = 391600.26	F_l = 7.56
Error model	4.491 E-4	p-2 = 4	F_{nl} = 3.67	F_{nl} = 4.02
Experimental error	9.156 E-4	p (n-1) = 30		
Total	11.953	np-1 = 35		

and 0, 20, 40, 60, 80, and 100 ppm for scandium; the results are summarized in *Tables* 2 and 3. The intensity obtained at each concentration was plotted against the initial concentration of yttrium and scandium. Microsoft Excel™ was used to compute the regression characteristics. *Tables* 4 and 5 present a summary of the results obtained.

Error model: error of the selected model ($y = b_0 + b_1x$) for linear regression.

Experimental error: represents the experimental errors made on the measures.

4.1.1. Interpretation

Step 1: F_1 observed ratio is greater than the critical value for a variable F_1 Fisher, risk $\alpha = 1\%$ for 1 and $p(n-1)$ degrees of freedom. The regression model is acceptable, and we can proceed to the next stage.

Step 2: F_{nl} observed ratio is less than or equal to the critical value corresponding to a variable F_{nl} Fisher, risk $\alpha = 1\%$ for p-2 and $p(n-1)$ degrees of freedom. The linear range can be selected validated.

And by drawing the calibration curves of yttrium and scandium while wearing the intensity according to content in yttrium and scandium, we get the curves shown in *Figs.* 3 and 4.

The linearity measurements can be used to calculate the sensitivity (b_1) and its standard deviation $S(b_1)$, the blank value b_0 and its standard deviation $S(b_0)$.

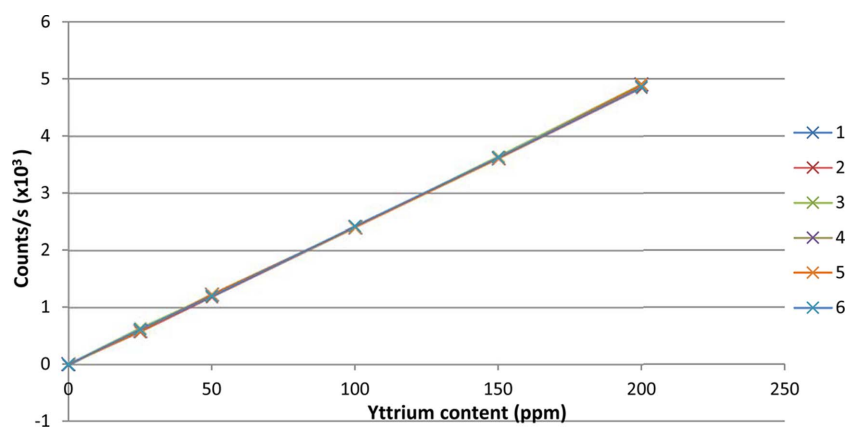$$\text{Limit of detection: } LD = \frac{b_0 + 3.S(b_0)}{b_1} \qquad (2)$$

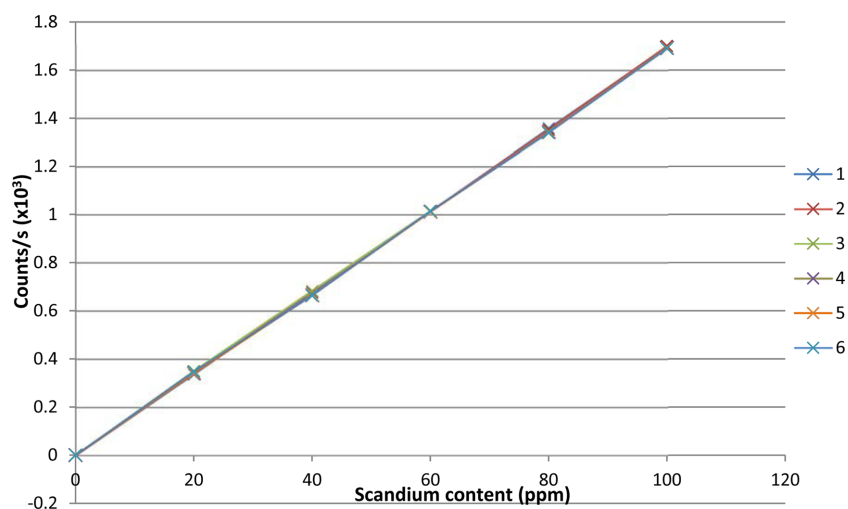*Fig.* 3. Calibration of the method for the determination of yttrium.

Fig. 4. Calibration of the method for the determination of scandium.

Table 6. Statistical results of the calibration

Designation	Observed value for yttrium	Observed value for scandium
Number of levels (p)	6	6
Total number of measurements	36	36
sensitivity b_1	0.024 ppm	0.017 ppm
blank value b_0	-0.011 ppm	0.001 ppm
Equation of linear regression	$Y = 0.024X - 0.011$	$Y = 0.017X + 0.001$
Correlation coefficient	0.9997	0.9998
Standard deviation of sensitivity $S(b_1)$	5.158×10^{-5}	3.091×10^{-5}
Standard deviation of the blank value $S(b_0)$	0.005	0.002
Detection limit (DL)	0.238 ppm	0.418 ppm
Quantification limit (QL)	1.903 ppm	1.195 ppm

Limit of quantification: $LQ = \dfrac{b_0 + 10.S(b_0)}{b_1}$ (3)

$b_1 = \dfrac{SPE(x,y)}{SCE(x)}$ (4)

$b_0 = \bar{y} - b_1 \cdot \bar{x}$ (5)

$S(b_1) = \sqrt{\dfrac{s^2(e)}{SCE(x)}}$

Sensitivity b_1 standard deviation (6)

$S(b_0) = \sqrt{s^2(e)\left(\dfrac{1}{np} + \dfrac{\bar{\bar{x}}^2}{SCE(x)}\right)}$

Blank b_0 standard deviation (7)

$s^2(e)$: Regression experimental variance.

$SEC(x)$: Sum of squared deviations for the variable x.

$SPE(x, y)$: Sum of the products of deviations for the variable x and y.

The findings of the linearity test are summarized in *Table* 6:

By calculating the analytical blank's confidence interval (IC) for yttrium and scandium:

$IC = \left[b_0 - t_{V,1-\frac{\alpha}{2}} \times S(b_0);\ b_0 + t_{V,1-\frac{\alpha}{2}} \times S(b_0)\right]$ (8)

We got: IC $_{for\ yttrium}$ = [-0.027; 0.004]

IC $_{for\ scandium}$ = [-0.004; 0.007]

* where $t_{V,1-\frac{\alpha}{2}}$ is the Student value variable the risk $1 - \alpha/2$ with $v = (n \times p) - 2$ degrees of freedom ($\alpha = 1\ \%$).

The value 0 is included in the confidence intervals for both yttrium and scandium, so the model is correct. The linearity domain for yttrium is between 0 and 200 ppm, and for scandium it is between 0 and 100 ppm and that the domain of linearity is validated.

4.2. The specificity

To cover the method's scope, we performed 16 ($p = 16$) standard additions on selected samples. The regression line that connects the points in the following equation is established:

$r_i = C_0 + C_1 . v_i$ (9)

C_0 is the regression line's intercept.

Table 7. Results of specificity test for yttrium

Sample	Content before addition x_i (ppm)	Added content v_i (ppm)	Content after addition w_i (ppm)	Found content $r_i = w_i - x_i$ (ppm)
1	20.035	20.000	40.341	20.306
	20.035	40.000	61.013	40.978
	20.035	80.000	100.173	80.138
	20.035	100.000	120.841	100.806
2	30.524	20.000	49.995	19.471
	30.524	30.000	60.621	30.097
	30.524	60.000	90.236	59.712
	30.524	80.000	110.528	80.004
3	40.329	15.000	55.485	15.156
	40.329	30.000	71.007	30.678
	40.329	60.000	101.003	60.674
	40.329	80.000	120.012	79.683
4	60.346	15.000	75.034	14.688
	60.346	25.000	84.985	24.639
	60.346	50.000	109.898	49.552
	60.346	60.000	119.779	59.433

C_1 represents the slope of the regression line.

v_i added content of yttrium or scandium in the samples.

r_i found yttrium or scandium content = content measured after addition - content measured before addition.

Tables 7 and 8 present a summary of the measure-ments.

We plot the values of vi additions and founded values ri, as well as the calculated straight recovery and slope 1 (equation y = x) on a graph. *Figs.* 5 and 6 show the curves and the 16 points that correspond to the 16 standard additions for yttrium and scandium, respectively.

Table 8. Results of specificity test for scandium

Sample	Content before addition x_i (ppm)	Added content v_i (ppm)	Content after addition w_i (ppm)	Found content $r_i = w_i - x_i$ (ppm)
1	14.349	20.000	34.213	19.864
	14.349	40.000	55.012	40.663
	14.349	60.000	73.984	59.635
	14.349	80.000	94.869	80.520
2	7.168	20.000	27.256	20.088
	7.168	40.000	47.345	40.177
	7.168	60.000	66.034	58.866
	7.168	80.000	87.431	80.263
3	10.542	15.000	25.648	15.106
	10.542	30.000	40.445	29.903
	10.542	60.000	70.497	59.955
	10.542	80.000	90.612	80.070
4	5.254	15.000	20.314	15.060
	5.254	25.000	30.427	25.173
	5.254	50.000	55.341	50.087
	5.254	60.000	64.975	59.721

4.2.1. Interpretation

A test is performed to determine whether the slope of the regression line is equal to one by calculating the t_{obs}, which follows a Student distribution with $p - 2$ degrees of freedom. t_{obs} is a criterion calculated to ensure that the slope matches the description in the validation standard.

$$t_{obs} = \frac{|C_1 - 1|}{\sqrt{\dfrac{s^2(e)}{SCE(v)}}} = \frac{|C_1 - 1|}{s(C_1)} \tag{10}$$

$s^2(e)$: Regression experimental.

$SEC(v)$: Sum of squared deviations for the variable v.

$s(C_1)$: Slope (C_1) standard deviation.

a) If t_{obs} is less than or equal the Student table value (risk $1 - \alpha / 2$ with $v = p - 2 = 14$ degrees of freedom), so no interference and the specificity is acceptable.

b) If t_{obs} is greater than the Student table value, the method is not specific.
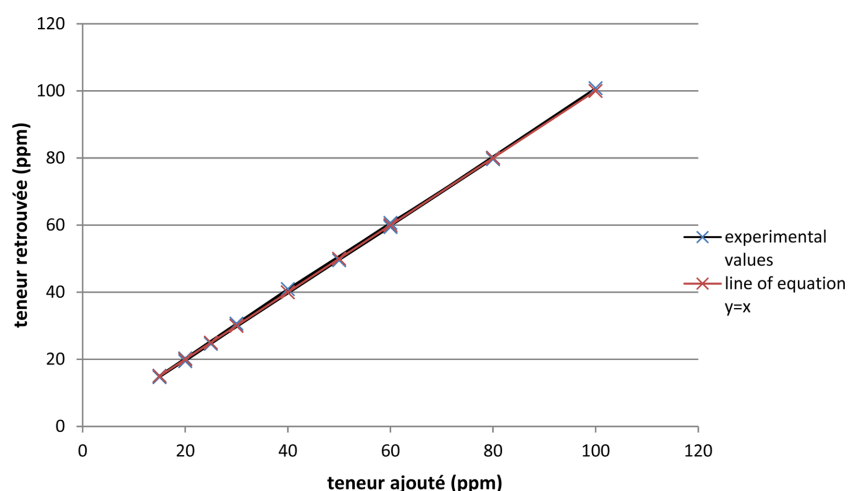

Fig. 5. Study of the specificity of the method for the determination of yttrium.
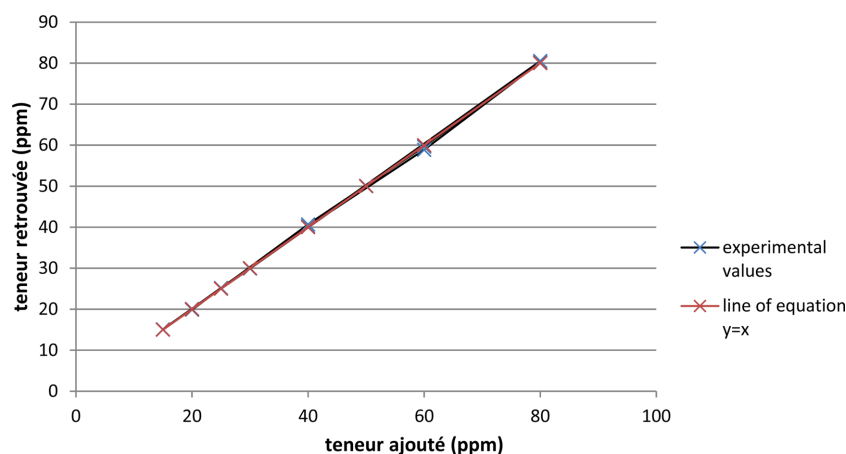
Fig. 6. Study of the specificity of the method for the determination of scandium.

The risk of error α is taken to 1 % ($t_{crit} = 2.977$ from the Student table).

▶ We obtain $t_{obs\ for\ yttrium} = 0.320$ and $t_{obs\ for\ scandium} = 0.362$

A test is performed to determine whether the intercept is equal to zero by calculating the t'_{obs}, which follows a Student distribution with p − 2 degrees of freedom. It is a criterion calculated to verify the intercept as described in the validation standard.

$$t'_{obs} = \frac{|C_0|}{s(C_0)} \qquad (11)$$

$s(C_0)$: The standard deviation of the intercept C_0

a) If t'_{obs} is less than or equal to the value of the Student table to the risk $1 − α/2$ with p − 2 degrees of freedom, so the intercept is equal to 0.

b) If t'_{obs} is greater than the Student table value, so the method is not specific.

▶ We obtain $t'_{obs\ for\ yttrium} = 0.147$ and $t'_{obs\ for\ scandium} = 0.344$

- $t_{obs} < t_{crit}$: No interference, so the specificity is acceptable for yttrium and for scandium.
- $t'_{obs} < t_{crit}$: The intercept equal to zero for yttrium and for scandium.

▶ The specificity for these two elements is acceptable.

4.3. The fidelity (repeatability & reproducibility)

4.3.1. Repeatability

We analyzed 10 samples in triplicate repeatability conditions. *Tables* 9 and 10 summarize the results for yttrium and scandium, respectively.

Table 9. Results of repeatability test for yttrium

Sample	Replicates			Average	Variance
	1	2	3		
1	60.653	61.945	61.040	61.212	0.439
2	61.002	62.067	60.945	61.338	0.399
3	63.054	62.080	60.978	62.037	1.078
4	60.897	60.798	61.542	61.079	0.163
5	61.012	62.084	62.060	61.718	0.374
6	62.943	61.037	60.348	61.442	1.806
7	62.812	60.938	62.047	61.932	0.887
8	62.031	60.941	63.004	61.992	1.065
9	60.948	61.785	61.104	61.279	0.198
10	61.075	60.973	62.005	61.351	0.323

Table 10. Results of repeatability test for scandium

Sample	Replicates			Average	Variance
	1	2	3		
1	14.235	14.986	15.043	14.754	0.203
2	12.567	13.027	12.876	12.823	0.055
3	13.987	13.274	14.001	13.754	0.172
4	15.055	15.127	14.899	15.027	0.013
5	14.568	14.267	14.873	14.569	0.092
6	13.994	14.239	14.364	14.199	0.035
7	14.755	14.205	14.679	14.546	0.089
8	13.944	14.318	14.068	14.110	0.036
9	15.021	15.009	14.873	14.967	0.007
10	14.539	14.061	14.973	14.524	0.208

$$S_r^2(x) = \frac{SCE_r(x)}{N-p} \text{ Internal repeatability variance}$$ (12)

$$SEC_r(x) = \sum_{i=1}^{p}\sum_{j=1}^{n}(x_{ij}-\bar{x}_i)^2 \text{ Sum of squared}$$

intra-sample differences (13)

$$\bar{x}_i = \frac{\sum_{j=1}^{n_j} x_{ij}}{n_i} \text{ Sample Average}$$ (14)

$$N = \sum_{j=1}^{p} n_j \text{ Total measurements}$$ (15)

$$S_r(x) = \sqrt{S_r^2(x)} \text{ repeatability standard deviation}$$ (16)

We calculate the repeatability coefficient of variation:

$$CV_r(\%) = \frac{S_r(x)}{\bar{\bar{x}}} \times 100$$ (17)

We have the standard deviation of repeatability value $S_r(x)$:

$S_r(x)_{\text{for yttrium}} = 0.820$ and $S_r(x)_{\text{for scandium}} = 0.302$

And the coefficient of variation of repeatability intra-laboratory CV_r :

$CV_{r\,\text{for yttrium}} = 1.33\,\%$ and
$CV_{r\,\text{for scandium}} = 2.11\,\%$.

◆ Checking the stability of fidelity

It is carried out using the Cochran test with a risk error equal to 1 %. This test determines whether fidelity is consistent across the application domain.

$$C_{obs} = \frac{S_{\max}^2(x)}{\sum_{i=1}^{p} S_i^2(x)}$$ (18)

$S_{\max}^2(x)$ Maximum experimental variance.
$\sum_{i=1}^{p} S_i^2(x)$ Sum of experimental variances.
C_{obs} Ratio calculated from the above-mentioned equation.

C_{crit} The Cochran value variable to the risk 1 % with n distributions and p samples.

Table 11 displays the statistical results of the fidelity stability verification.

▶ C_{obs} for yttrium and scandium is less than the table value at 1 % margin of error. So the fidelity in terms of intra-laboratory repeatability is constant across the entire field of application for these two elements.

4.3.2. Reproducibility

A sample of industrial phosphoric acid was tested for 10 days (p = 10) with three replicates (n = 3). *Table* 12 summarizes the yttrium results, while *Table* 13

Table 11. Statistical results of the verification of the stability of fidelity

Designation	Observed value for yttrium	Observed value for scandium
$S_{\max}^2(x)$	1.806	0.208
C_{obs}	0.268	0.039
Number of samples (p)	10	10
Number of replicates (*n*)	3	3
C_{crit} (1 %)	0.536	0.536

Table 12. Results of reproducibility test for yttrium

Day	Replicates			Average	Variance	$S_r^2(x)$	$S_L^2(x)$	$S_R(x)$	CV_R (%)
	1	2	3						
1	62.653	61.845	61.140	61.879	0.573				
2	61.102	62.067	60.945	61.371	0.369				
3	62.254	62.354	61.978	62.195	0.038				
4	61.897	60.998	61.042	61.312	0.257				
5	61.572	62.354	62.237	62.054	0.178	0.436	0.016	0.672	1.089
6	62.873	61.457	60.793	61.707	1.128				
7	62.731	61.538	62.108	62.125	0.356				
8	62.458	60.981	63.104	62.181	1.184				
9	60.978	61.095	61.184	61.085	0.011				
10	61.585	60.998	62.037	61.540	0.271				

Table 13. Results of reproducibility test for scandium

Day	Replicates			Average	Variance	$S_r^2(x)$	$S_L^2(x)$	$S_R(x)$	CV_R (%)
	1	2	3						
1	14.349	14.721	14.543	14.537	0.035				
2	14.298	14.614	14.876	14.596	0.084				
3	14.824	14.598	14.623	14.981	0.015				
4	14.235	14.398	14.456	14.363	0.013				
5	14.983	14.789	14.655	14.809	0.027	0.025	0.012	0.192	1.328
6	14.534	14.442	14.497	14.491	0.002				
7	14.654	14.397	14.376	14.475	0.024				
8	14.394	14.236	14.578	14.402	0.029				
9	14.367	14.279	14.521	14.389	0.015				
10	14.328	14.443	14.497	14.422	0.007				

summarizes the scandium results.

We have :

$$N' = N - \frac{\sum_{i=1}^{p} n_i^2}{N}$$ Corrected average number of repetitions $\qquad$ (19)

$$S_L^2(x) = \frac{(p-1)\left(\frac{SEC_L(x)}{p-1} - S_r^2(x)\right)}{N'}$$

Variance inter-sample. $\qquad$ (20)

$$S_R^2(x) = S_L^2(x) + S_r^2(x)$$ Reproducibility Variance. $\qquad$ (21)

$$CV_R(\%) = \frac{S_R(x)}{\bar{\bar{x}}} \times 100$$ Coefficient of variation of reproducibility. $\qquad$ (22)

n_i : Number of repetition per day ($n = 3$).
N: Total measurements.

$SCE_L(x)$: Squared inter-sample differences sum.
$S_r^2(x)$: Variance of repeatability.
$S_R(x)$: Internal reproducibility standard deviation.

$CV_{R\,for\,yttrium}$ = 1.09 % and $CV_{R\,for\,scandium}$ = 1.33 %.

▶ So, the fidelity in terms of reproducibility is acceptable.

4.4. The accuracy

We make 10 repetitions on NIST standards (National Institute of Standards and Technology) for yttrium (Y) 50 ppm and scandium (Sc) 20 ppm.

Table 14 summarizes the results for yttrium and *Table* 15 summarizes the results for scandium.

• Calculate $t_{cal} = \dfrac{\dfrac{|\bar{x} - x_{SR}|}{S_R(x)}}{\sqrt{n}}$ $\qquad$ (23)

Table 14. Results of accuracy test for yttrium

Repetition	Concentration of yttrium (ppm)	Average of *n* (ppm)	Variance	t_{cal}	t_{crit}
1	50.178				
2	50.235				
3	49.878				
4	50.984				
5	51.543	50.307	0.331	2.94	3.355
6	50.056				
7	49.855				
8	50.087				
9	49.678				
10	50.578				

Table 15. Results of accuracy test for scandium

Repetition	Concentration of scandium (ppm)	Average of n (ppm)	Variance	t_{cal}	t_{crit}
1	19.978				
2	20.234				
3	20.198				
4	19.697				
5	20.758	20.072	0.085	2.723	3.355
6	19.947				
7	19.998				
8	20.154				
9	19.892				
10	19.873				

t_{cal} : Ratio calculated from the equation cited above to verify the accuracy.

- Obtain $t_{crit} = t_{V,1-\frac{\alpha}{2}}$ from the Student table.
- Compare t_{cal} to t_{crit}

We decide as follows:

- If $t_{cal} > t_{crit}$: error accuracy is significant, so the method is not justified.
- If : $t_{cal} \leq t_{crit}$ error accuracy is not significant, so the method is justified.
- ▶ The value of t_{cal} for yttrium and scandium is less than the Student table value. So the method is considered justified.

5. Conclusions

The current study has developed and validated a method for determining yttrium and scandium in industrial phosphoric acid obtained through a wet process. It has several advantages, including measurement speed, accuracy, and low operating costs. The proposed method has the advantage of not requiring the use of reagents to prepare samples for analysis, moreover, the samples were analyzed directly without dilution or preparation, increasing the accuracy of the analyzes. The method is accurate, fast, and useful for industrial phosphoric acid quality control and determining the precise concentration of valuable elements such as yttrium and scandium present in industrial phosphoric acid before extraction. The proposed method for determining yttrium and scandium

in industrial phosphoric acid reveals that it contains more yttrium than scandium (about 60 ppm yttrium and 15 ppm scandium).

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