Figure 3.6. MEASURING: An Introduction

Measurements are made to answer questions such as: How long is this object? How heavy is it? How much chlorine is there in this water?

In order to make measurements we need suitable units of measure. When we ask the length of an object, we expect an answer that will tell us how many millimetres it is from one end of the object to the other end. We need some way to find out how many times a unit quantity, such as a millimetre, is contained in the length of a particular object. Rarely will a unit of length go into the length of the object a whole number of times. Almost always our answer will be, "so many units plus some fractional part of a unit." If a quantitative measurement of length is to be trusted, we must take great care that the unit we choose is invariable and suitable for the task. We must also have devised a method of measuring the object with this unit.

Some measurements require only a simple procedure and little equipment. The apparatus may be no more than a scale marked off in the desired units. It is easy to measure the width of a table by using a metre stick marked off in centimetres and millimetres. The air temperature of a room is found by looking at a thermometer and reading the position of the mercury on the scale. The pressure in an automobile tire is found by applying a tire guage to the valve and looking at the scale to read the pounds of air pressure per square inch of surface of the tire.

When the proper instrument is available and used carefully, many measurements require no more than a careful reading of a scale. On the other hand, most scientific measurements involve elaborate equipment and a complicated technique of using it.

If a chemist wants to determine the amount of chlorine in a material, he may perform a fairly lengthy sequence of operations. He must first weigh out a sample of the material and record the weight. The sample must be treated with an acid that will dissolve out all of the chlorine. Any insoluble residue must be filtered off to obtain a clear solution, and the filter paper must be washed carefully with excess acid to make sure that none of the chlorine is left behind.

It may then be necessary to adjust the acid concentration or the volume of the solution – or both – before adding a second reagent to precipitate the chlorine. The usual reagent is silver nitrate. Enough must be added to precipitate all the chlorine as insoluble silver chloride. This precipitate of silver chloride is separated from the acid by filtering the suspension through a crucible with a porous bottom.

Before doing this, however, it will be necessary to weigh the crucible, making sure that it is dry. The precipitate collected in the crucible should be washed with distilled water to remove all traces of reagent, and then dried. The weight of the empty crucible subtrac- ted from the weight of the crucible and the precipitate gives the weight of the silver chloride.

By using the atomic weights of silver and chlorine, the proportion of chlorine in the silver chloride molecule can be determined. The weight of silver chloride precipitate multiplied by this proportion gives the weight of chlorine in the precipitate. This, of course, is also the weight of the chlorine in the original sample. The weight of chlorine divided by the weight of the sample and multiplied by 100 gives the percent of chlorine in the sample, thus completing the determination of chlorine.

The Errors in Measurements

If we consider that each weighing (sample, empty crucible, and crucible plus precipitate) is a measurement, we see that three measurements are necessary to measure the amount of chlorine in the material. This sketch of the analytical procedure reveals that there are several steps, all of which must be taken with great care. If the silver chloride precipitate is not carefully washed, the silver chloride may be contaminated and appear too heavy. If the precipitate is not transferred completely to the crucible, some may be lost. None of these steps can be carried out so that they are absolutely free of error. For example, since silver chloride is very slightly soluble, some of the chloride will not be precipitated. This results in error.

Evidently a measurement is subject to many sources of error, some of which may make the measurement too large, while others may tend to make the measurement too small. It is the aim of the experimenter to keep these sources of error as small as possible. They cannot be reduced to zero. Thus in this or any measuring procedure, the task remains to try to find out how large an error there may be. For this reason, information about the sources of error in measurements is indispensable.

In order to decide which one of two materials contains the larger amount of chlorine, we need accurate measurements. If the difference in chlorine content between the materials is small and the measurement is subject to large error, the wrong material may be selected as the one having the larger amount of chlorine. There also may be an alternative procedure for determining chlorine content. How can we know which procedure is the more accurate unless the errors in the measuring have been carefully studied?

1 Youden describes a procedure for measuring chlorine content. What are the similarities and the differences between this data-based investigating and the one described in Figure 3.4. SAMPLING: *How Polls are Conducted*?

2 Was a *measuring instrument* used in the investigations described in Figure 3.4. SAMPLING: *How Polls are Conducted*?
- If *Yes*, identify it and compare it briefly with the types of measuring instruments mentioned by Youden;
- if *No*, briefly justify your answer.

3 Youden discusses *measurement error* in the last three paragraphs above. Are there situations in which measurement error can be *eliminated*? Explain briefly.

4 Youden says in his fifth paragraph: *He must first weigh out a sample ....*; is there a corresponding *population*?
- if *Yes*, describe it briefly;
- if *No*, justify your answer and explain whether the word *sample* is being used correctly in the statistical sense.

(*continued overleaf*)

Small Differences in Measurements

The detection of small differences with respect to some property is a major problem in science and industry. Two or more companies may submit samples of a material to prospective purchasers. Naturally the purchasers will want first of all to make sure that the quality of the material they buy meets their requirements. Secondly, they will want to select the best material, other things, such as cost, being equal.

When we buy a gold object that is stated to be 14 carats *fine* this means that the gold should constitute 14/24 of the weight. We accept this claim because we know that various official agencies occasionally take specimens for chemical analysis to verify the gold content.

An inaccurate method of analysis may lead to an erroneous conclusion. Assuming that the error is in the technique and not some constant error in the scales or chemicals used, the chemical analysis is equally likely to be too high as it is to be too low. If all the items were exactly 14 carats, then chemical analysis would show half of them to be below the specified gold content. Thus an article that is actually 14 carats fine might be unjustly rejected, or an article below the required content may be mistakenly accepted. A little thought will show that if the error in the analysis is large, the manufacturer of the article must make the gold content considerably more than 14/24 to ensure acceptance of nearly all the items tested.

There are two ways around this dilemma. The manufacturer may purposely increase the gold content above the specified level. This is an expensive solution and the manufacturer must pass on this increased cost. Alternatively, the parties concerned may agree upon a certain permissible *tolerance* or departure from the specified gold content. Inasmuch as the gold content cannot be determined without some uncertainty, it appears reasonable to make allowance for this uncertainty. How large a tolerance should be set? This will depend primarily on the accuracy of the chemical analysis. The point is that, besides the problem of devising a method for the analysis of gold articles, there is the equally important problem of determining the sources of error and the size of the error of the method of analysis. This is a recurrent problem of measurement, regardless of the material or phenomenon being measured.

There may be some who feel that small differences are unimportant because, for example, the gold article will give acceptable service even if it is slighlty below 14 carats. But small differences may be important for a number of reasons. If one variety of wheat yields just one percent more grain than another variety, the difference may be unimportant to a small farmer. But added up for the whole of the United States this small difference would mean at least ten million more bushels of wheat to feed a hungry world.

Sometimes a small difference has tremendous scientific consequences. Our atmosphere is about 80 percent nitrogen. Chemists can remove the oxygen, carbon dioxide and moisture. At one time the residual gas was believed to consist solely of nitrogen. There is an interesting chemical, ammonium nitrite, NH_4NO_2. This chemical can be prepared in a very pure form. When heated, ammonium nitrite decomposes to give nitrogen (N_2) and water (H_2O). Now pure nitrogen, whether obtained from air or by the decomposition of NH_4NO_2, should have identical chemical and physical properties. In 1890, a British scientist, Lord Rayleigh, undertook a study in which he compared nitrogen obtained from the air with nitrogen released by heating ammonium nitrite. He wanted to compare the densities of the two gases; that is, their weights per unit volume. He did this by filling a bulb of carefully determined volume with each gas in turn under standard conditions: sea level pressure at 0^o celsius. The weight of the bulb when full minus its weight when the nitrogen was exhausted gave the weight of the nitrogen. One measurement of the weight of atmospheric nitrogen gave 2.31001 grams. Another measurement of nitrogen from ammonium nitrite gave 2.29849 grams. The difference, 0.01152, is small. Lord Rayleigh was faced with a problem: was the difference measurement error or was there a real difference in the densities? On the basis of existing chemical knowledge there should have been no difference in densities. Several additional measurements were made with each gas, and Lord Rayleigh concluded that his data were convincing evidence that the observed small difference in densities was in excess of the experimental error of measurement and therefore actually existed.

There now arose the intriguing scientific problem of finding a reason for the observed difference in density. Further study finally led Lord Rayleigh to believe that the nitrogen from the air contained some hitherto unknown gas or gases that were heavier than nitrogen, and which had not been removed by the means used to remove the other known gases. Proceeding on this assumption, he soon isolated the gaseous element argon. Then followed the discovery of the whole family of the rare gases, the existence of which had not even been suspected. The small difference in densities, carefully evaluated as not accidental, led to a scientific discovery of major importance.

1 What step(s) did Lord Rayleigh take to assess the size of the error in his measuring process?
- How *generally* useful are the matter(s) you have identified in Lord Rayleigh's work for dealing with measurement error?

2 What does Youden say are the likely consequence(s) of excessive measurement error in data-based investigating?

3 Identify a situation, involving measuring *weight* in a laboratory, where an important small difference arises? Explain briefly.
- What would be the practical problem(s) associated with a small difference like this?

4 What does Youden indicate as the distinction between *imprecision* and *inaccuracy* in a measuring process? Indicate explicitly where Youden mentions this distinction.

5 How did Lord Rayleigh deduce that argon is *heavier* than nitrogen?

6 What factor(s) would make it considerably easier for us, if we were to repeat Lord Rayleigh's work *now*, than it was for him late in the nineteenth century?