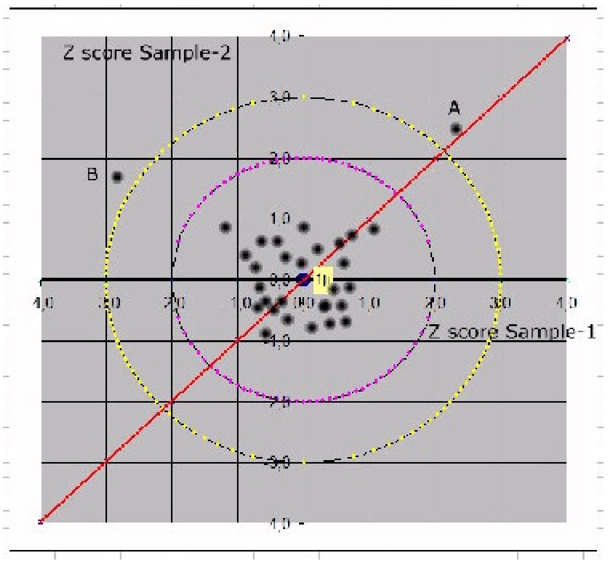
QUALITY ASSURANCE
Applying statistics to analytical data



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Languages available
English

Summary
Laboratories analyse, for example, raw materials, food ingredients, air pollution or, in hospitals, serum. You can imagine how very important it is that the results of the analysis are the right results. You do not want to be poisoned by your food!
To compare the results within a laboratory or among various laboratories, a standard method of analysis is used for the same sample. You might think the results are identical, and fall within the range of random errors. But no, systematic errors can cause differences of 200 % and more!
A well-established method for visualising variability of results is the Youden plot. In this project, you determine the iron content spectrophotometrically in two samples, and try to establish the random and systematic error. Planning your time and your workload are a part of the project.

Activity type C
Use of scientific knowledge and understanding to solve problems
Working in teams to solve problems
Time and workload management

Techniques
UV-VIS spectroscopy

Field
Quality assurance in analytical chemistry

Time
Practical lessons: 180 minutes
Theory lessons: 45 minutes
Out of class time: 45 minutes

StandardBase procedures
Determination of iron in water using visible spectrophotometry

StandardBase techniques
Ultraviolet and Visible (UV-VIS) absorption spectroscopy

Other resources
Waterschap Hunze en Aa's, the Netherlands; www.hunzeenaas.nl
http://en.wikipedia.org/wiki/Quality_control#Quality_assurance
http://deming.eng.clemson.edu/pub/tutorials/qctools/homepg.htm
http://www.st.com/stonline/press/news/glossary/q.htm

Student’s document

QUALITY ASSURANCE: Applying statistics to analytical data

Why Quality Assurance (QA)? Do we really need all the extra paperwork, supervision, verification and audits? We did without QA for a long time. So why bother now?

Suppose you are ill and lying in a hospital. Every day they take a blood sample to measure your potassium value. Blood potassium levels vary - for adults it should be 3.5 -5.0 mmol/L. And there are the results, different every day, too high or too low. Are these results reliable? You hope so, otherwise the physician will be prescribing medication that you do not need and that may not cure you.

This is where QA comes in. With QA you can minimise mistakes, wrong results etc. It is why, in fields such as medical, pharmaceutical, food analysis etc., there are strict formal regulations on the QA of analysis. QA is part of the daily routine in laboratories nowadays. Have a taste of QA in this project.

An example of a Quality Assurance plan for a laboratory can be found at http://www.anr.state.vt.us/dec/lab/docs/Section1.pdf

Your brief

You work in an environmental laboratory and a student from a vocational school has to complete a traineeship in your laboratory. The determination of iron in water, using visible spectrophotometry, is assigned to the student. To your surprise and concern, the student’s results for the iron content differ significantly from the ‘old’ results. You go into action!

You will establish the random and systematic error of the determination of iron in water, using visible spectrophotometry.

To begin the check, you perform the same method on two different samples, both volumetric standards, of which you know the exact iron content. You then draw a Youden plot and establish the random and systematic error.

The group’s tasks are to determine the iron content in two different samples:

1. ammonium iron(II) sulfate hexahydrate
2. iron(II) ethylenediammonium sulfate tetra hydrate

Each student determines both samples twice.

Your investigation

Task 1

Use **www.standardbase.com**: *Determination of iron in water using visible spectrophotometry* (the procedure for pure $Fe(NH_4)_2(SO_4)_2.6H_2O$ and $(CH_2NH_3)_2Fe(SO_4)_2.4H_2O$ has to be adjusted, see **Student sheet 1**).

Task 2

Summarise the group’s results of the iron content in the samples. Draw the Youden plot and put in the results, use **ProBase** Zscores Youdenplot 2008.xls Establish the random and possible systematic error (see **Student sheet 2**: *Youden Plot*).

Make a plan for all tasks and book the necessary instruments and chemicals.
Discuss the plan with your teacher, including instruments and chemicals.
Gather information about the technique to be used.

Remember that a risk assessment must have been carried out before you start any practical work. Attention: the glacial ethanoic acid is very dangerous. Protective gloves and safety goggles must be worn.

Your findings
Write a report with your results and conclusions. Use your data to explain the existence of random and possible systematic error in your laboratory.

Students self assessment
Use the file *Evaluating skills.doc* from the **ProBase** website

Student sheet 1

Use **www.standardbase.com**: *Determination of iron in water using visible spectrophotometry.* Follow the instructions in the experiment but, in the step-by-step, adjust number **5. Procedure** for pure $Fe(NH_4)_2(SO_4)_2.6H_2O$ (5.1) and $(CH_2NH_3)_2Fe(SO_4)_2.4H_2O$ (5.2) as follows.

5.1 Procedure

Sample ammonium iron(II) sulfate hexahydrate
Weigh out accurately about 105 mg $Fe(NH_4)_2(SO_4)_2.6H_2O$, and dissolve it in 25 cm^3 of 1 mol/dm^3 sulfuric acid. Transfer to a 100 cm^3 volumetric flask and make up to the mark with distilled water. Mix the solution completely and then pipette 1.00 cm^3 portions of this solution into a 100 cm^3 standard flask.
Into this 100 cm^3 standard flask add 10 cm^3 ammonium ethanoate buffer and 20 cm^3 of 1,10-phenanthroline solution. Make up to the mark with distilled water. Prepare 2 different samples.

Prepare a blank by adding the 10 cm^3 ammonium ethanoate solution and 20 cm^3 of 1,10-phenanthroline solution and making up to the mark with distilled water.

Determine the absorbance, at 515 nm, of the six standard solutions and the two samples of ammonium iron(II) sulfate hexahydrate, using the 1 cm cuvettes.

5.2 Procedure

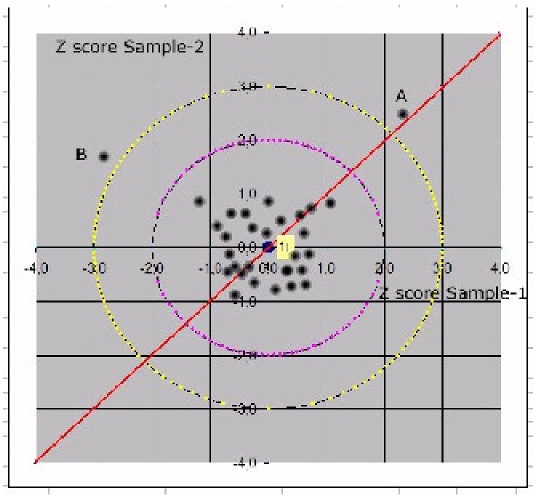
Sample iron(II) ethylenediammonium sulfate tetra hydrate
Weigh out accurately about 105 mg $(CH_2NH_3)_2Fe(SO_4)_2.4H_2O$, and dissolve it in 25 cm^3 of 1 mol dm^3 sulfuric acid. Transfer to a 100 cm^3 volumetric flask and make up to the mark with distilled water. Mix the solution completely and then pipette 1.00 cm^3 portions of this solution into a 100 cm^3 standard flask.
Into this 100 cm^3 standard flask add 10 cm^3 ammonium ethanoate buffer and 20 cm^3 of 1,10-phenanthroline solution. Make up each to the mark with distilled water.

Use the same blank prepared in **5.1 Procedure**.

Determine the absorbance at 515 nm of the six standard solutions and the two samples of iron(II) ethylenediammonium sulfate tetrahydrate, using the 1 cm cuvettes.

Student sheet 2: Youden Plot

The Youden plot is a graphical method used to analyse laboratory data, where all students (laboratories) have analysed two samples. The plot visualises systematic as well as random errors.



For the Youden plot (Youden, 1959) the two samples must be similar and reasonably close in the magnitude of the property being evaluated. The axes for this plot are drawn on the same scale: one unit on the *x*-axis has the same length as one unit on the *y*-axis.

Each point on the plot corresponds to the results of one student and is defined by a first response variable on the horizontal axis (i.e. *sample 1* response value) and a second response variable 2 (i.e., *sample 2* response value) on the vertical axis.

A circle is drawn, as shown in the figure, that usually includes 95% of the measurements, if individual constant errors could be eliminated. (2s-border or *Z*=2. A 45-degree reference line is drawn.

Interpretation

Points that lie near the 45-degree reference line but far from the centre of the circle median indicate large systematic error. Points that lie far from the 45-degree line indicate large random error. Points outside the circle indicate large total error. Examine the plot: *sample A* on the upper right has systematic errors while *sample B* has random errors.

Using *Excel*

This activity is supported by a worksheet in Excel:
http://www.herbies.nl/getfile.asp?FILE_ID=315

To make it usable, even in cases where the two samples have a quite different magnitude, it is not the actual values (results) that are displayed, but the *Z*-score. This *Z*-score is the difference between the measurement value and the mean or expected value, divided by standard deviation *σ*.

$$Z = \frac{(x \quad \mu)}{\sigma}$$

So when, for instance, the expected value of *sample 1* is 14.5 and σ = 0.5, then a result of 13.0 means *Z* = (13.0-14.5)/0.5 = -3. For a *Z*-score of −3, it means that the *sample 1* value is 3 times the standard deviation below the mean. When *Z*= +1 it means that it is just one σ above the mean value. When measurements are entered in page 2 of the *Excel* worksheet (yellow square), the *Z*-scores are automatically calculated.

It is recommended that the results from a whole group are used.

Teacher's document

Overview

Students work as analysts in an environmental laboratory. They carry out determinations of iron in pure ammonium iron(II) sulfate hexahydrate and iron(II) ethylenediammonium sulfate tetrahydrate.
They put their results onto a Youden plot, to establish the random and possible systematic error in the determination of iron in their laboratory.
To be effective, they need scientific skills and knowledge, they have to work in a team and communicate effectively.
Students learn to:

- tackle scientific problems by applying their practical skills and their knowledge and understanding about visible spectrophotometry.
- observe, measure and analyse data collected from visible spectrophotometry and evaluate these
- use statistics to evaluate data (Youden plot)
- work with others and manage time and workload.

Developing student's skills

Each student will measure both samples twice.
The groups draw the Youden Plot; they should receive feedback on their evaluation of the data, to establish random and/or systematic error.

Organising and managing the class

Students should have experience of visible spectrophotometry.

It is suggested that students work in groups of four to five, preferably in two or more groups. Each student will analyse both samples twice. Make sure students have sufficient time to understand the Youden Plot, and to share and discuss their results before drawing the plot.

Students need to recognise the importance of taking care and pride in their work. They need gently reminding of this while they are working. They may need three types of help:

- help with technical details, including manual skills and correct handling of chemicals and equipment
- help with, and vigilance over, health and safety issues
- help with working relations in their group.

Students from the different groups should draw one Youden Plot. They can comment on the random and/or systematic error individually and as a group.

Session plan for teachers

A suggested approach is:

- introduce the activity and check prior knowledge (35 minutes)
- arrange students into groups to discuss and allocate the work (10 minutes)
- carry out practical work (180 minutes)

(the same calibration solution can be used by more than 1 student)

- groups come together to share results, complete reporting forms, draw Youden Plot and draw conclusions (45 minutes).

Technical notes

Equipment and materials

Materials and their CAS numbers

Name	Grade	CAS number
glacial ethanoic acid	Reagent	64-19-7
ammonium ethanoate	Reagent	631-61-8
concentrated hydrochloric acid	Reagent	7647-01-0
concentrated sulphuric acid	Reagent	7664-93-9
ammonium iron(II) sulphate hexahydrate	AR	7783-85-9
iron(II) ethylenediammonium sulfate tetrahydrate	AR	113193-60-5
1,10-phenanthroline	Reagent	66-71-7
iron-free distilled water	-	

Note 1: 1,10-phenanthroline chloride monohydrate (CAS number 18851-33-7) can be used in place of 1,10-phenanthroline.

Note 2: Glacial ethanoic acid is very dangerous. Protective gloves and safety goggles must be worn. The chemicals for the buffer are of such high concentration and volume that they are rather expensive.

Equipment

Instruments

- UV-VIS spectrometer for use at 515 nm
- analytical balance capable of weighing to 0.0001 g

Glassware and other equipment

- disposable 1 cm cuvettes
- 2 x 1 dm^3 standard volumetric flask
- 15 x 100 cm^3 standard volumetric flasks
- 1 x 250 cm^3 measuring cylinder
- 1 x 50 cm^3 measuring cylinder
- 2 x 50 cm^3 burettes
- 2 x 10 cm^3 pipette
- 2 x 1 cm^3 pipette

Preparation

Prepare the following solutions for the students:

Ammonium ethanoate buffer solution

Dissolve 250 g of ammonium ethanoate in 100 cm^3 distilled water. Carefully add 700 cm^3 of glacial ethanoic acid. Homogenise the solution.

1,10-phenanthroline solution

Dissolve 1.00 g of 1,10-phenanthroline in 1 dm^3 of water to which has been added 20 drops of concentrated hydrochloric acid.
Note: Use 1 cm^3 of reagent to no more than 0.1 mg of standard iron solution.

TESTING PRIOR KNOWLEDGE

Choose the correct answer.

1. $Fe(NH_4)_2(SO_4)_2.6H_2O$ must be dissolved in acidic water because:
   a. H^+ ions form a soluble complex with Fe^{2+} ions
   b. $Fe(H_2O)_4^{2+}$ is a strong cationic acid and hydrolyses in water to an insoluble complex
   c. H^+ ions react with SO_4^{2-} to H_2SO_4
   d. answers a, b and c are all true

2. What mass of iron (in milligrams) is present in 0.5267 g of ammonium iron(II) sulfate-6-water?
   a. 25.00
   b. 75.00
   c. 150.0
   d. 200.0

3. The mass concentration of iron in the stock solution is $c(Fe^{2+})$ = 25 mg L^{-1}. What is the mass concentration in a standard solution if 10.00 mL of this solution is diluted to 250 mL?
   a. 1 mg L^{-1}
   b. 2 mg L^{-1}
   c. 3 mg L^{-1}
   d. 4 mg L^{-1}

4. In a Youden plot you can determine:
   a. the systematic error
   b. correctness
   c. random error
   d. both a and c

5. If the absorbance of a solution is 0.4, the transmittance is:
   a. 5.89%
   b. 67.4%
   c. 39.8%
   d. 40.0%

Note: answers are given in red. These need to be removed before the test is used.

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