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Soil quality — Detection of water soluble chromium(VI) using a ready-to-use test-kit method

Qualité du sol — Détection du chrome(VI) soluble dans l'eau en utilisant un kit d'essai prêt à l'emploi

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Foreword

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information.

The committee responsible for this document is ISO/TC 190, *Soil quality*, Subcommittee SC 3, *Chemical methods and soil characteristics*.

Introduction

A test-kit method uses reagents stored in plastic or glass vials prepared for colorimetric detection of specific compounds soluble with water. There is a lot of varieties of test-kits developed mainly for the compounds in water samples based on well-known reactions with commonly-used and chemically stable reagents indicating constant magnitudes of intensities of the signals from target compounds. The common reactions employed for the test-kit usually give colour, by which the user can recognize the concentration level of the compound without absorption spectrophotometers even in the situation when such instruments are not available. Thus, the test-kit determination of the compound in water samples can be used to screen specific compounds in soil samples, if they are easily dissolved into water.

The reaction applied depends on the target compounds. For chromium(VI), a reaction is used, where 1,5-diphenylcarbazide is used, its isomer or derivatives. When other chemicals or derivatives are used, the performance is intended to be similar to that obtained with the original reagents. The test-kit consisting of the reagents has to be identified by confirming the spectrum including intensities at a specific wavelength. The spectrum shape should be similar to each other between those from test-kits and bulk reagents commonly used for absorptiometry in laboratories. The intensities and varieties of interferences to the test-kit method should be within those taking place to absorptiometry test methods with bulk reagents. The quality or purity of the reagents packed in test-kits should keep constant with a deviation around that for the bulk reagents for absorptiometry. The detection limit and working curves available with test-kits should be confirmed in prior of the use.

When screening contaminated sites for Cr(VI) by test-kit detection, Cr(VI) is extracted from soil into water. The recovery of extracted Cr(VI) would be slightly lower than that when extracting with alkali solution; however, the repeatability of test-kit detection for Cr(VI) is high enough to apply the detection manner to contaminated sites as a screening method. Basically, laboratory analysis provides with precise concentration values but takes longer time and higher costs than those of test-kit detection. Furthermore, under the conditions that survey time and the total costs are restricted, test-kit detection is more useful and practical as it can cover more inspection spots, resulting in precise information on the pollution at investigation sites, compared with a conventional manner applying samples to laboratory analysis that costs and limits the numbers of samples to be analysed due to a lean budget for financial reasons.

The two investigation manners, or the conventional methods and the screening work, have their specific advantages and characters. Then, it is quite natural to choose one of the two options. In short, one gives precise concentration values at selected spots within a limited number but calling for high costs while the other provides concentration levels at spots with no limits in number but showing good cost performance.

This Technical Report describes the procedure to screen soil for Cr(VI) using a method with test-kits developed for water samples.

Soil quality — Detection of water soluble chromium(VI) using a ready-to-use test-kit method

1 Scope

This Technical Report describes the procedure to screen soil samples to detect Cr(VI) using test-kits based on water extraction of Cr(VI) in soil. The test-kit approach in this method is designed to quickly screen soil samples using calibration to indicate the concentration level. A batch test at a liquid to solid ratio of 10 l/kg, designated by ISO/TS 21268-2, has been used in Japan for over 30 years to evaluate the risk of Cr(VI) contamination in soil. The Cr(VI) detection by a ready-to-use test-kit method follows ISO/TS 21268-2.

This screening technique is applicable in laboratories but can also be applied for site screening in the field. The standard system detection covers the range mg/kg to % for Cr(VI).

This method is expected as a screening technique because of the significant colour change given by 1,5-diphenylcarbazide in the existence of Cr(VI). The method may be especially useful in quickly detecting Cr(VI) where a site is assumed to have no Cr(VI) contamination. As with other screening techniques, it is advisable to confirm a certain percentage of both positive and negative test results in another technique, especially when the detected level is near or above a regulatory action limit or when the presence of background or interfering materials is suspected.

Basically, laboratory analysis requires longer time and higher costs than those of test-kit detection. If the same survey time and the costs are allowed with test-kit screening work and conventional investigation methods including laboratory analysis, the former way can work on more inspection spots than the latter. However, test-kit detection should carefully be adopted for site investigation because the recovery of Cr(VI) from soil into water dependent on soil matrices changes the performance of test-kit detection.

2 References

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 11074, *Soil quality — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 11074 and the following apply.

3.1
ready-to-use method
analytical method that is ready-made for use, and may be employed in the field

Note 1 to entry: A more familiar name is “field method”.

[SOURCE: ISO 17381:2003, 3.2, modified — definition shortened]

4 Principle

Chromium(VI) in solution reacts with 1,5-diphenylcarbazide to form a red-violet complex of chromium-1,5, diphenylcarbazone resulting in colour changes of the solution due to the formation. Spectrometry and colour charts are applied to determine the complex. The test determines Cr(VI) present in the soil extract as chromate or dichromate ions. The test-kit method to detect the Cr(VI) in soil consists of three basic steps: extraction, filtration and detection.

5 Reagents

5.1 **Water**, de-ionized, as an extraction solvent to extract Cr(VI) from soil samples.

5.2 **Test-kit reagent**, i.e. 1,5-diphenylcarbazide.

6 Interferences

Arsenic, cobalt, iron(II), iron(III), tin, vanadium, lead and phenol may give colour changes by reacting with 1,5-diphenylcarbazide. Reducing agents like iron(II) and ascorbic acid effect to reduce Cr(VI) to Cr(III). Thus, they also interfere with a chromium(VI)/1,5-diphenylcarbazone reaction.

7 Apparatus

7.1 **Spectrometer**, hand-held or portable photometer working at a wavelength of 540 nm.

7.2 **Colour chart**, with colour bars indicating a value on a reference concentration.

7.3 **Spoon**, non-metal to take soil samples.

7.4 **Sample tube and vial**, e.g. plastic or glass tube for the extraction operation by shaking and a transparent glass vial for the test-kit observation.

8 Procedure

8.1 Calibration

When using a photometer for photometric observation of Cr(VI) in the sample solution, prepare a calibration curve using blank and working standards. The working standards should be prepared by spiking an appropriate amount of Cr(VI) solution into de-ionized water.

When using a colour chart for the detection of Cr(VI), the calibration process is not necessary.

8.2 Sample detection

Weigh out 1 g of a soil sample and put into 10 ml of water. Shake the mixture for 1 min and then filtrate using a 0,45 µm pored membrane filter. Dilute 1 ml of the filtrate with water to give at least 10 ml, when the colour of the sample is out of the range of the colour chart supplied by the manufacturer due to too high concentration of Cr(VI) in the filtrate.

8.3 Measurement

Introduce a certain volume of the diluted sample (7.2) into the test-kit apparatus. Measure the absorbance of the solution at a wavelength of 540 nm using a suitable cell with a 10 mm optical path length or observe the colour comparing with the colour chart.

9 Quality assurance (QA) and quality control (QC)

A program of field QA/QC should include a minimum of periodic soil blanks, equipment blanks, soil spikes and duplicates. Other procedures should be implemented depending on the specific requirements of each site.

To ensure accurate quantification and repeatable results, it is recommended that a recalibration be run at a certain interval or at least daily.

The analytical results contain uncertainty arising from numerous sources, heterogeneity of soil sample, difficulty in using matrix matched reference samples, etc. The expanded uncertainty of measurement can be estimated from the uncertainty budget with standard uncertainties. See ISO/IEC Guide 98 for the guidance on the estimation of expanded uncertainty.

10 Test report

The test report (see ISO 12404) should contain at least the following information:

a) a reference to this Technical Report;

b) complete identification of samples;

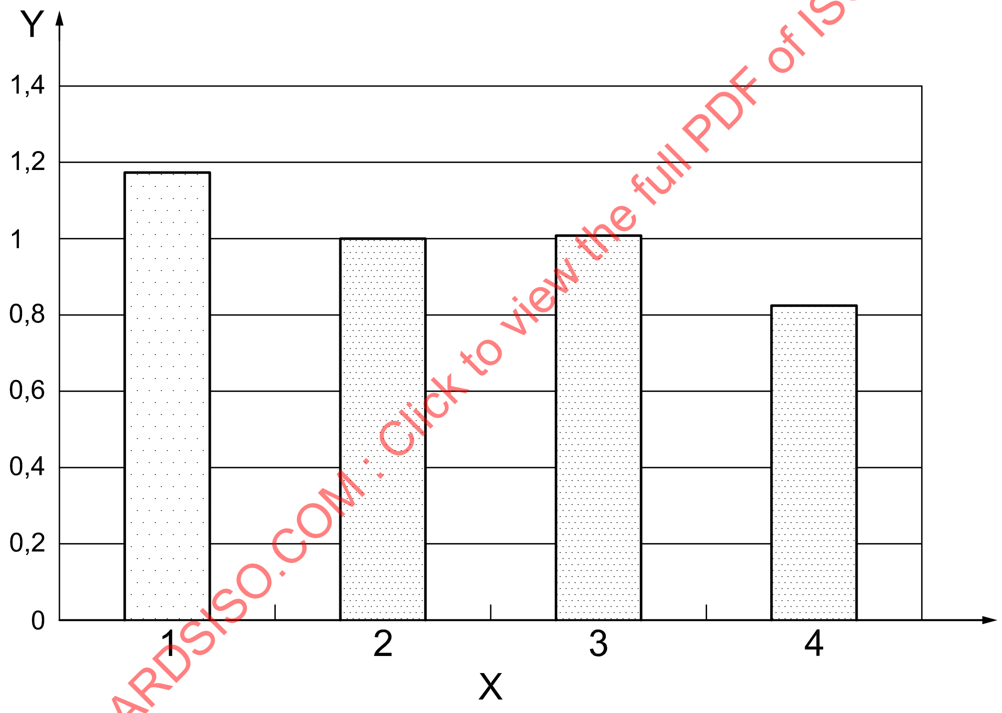
c) the results of the determination;

d) any details not mentioned in this Technical Report or which are optional, as well as any factor which may have affected the results.

Annex A
(informative)

Extraction of Cr(VI) from soil CRMs

A preliminary evaluation of test-kit detection performance with certified reference materials (CRMs) showed that test-kits effectively work as a screening method. Figure A.1 and Figure A.2 show the relative concentrations of Cr(VI) in sandy loam and clay CRMs when Cr(VI) was extracted with alkaline solution as designated by ISO 15192 and EPA 3060 as well as with water as designated in this Technical Report. The Cr(VI) recovery when applying the test-kits to the detection of Cr(VI) in the CRMs was high for the sandy loam CRM, even when the Cr(VI) extraction was performed with water. With the clay CRM, the recovery by detection with water extraction was half that with alkaline extraction. However, the standard deviation ($n = 5$) is less than 10 % under each condition. Figure A.3 shows the improvement of the recovery achieved by adding salts when extracting Cr(VI) from clayey soil into water. In this case, it was found that addition of Na_2SO_4 and $Al_2(SO_4)_3$ improved the Cr(VI) recovery.



Key

Y C/C ISO 15192

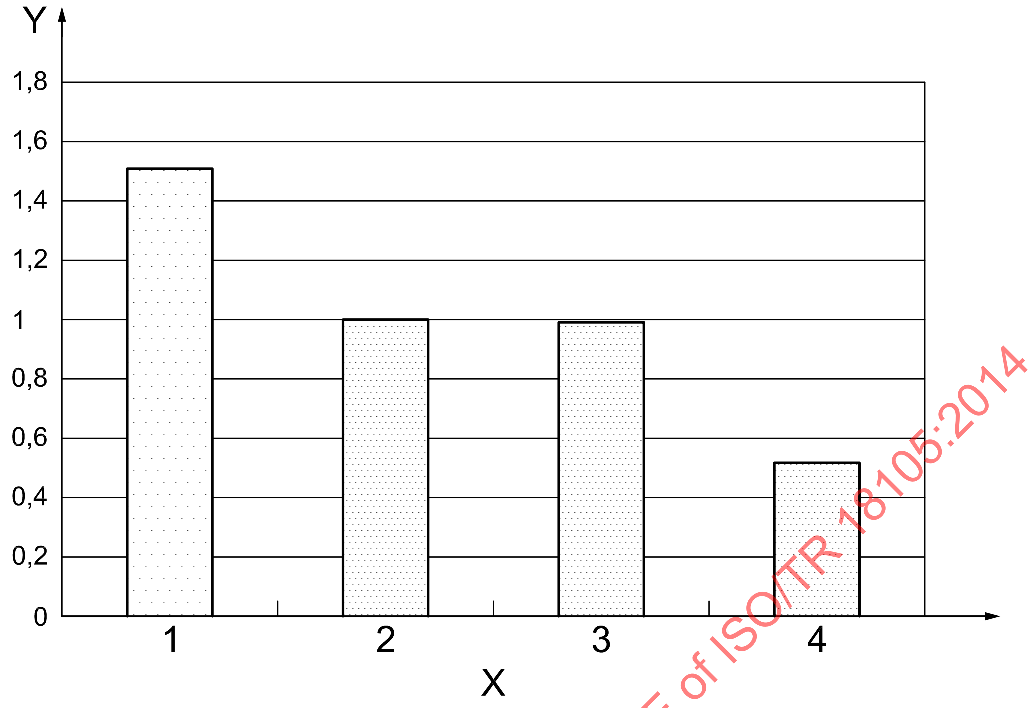
X 1 certified value

2 by ISO 15192

3 by EPA 3060

4 by TK proposed

Figure A.1 — Cr(VI) determined in the CRM (sandy loam) — Test-kit (TK)



Key

Y C/C ISO 15192

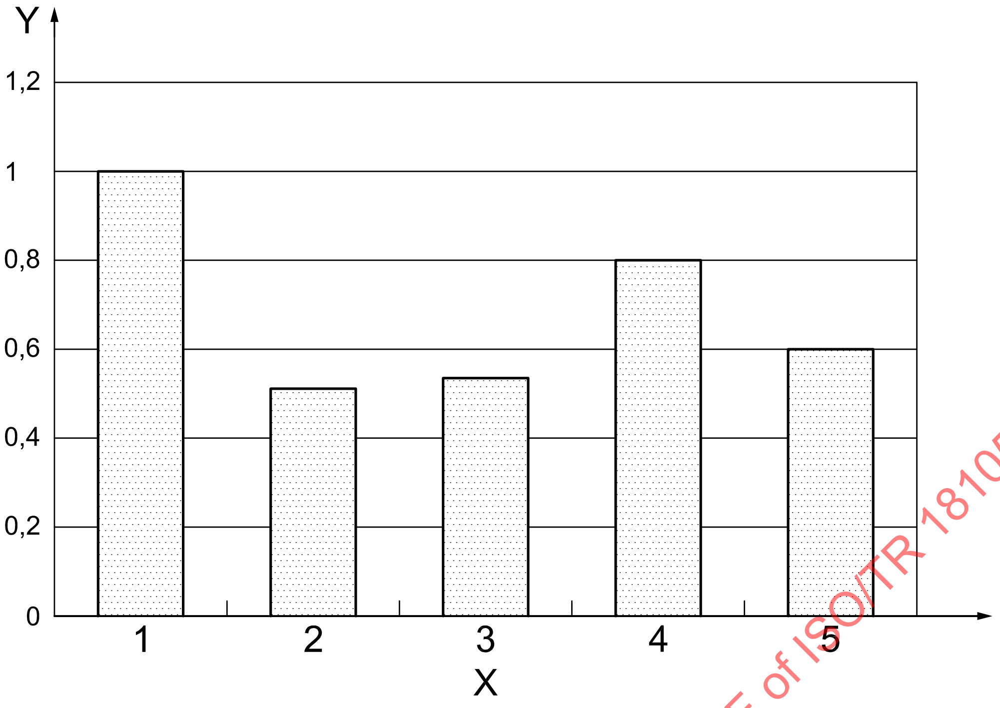
X 1 certified value

2 by ISO 15192

3 by EPA 3060

4 by TK proposed

Figure A.2 — Cr(VI) determined in the CRM (clay) — Test-kit (TK)



Key

Y C/C ISO 15192

X 1 by ISO 15192

2 by TK proposed

3 by TK with NA_2SO_4

4 by TK with Na_2SO_4, extracted for 12 h

5 by TK with $AI_2(SO_4)_3$

Figure A.3 — Improvement of the recovery with salts for clayey soil — Test-kit (TK)

Annex B
(informative)

Comparison of Cr(VI) results obtained with commercially available test-kits

Using a soil material spiked with a known amount of Cr(VI), three kinds of commercially available test-kits[1] were applied to the same soil material to check their performance as screening detection of Cr(VI) in soil. There was no significant difference in the indicated concentration value among the applied test-kits. Additionally, the results given when using colour charts for Cr(VI) determination were comparable to those obtained by photometer detection. See Table B.1.

Table B.1 — Chromium(VI) determined with commercially available test-kits

Cr(VI) concentration measured mg kg^{-1}			
Shibata[1] with a photometer	Shibata[1] with a colour chart	Dojin[1] with a colour chart	Merck[1] with a colour chart
2,4	5,0	5,0	4,0
4,8	10,0	10,0	10,0
11,2	20,0	20,0	22,0

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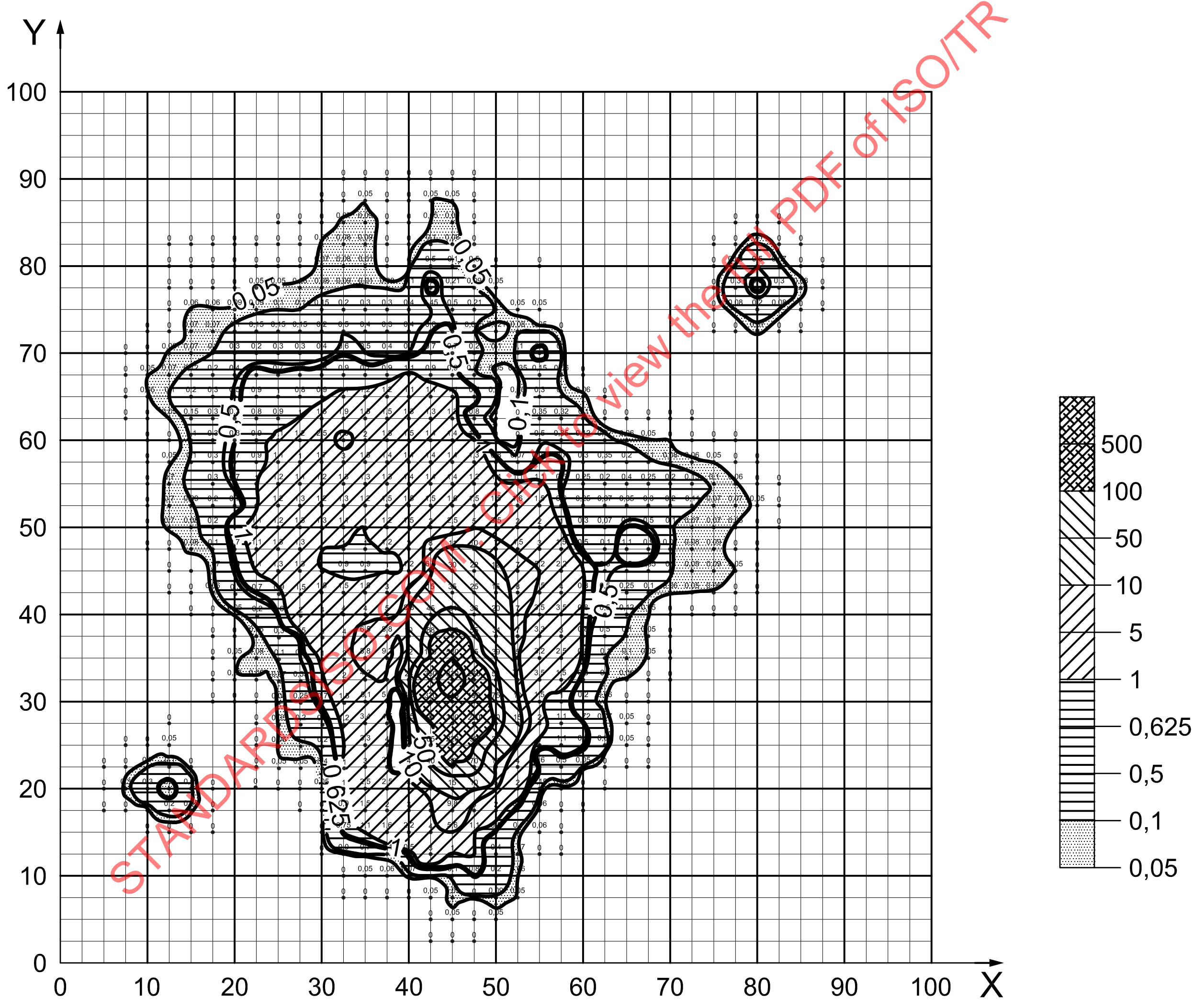
[1] Examples of products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

Annex C
(informative)

Simulation of mapping distributions of Cr(VI) contaminating potential land

The performance of conventional investigation methods with laboratory analysis and screening work by test-kit detection was compared to confirm which method is suitable to successfully find hot spots contaminated with Cr(VI) in investigation land. The distributions of Cr(VI) concentration in soil were simulated by illustrating a Cr(VI) concentration map expressed with concentration contours. Even if it gives precise concentration values, laboratory analysis normally takes longer time and higher cost than those by test-kit detection. Usually, investigation costs and time are restricted for financial reasons.



Key

X and Y distance, in m

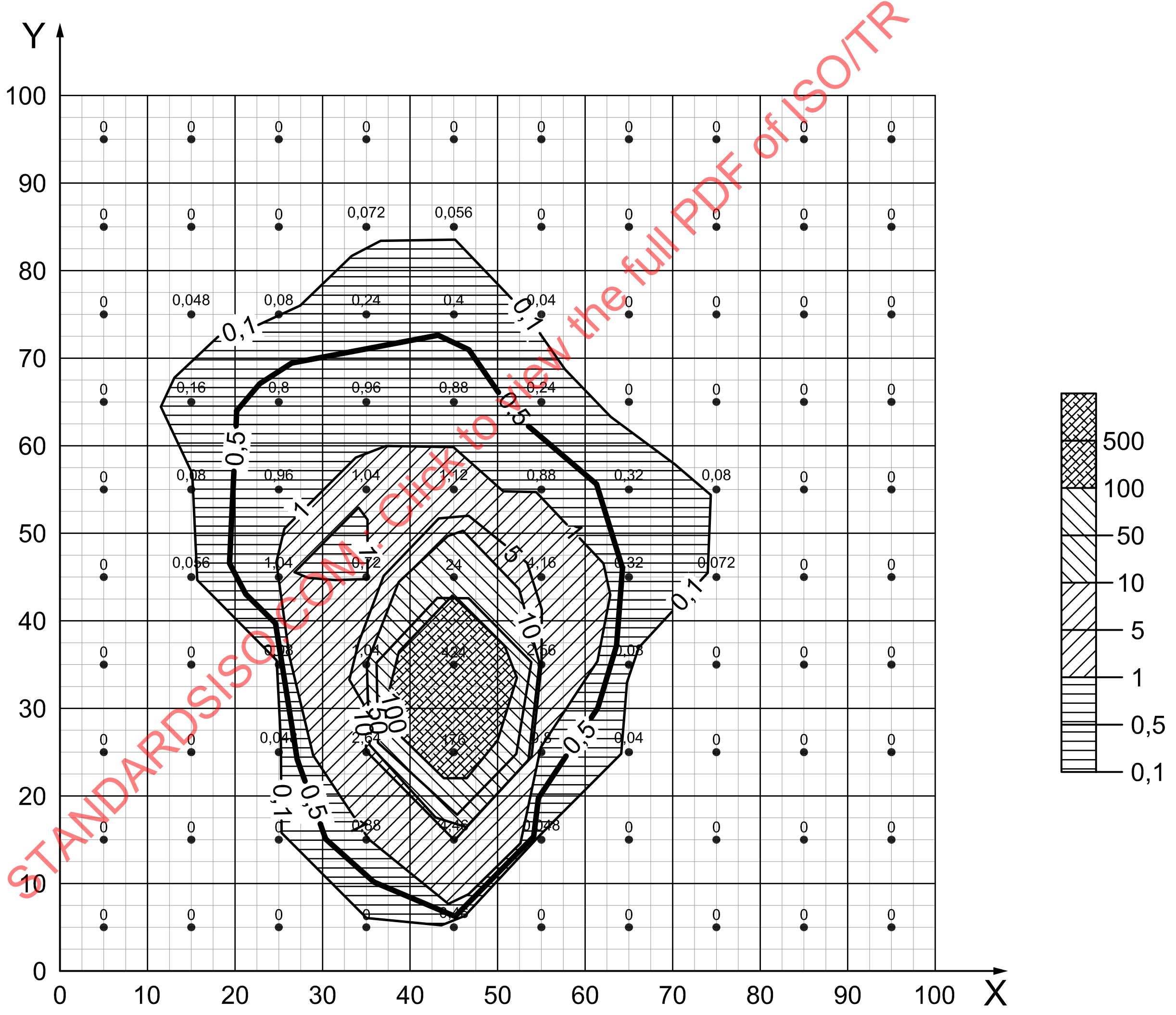
Figure C.1 — Basic conditions of Cr(VI) distributions potentially designed for simulation

Figure C.1 illustrates the feature of Cr(VI) distributions indicated at spots at 2,5 m intervals. The Cr(VI) recovery from the soil was set at 80 %.

Meanwhile, the Japanese government regulates the allowable limit concentration of Cr(VI) in soil as a value to be given through analytical procedures by laboratory reference methods. When the regulated allowable limit concentration is 0,5 mg kg^{-1} and the Cr(VI) recovery is 80 %, the true or actual Cr(VI) concentration in soil must be 0,625 mg kg^{-1}. In this case, for this Cr(VI) concentration, the government-regulated allowable limit is 0,5 mg kg^{-1} but the estimated concentration actually in soil is 0,625 mg kg^{-1}, which is obtained through calculation with the Cr(VI) recovery of 80 %. The former or the regulated value is not changed while the latter or the calculated one is changeable depending upon the Cr(VI) recoveries.

Consequently, based on the relationship between the two concentration values, the thick black lines in Figure C.1 show the contours of the threshold or the allowable limit concentration of Cr(VI), which is 0,625 mg kg^{-1} as the concentration of Cr(VI) actually existing in soil. The concentration value of 0,625 mg kg^{-1} is given with the regulated allowable limit concentration of 0,5 mg kg^{-1} and the Cr(VI) recovery of 80 % from the soil.

The true concentration value of Cr(VI) at the pollution source at the site is set at 0,625 mg kg^{-1} for this simulation.

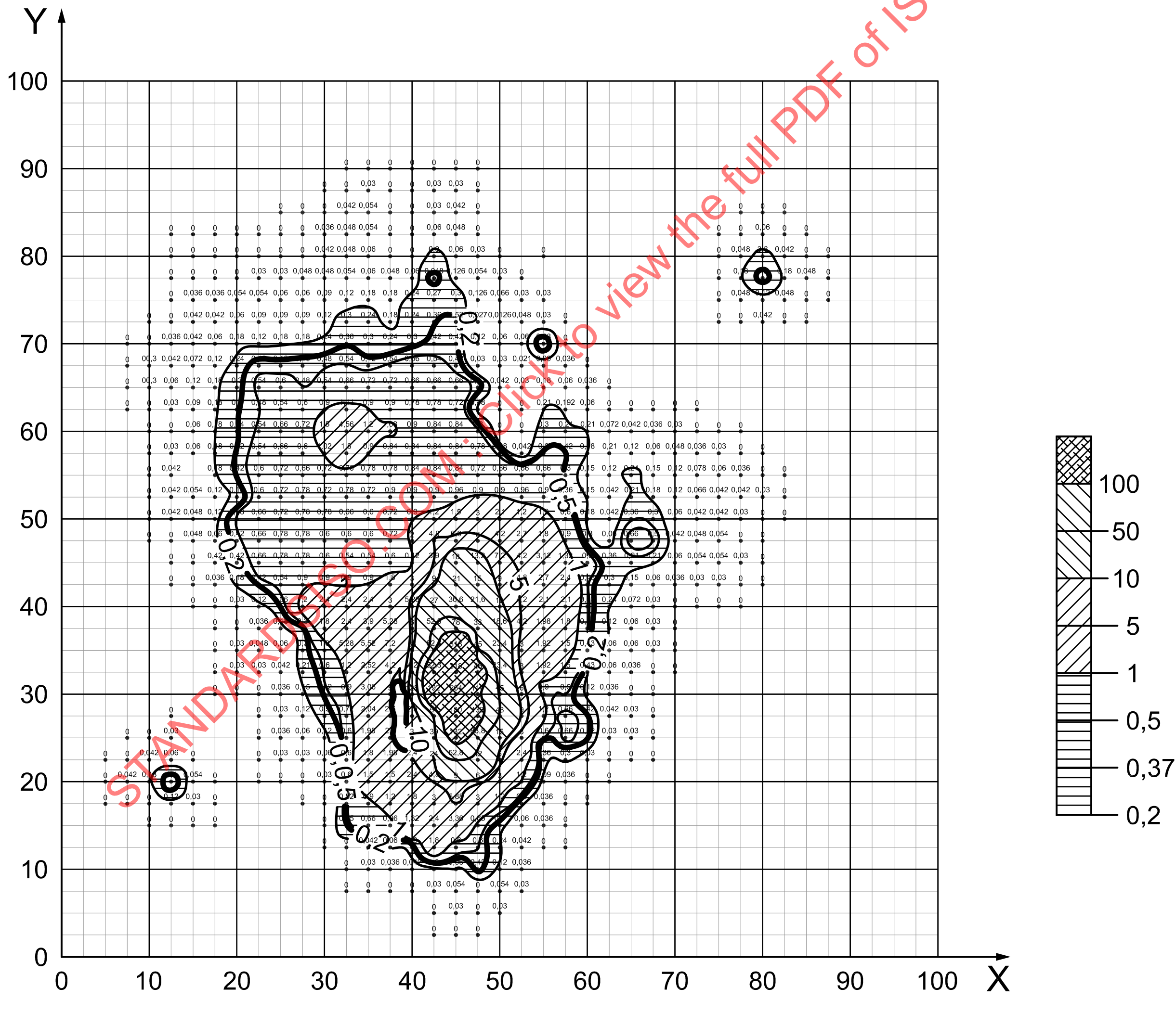


Key

X and Y distance, in m

Figure C.2 — Cr(VI) distributions mapped by laboratory reference methods with a Cr(VI) recovery of 80 %

Figure C.2 shows the mapping results obtained through conventional investigation manners with soil samples collected at spots at 10 m intervals and analysed by laboratory reference methods having the detection limit of Cr(VI) 0,05 mg kg^{-1} by the laboratory reference method. The Cr(VI) recovery set at 80 % is the same as that under the basic conditions designed for this simulation, see Figure C.1. However, the laboratory reference analysis gives the Cr(VI) concentration of 0,5 mg kg^{-1} when analysing the same soil sample actually containing 0,625 mg kg^{-1} of Cr(VI). The Cr(VI) recovery of 80 % in the soil means that only 80 % of Cr(VI) therein can be detected. Then, 0,625 mg kg^{-1} is the threshold or allowable limit concentration in the actual soil as the true value but 0,5 mg kg^{-1} is still the allowable limit that is legislatively regulated for the reason that the Cr(VI) concentration value can be obtained only by an analytical procedure while the analytical value is changeable with the Cr(VI) recoveries. At this simulating potential site, 100 spots can be surveyed by conventional investigation methods through laboratory analysis. Contaminated spots are detectable but the spots where this manner is applicable are limited, since surveyed spots are those falling only on the location at 10 m intervals. This conventional investigation manner does not take into account the area situated between spots checked at 10 m intervals. It is difficult to identify the location of the most seriously contaminated spots or the centre thereof and the concentration at the spots, since these spots are stepped over in the sample collection work at such intervals. It is risky to take this sampling manner since small areas contaminated are supposed to be between spots at 10 m intervals and the spread of contaminated areas be overlooked or underestimated.



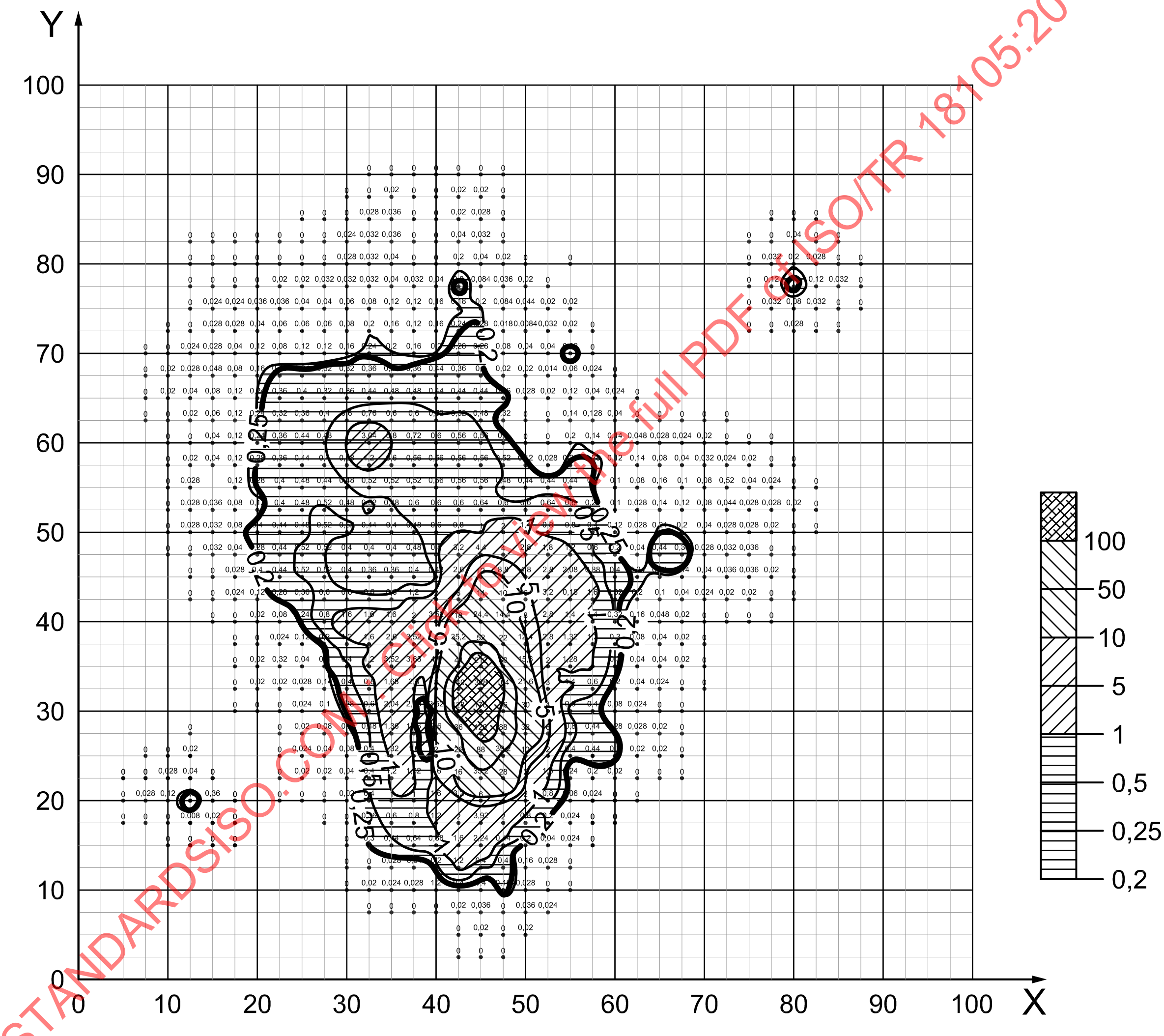
Key

X and Y distance, in m

Figure C.3 — Cr(VI) distributions mapped through test-kit screening work in the sandy soil ground having a Cr(VI) recovery of 60 %

Figure C.3 illustrates the Cr(VI) distributions mapped by test-kit detection with its detection limit of 0,2 mg kg^{-1}, which is carried out at 2,5 m intervals in the ground of sandy soil. The Cr(VI) recovery from the sandy soil is set at 60 % as the soil is sandy or contains large particles. The legislative threshold (allowable limit) of 0,5 mg kg^{-1} or the actual concentration of 0,625 mg kg^{-1} in soil is indicated as a concentration value of 0,375 mg kg^{-1} to be given by test-kit methods as a result of the Cr(VI) recovery of 60 %. Thus, 1 600 spots can be surveyed in test-kit screening work at the same site, since the method can be applied at short or 2,5 m intervals.

Contaminated spots are thoroughly detectable with test-kits. The location of the most seriously contaminated spots and the concentration thereof can also be identified. Small areas even between spots at 10 m intervals can be inspected. Then, the areas contaminated are more perfectly estimated without failure.



Key

X and Y distance, in m

Figure C.4 — Cr(VI) distributions mapped through test-kit screening work in the common-type soil ground having a Cr(VI) recovery of 40 %

Figure C.4 shows the Cr(VI) distributions mapped by test-kit detection with its detection limit of 0,2 mg kg^{-1}, which is carried out at 2,5 m intervals in the ground of common-type soil. The Cr(VI) recovery from the soil is set at 40 % as the soil is of a common type. The legislative threshold (allowable limit) of 0,5 mg kg^{-1} or the actual concentration of 0,625 mg kg^{-1} in soil is indicated as a concentration value of 0,25 mg kg^{-1} to be given by test-kit detection, since the recovery is 40 %. Therefore, 1 600 spots can still be surveyed at the site. Contaminated spots are also thoroughly detectable in test-kit screening