

## Determination of cyanide in soil - Pilot testing of ISO/DIS 11 262

### Introduction

The aim of the present experiments is to test the draft ISO method, ISO/DIS 11 262, in one single laboratory before sending the method out for method testing as an interlaboratory comparison. A number of factors based on previous experience which could influence the analytical quality have been tested by ruggedness tests.

### Methods and materials

The ISO/DIS 11 262 method from 22 September 1997 with corrections received from the convenor in October 1997 was tested, using the colorimetric end-point determination.

The samples that were tested were non-polluted freeze-dried oxidised clay and non-polluted freeze-dried blue clay. The samples were spiked with 1.00 ml 100 mg/l  $K_3Fe(CN)_6$  per 10,0 g soil the afternoon before analysis, and stored at 0-4 °C overnight. Quality control samples were non-spiked soil samples, 1.00 ml of 100 mg/l  $K_3Fe(CN)_6$  spike solution without soil. Non-digested NaCN standards were used for checking the colour reaction and the calibrants (KCN standards).

Ruggedness tests were performed mainly to test the digestion procedure, where the effects of several factors were tested in each batch of 5 or 10 digestions. Three tests were performed as 2 level fractional factorial designs. Up to 7 factors can be tested in 8 digestions, thus allowing for one soil blank and one quality control per batch. The main tendencies observed were re-tested for confirmation.

The factors tested were:

- the quantity of phosphoric acid (20 ml (ISO/DIS 11 262) versus 40 ml)
- the type of acid (concentrated phosphoric acid (ISO/DIS 11 262) versus concentrated sulphuric acid)
- sulphide interference (tests with addition of 200 mg/kg and 1000 mg/kg versus no addition)
- addition of zinc sulphate reagent in the determination of total cyanide as a one step digestion procedure (only specified in ISO/DIS 11 262 for the determination of easy-liberatable cyanide)
- the volume of the digestion flask (500 ml versus 1000 ml), the quantity of soil (5 g, 10 g as in ISO/DIS 11 262, and 15 g)
- the time and temperature of the colour reaction (room temperature (ISO/DIS 11 262) versus 37°C)
- the time of digestion for total cyanide as a one step digestion procedure (2 hours (ISO/DIS 11 262) versus 3 hours).

In the first 2-factorial test the sample volume, soil type, digestion time, addition of zinc sulphate, addition of sulphide (10 g/kg soil) and the digestion vessel volume were tested. In the second 2-factorial test the flow rate, the sample size, sulphide addition (10 g/kg (re-testing), colour development temperature, and the one versus two step

digestion procedure were tested, while the flow rate and acid-type tests were attempted, but omitted (see discussion below).

The last 2-factorial test covered tests with acid-types, sulphide (200 mg/kg), soil types (re-testing), and addition of zinc reagent.

The colour reaction was followed in detail for selected samples as a separate test and the re-testing with varying soil quantities was also performed separately.

## Results

The average recovery of the samples digested by phosphoric acid was 108% in samples that did not contain large quantities of sulphide (see figures 1, 2 and 3). The relative standard deviation of these samples was 5%. In comparison the average recovery of the digested control solution was 107% on average. The slightly high recovery in these experiments is considered to be mainly due to the titration procedure for determining the strength of the cyanide calibrant solution, where changing the method normally applied by the reference laboratory to the proposed ISO/DIS 11 262 method was not optimised (sub-optimal burette and sample volumes); this implied a relatively larger uncertainty of this step of the procedure. Further specifications of this standard titration procedure are not considered to be necessary in the ISO/DIS 11 262 standard.

### *Acid type*

In the second 2-factorial test the addition of sulphuric acid in the second digestion step caused an excessive heat reaction, whereby the digestion mixture boiled explosively. It is therefore not recommended to substitute phosphoric acid with sulphuric acid in the two step digestion procedure.

There was a significantly lower recovery and a poorer reproducibility with digestion by sulphuric acid compared to phosphoric acid in the third 2-factorial test, with the one step digestion procedure (sulphuric acid: 66% recovery (CV: 35%) and phosphoric acid 112% recovery (CV: 6%)) (Figure 1). This was the largest effect observed in all the tests. The necessary quantity of 20 ml phosphoric acid costs approximately 5 DKK, which is approximately 1% of the total price of the analysis. In comparison sulphuric acid costs approximately 3 DKK.

### *Quantity of phosphoric acid*

There was no significant difference (approx. 2 %) between addition of 20 ml and 40 ml of concentrated phosphoric acid (Figure 1).

### *Soil type*

There was a slightly lower recovery for oxidised clay in the first test, but this tendency was only significant for 2 of the 4 oxidised clay samples (Figure 1), for the other two samples the difference was insignificant (2%) and for this reason the tests were repeated. The recovery was slightly lower for the oxidised samples, but again this was only significant for the samples that were digested with sulphuric acid. If these results are omitted the difference in recovery of cyanide from oxidised clay and blue clay was not significant. It is concluded that unless the effects were coinciding such as large quantities of sulphide or application of sulphuric acid, there was no significant effect of the tested soil matrices on the recovery,

### *Sulphide*

The results showed a tendency to be 10-20 % lower with the addition of a high concentration of sulphide (10 g/kg soil) in both of the first 2-factorial tests (Figure 2). In the final test with sulphide quantities that normally occur in soil (200 mg/l) this tendency was not significant in the tests with phosphoric acid, and with sulphuric acid the recovery of cyanide was higher in the samples with sulphide. The tendency was only evident in two of the four replicates in both of the first 2 factorial tests. This indicates that there could be an interactive-effect between sulphide and the other factors that were tested. The coinciding effects were in the first test a higher concentration with 3 hours digestion contra 2 hours digestion and with blue clay.

In the second test a higher concentration was achieved with sulphide in combination with determination of total cyanide as a two step digestion procedure (versus a one step digestion) and with determination with 5 g sample (versus 15 g sample). This could indicate that for some samples with an extreme matrix composition, the digestion procedure should be tested, and if necessary modified for example by prolongation. However, on the basis of these experiments it was not possible to achieve a clear indication of how the procedure should be modified.

### *Addition of zinc sulphate*

In accordance with ISO/DIS 11 262 zinc sulphate is added in the first step of the determination of easily-liberatable cyanide, but it is not added when total cyanide is determined as a one step digestion of the sum of easy liberatable and complex cyanide. The effect of adding zinc sulphate (reagent 4.3) in the determination was tested and found to give no significant effect in the first 2-factorial test, and slightly lower results in the final factorial test (9 %) (Figure 2). It is therefore concluded that it is not necessary to add zinc sulphate reagent to the determination of total cyanide as a one step digestion procedure.

### *Vacuum rate*

The vacuum rate indicated in ISO/DIS 11 262 is 25 ml/min. The laboratory tests showed an average flow rate of 400 ml/min. At average flow rates below 300 ml/min there was a tendency that the absorption liquid to flow back into the digestion vessel. It is therefore recommended that the standard is modified to allow for a suitable vacuum flow rate that hinders back flowing of the absorption liquid, and that the specification of 25 ml/min is omitted.

### *Bottle size*

It is concluded from experiment with different bottle sizes (figure 3) that a difference in bottle size from 500 to 1000 ml does not effect the recovery of cyanide with this proposed method and these samples.

### *Colour reaction*

The time and temperature of the colour reaction was tested at room temperature and at 37°C on a KCN standard, and a digested Fe(III)-cyanide spiked soil sample control solution determined as easily-liberatable and complex cyanide respectively (Figure 4). Together with the 2 level factor tests (Figure 3), this shows that the temperature does

not influence the colour reaction time. The time of reaction seems to be less than the specified 60 minutes given in ISO/DIS 11 262, and tests with measurements every 5 minutes (Fig. 5) with a KCN standard, a digested Fe(III)-control solution and a spiked soil solution showed that the colour development had a maximum between 30 and 40 minutes. The colour decreased after the colour maximum had been reached at a rate of 2 pct per 10 minutes. It is therefore recommended that the samples are measured from 30 - 45 minutes after addition of the final reagent.

#### *Soil sample size*

In the tests combined with a high sulphide concentration (1,0 g/kg) and determination of total cyanide as a one step digestion, there was a lower recovery of a 15 g soil sample than of a 5 g soil sample (Figure 3). This was especially influenced by two samples where sulphide (10 g/kg) was added, and the digestion was performed as a single step digestion. The other two tests gave a satisfactory recovery. Follow up tests with 2,5 and 10 g soil (without sulphide) did not show any concentration dependant recovery. It is therefore concluded that digestion of a 10 g sample in accordance with the proposed ISO/DIS 11 262 gives a satisfactory recovery.

#### *Digestion time*

In the first series the digestion time was prolonged from two to three hours (Figure 3). For the two samples containing sulphide (10 g/kg) there was a lower recovery with 2 hours digestion time compared to 3 hours. For the other two samples there was no significant improvement obtained by applying a longer digestion time (5 % lower results after 3 hours than after two hours).

#### *Determination of total cyanide as a two step digestion versus a one step digestion.*

The determination of total cyanide determined as the digestion of easily-liberatable cyanide followed by the digestion of complex cyanide on the same sample was compared to the digestion of all cyanide in one step (Figure 3). The tests showed 5 pct higher results for determination by the 2 step digestion method, when all results were included. When the results of samples with 1,0 g/kg sulphide were eliminated, the results of the one step digestion procedure were slightly higher (8 pct). It is concluded that the recovery is not dependant on whether the digestion is performed in one or two steps.

#### **Conclusion**

The tests indicate that the proposed ISO/DIS 11 262 is a robust procedure. It is possible to change the time for measurement if the colour reaction is changed from 60 minutes to 35-45 minutes after addition of the final reagent. Samples with extreme matrices (10 g/kg sulphide) may give lower recoveries, and in this situation the procedure can be modified to obtain a satisfactory recovery. The method is, however, satisfactory at normally occurring sulphide pollution levels (below 200 mg/kg sulphide). The experiments with sulphuric acid compared to phosphoric acid for digestion showed a poorer recovery for sulphuric acid.

Figure 1

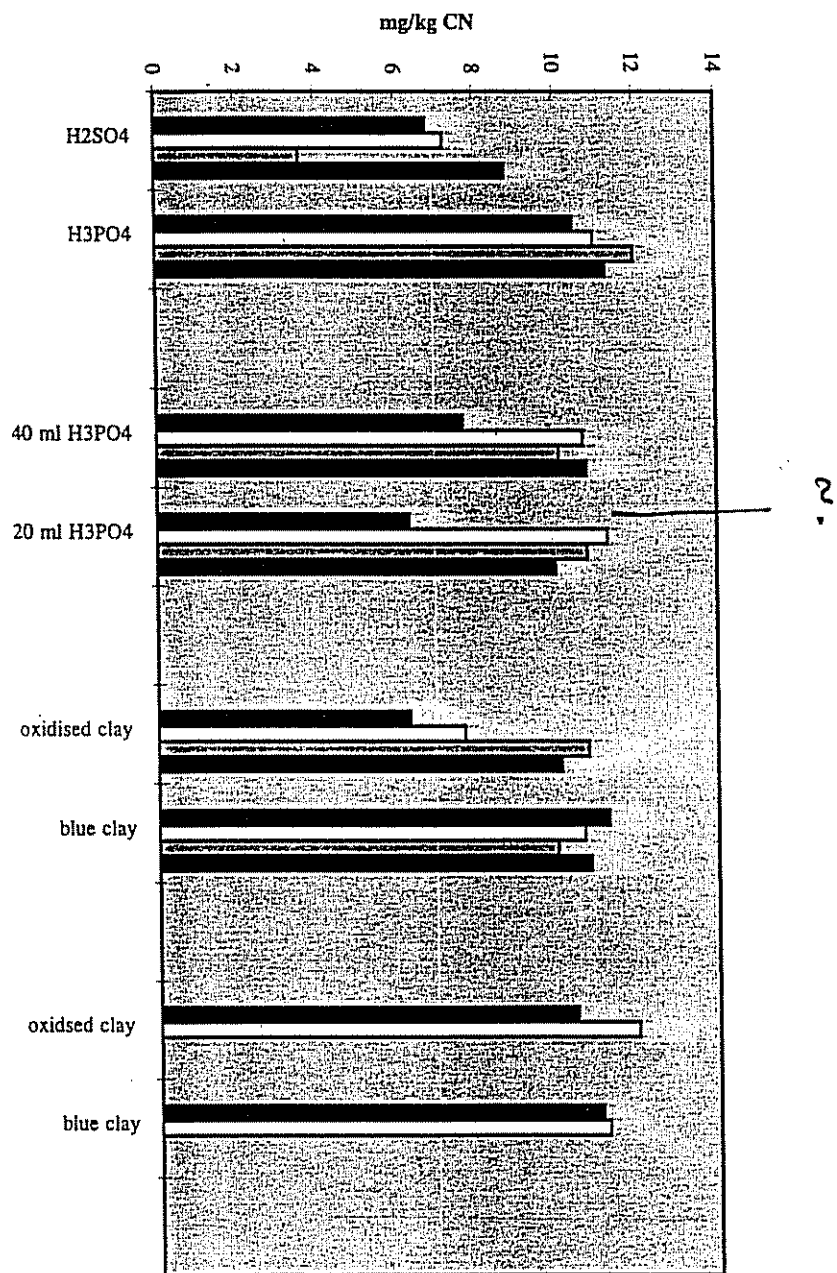


Figure 2

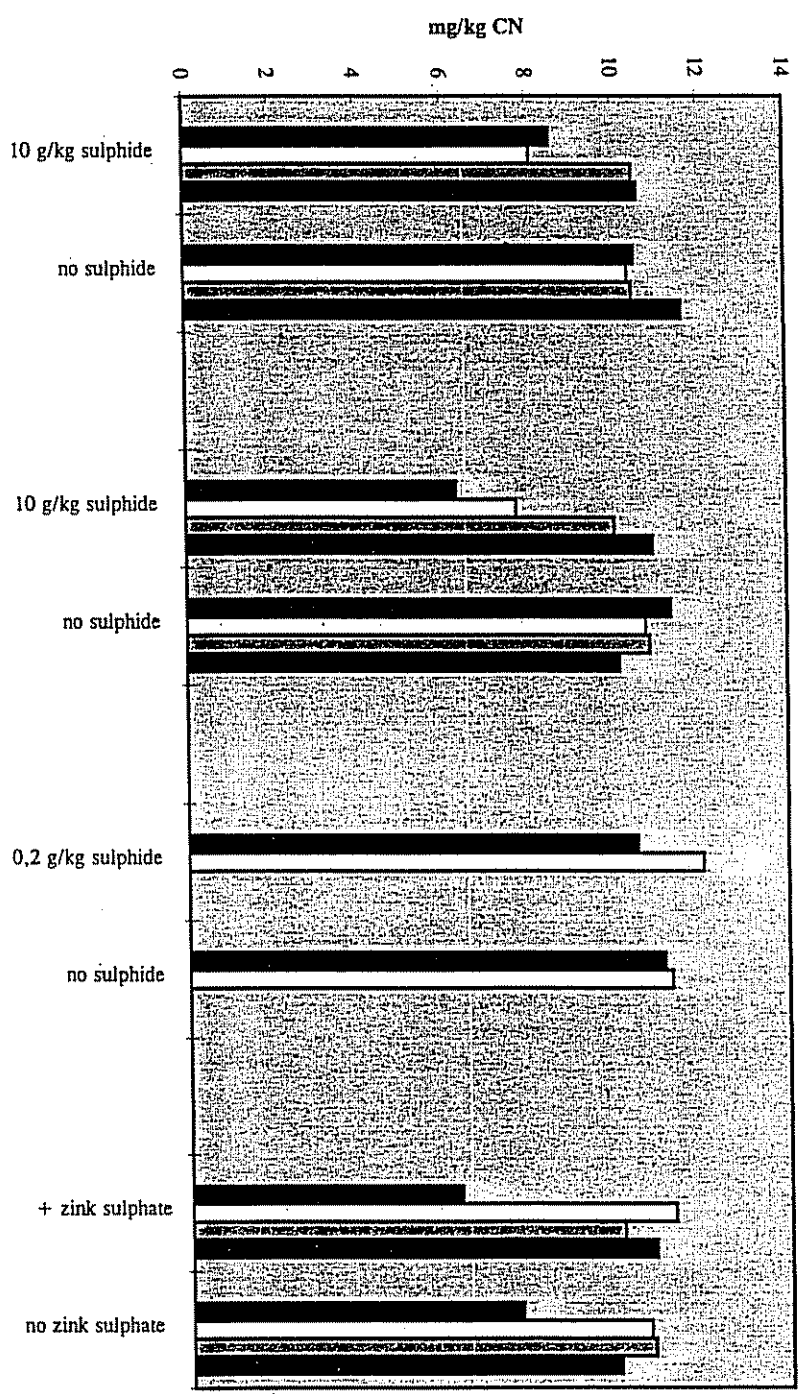
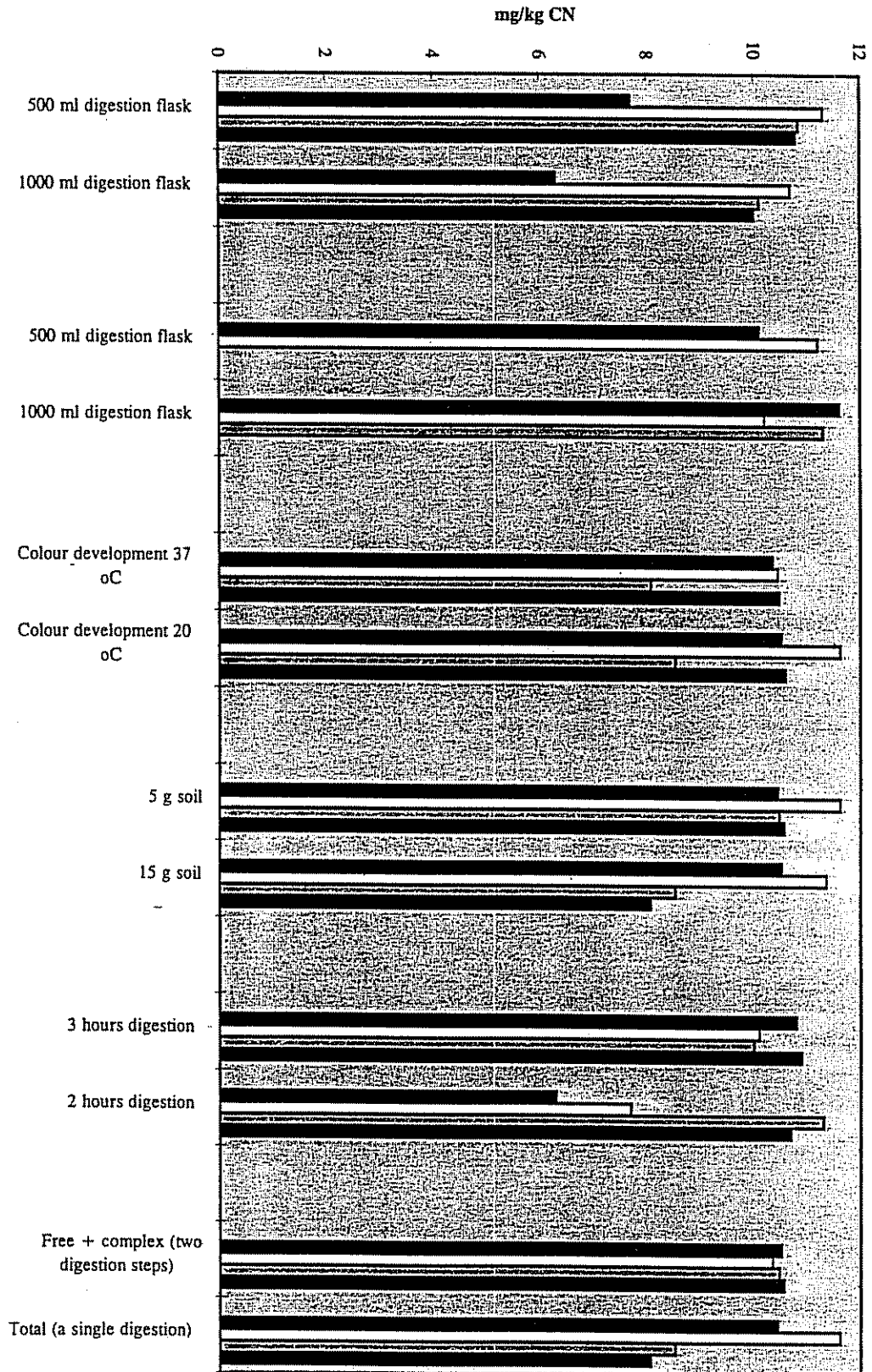


Figure 3



Cyanide colour reaction ISO/DIS 11 262

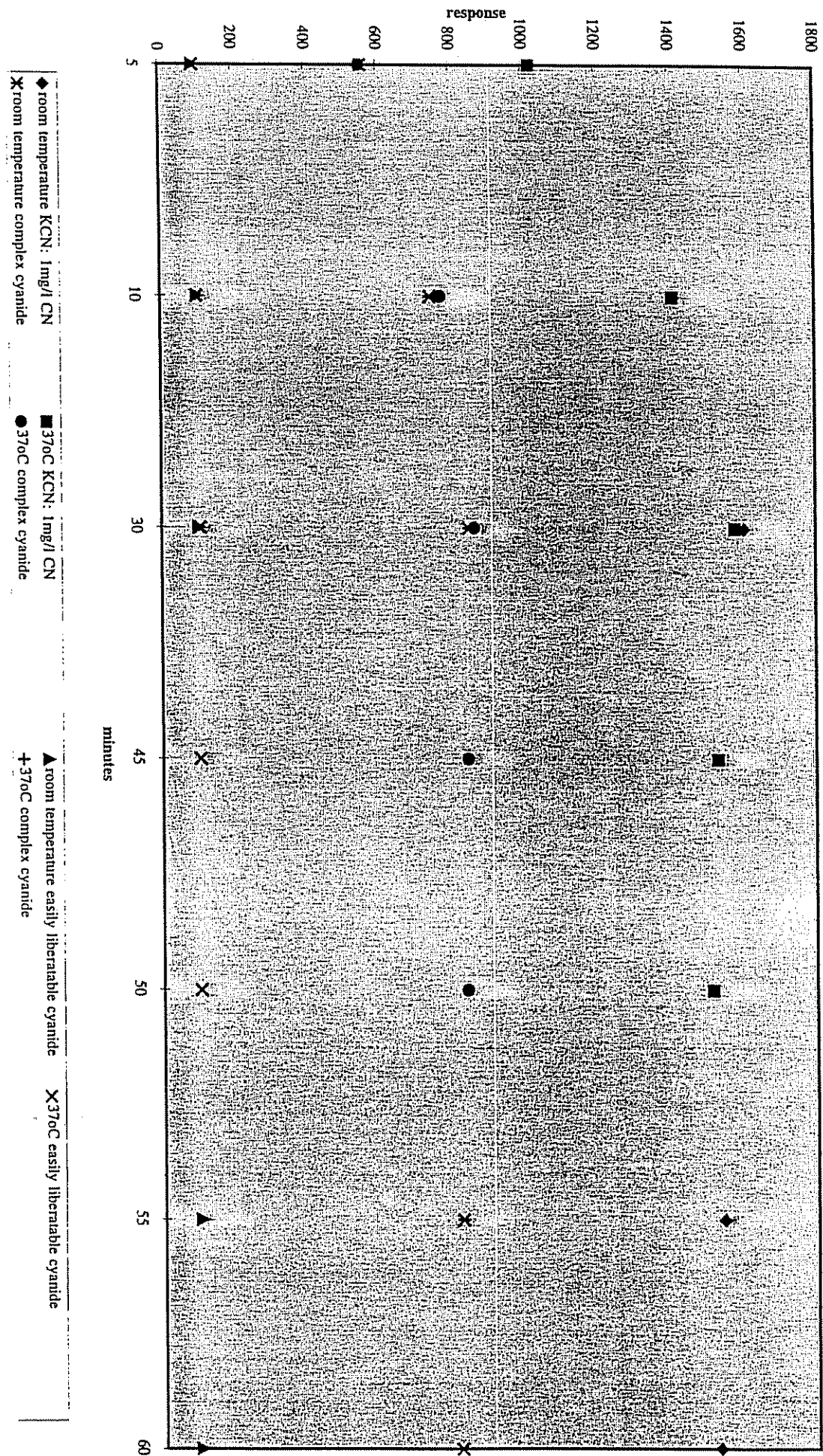


Figure 4

ISO/DIS 11262 Cyanide in soil

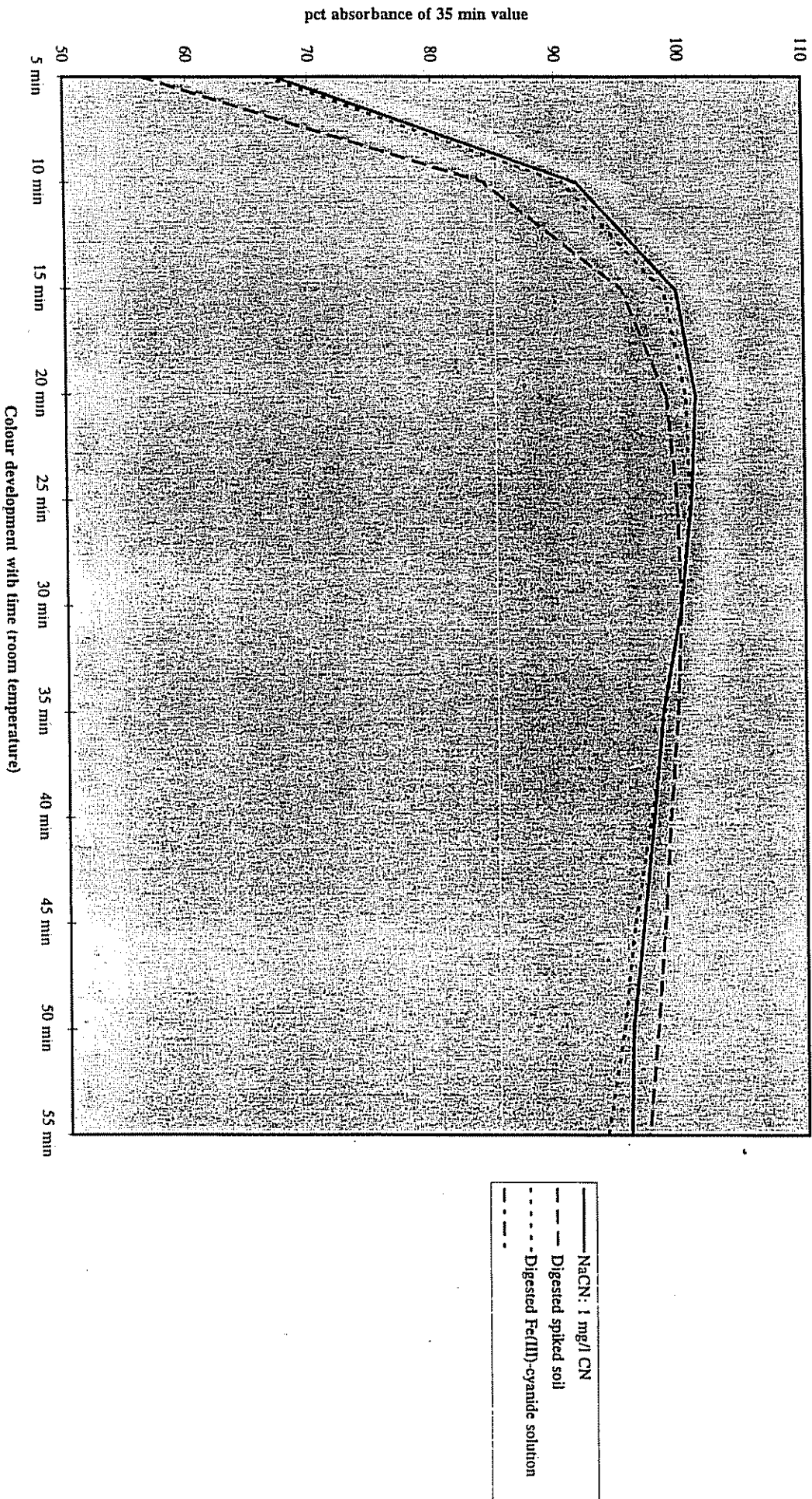


Figure 5