# INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

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**COMMISSION ON ATMOSPHERIC ENVIRONMENT\*** 

# SAMPLING PLAN FOR GASES AND **VAPOURS IN WORKING AREAS**

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# SAMPLING PLAN FOR GASES AND VAPOURS IN WORKING AREAS

This report gives basic practical information on the evaluation of the atmosphere in working areas. Only general guidelines have been included in this sampling plan and within this framework the measurements can be adapted to meet particular situations. Changes or supplementary measures will in practice be necessary but a comprehensive evaluation of the situation prevailing at the work place is possible only by systematically planning the sample-taking procedure.

#### I. GENERAL

Great advances have been made in analytical techniques resulting in an improved sensitivity and selectivity of the methods for the determination of air contaminants. Development of direct reading systems has to some extent solved the problems of separate sampling and analysis and has avoided any possible deterioration of samples during transportation or delay in analysis. Personal samplers have made possible a more objective and accurate assessment of individual exposures both in workers and in other population. But even the most sophisticated analytical method or monitoring instrument cannot give reliable results unless the sample reflects concentration levels and fluctuations at a given location, in a given area, or measures the actual exposure of the receptor. Full account must be taken of interferences or errors, and measures instituted to eliminate or evaluate them. Therefore, in general the problem of obtaining a representative sample must never be overlooked, and special attention should be devoted to the strategy of sampling, which is the most important single step in the measurement of air pollution.

The general approach for obtaining a representative sample in a working environment involves careful consideration of the following matters before the investigation is commenced.

- Recognition of the problem and definition of sampling objectives
- selection of sampling sites, sampling duration and sampling frequency which will adequately reflect the actual exposure pattern of the individual
- selection of the type of sampling equipment which can provide a reliable estimate with minimum cost and effort
- calibration and verification of sampling performance (including collection efficiency) of the sampling equipment
- control of sampling performance throughout the operation and the keeping of records of all the details relevant to the evaluation of such performance.

The general scheme for sampling in working areas (gases and vapours) should take into account the following specific points which are considered in detail under the appropriate Sections.

- Preparation of the sampling programme (Section II, e.g. detailed information about properties of raw materials)
- data to be included in the measurement record (Section III, e.g. all sources of contaminants)
- definition of sampling requirements (Section IV, e.g. measurement of contaminants at the work place)
- sampling procedures (Section V, e.g. evacuated flask, solid adsorbent)
- detector tubes (Section VI)
- measurement of gases and vapours at work places by means of short-term and long-term methods (Section VII).

#### II. PREPARATION OF THE SAMPLING PROGRAMME

(a). Consideration needs to be given to the following

- 1. Raw materials used in the work and production process
- 2. Sequence of production
- 3. Materials produced
- 4. Materials added during production
- 5. Intermediate products obtained during production
- 6. Side reactions during production
- 7. Persons working in the production area

# (b). Provision of detailed information about properties of all raw materials, intermediate products, side products, end products

- 8. Physical properties (e.g. melting point, boiling point, vapour pressure, solubility etc.)
- 9. Chemical properties of the substance (e.g. substance reacts with metal developing a gas, substance decomposes during heating, substance reacts with water, substance is sensitive to oxidants)
- 10. Physiological and toxic properties (e.g. threshold limit value), and possible short-or long-term effects and their importance to the sampling duration
- 11. Characteristic data on ignition hazards (e.g. flash point, lower ignition limit, ignition temperature).

## III. DATA TO BE INCLUDED IN THE MEASUREMENT RECORD

- 1. Name of laboratory conducting the measurement
- 2. Name of operator
- 3. Date
- 4. Name of work place
- 5. Name of monitored person
- 6. Description of room (e.g. size, height)
- 7. Type of work place
- 8. All sources of contaminants
- 9. Description of process
- 10. Type of ventilation (e.g. natural ventilation by windows, forced ventilation by fans)
- 11. Ventilation efficiency (e.g. air changes per hour, velocity of air, CO2 content, humidity)
- 12. Weather conditions (e.g. sunshine, rain)
- 13. Temperature (outdoor, indoor)
- 14. Atmospheric pressure
- 15. Working area of monitored person
- 16. Working position of monitored person
- 17. Duration of work and interruptions
- 18. Beginning and closing of sampling time
- 19. Sampling procedure (e.g. short-term in breathing zone)
- 20. Leak testing
- 21. Method of sampling and analysis used (e.g. adsorption on silica gel and analysis by gas chromatography
- 22. Result
- 23. Special observations.

# IV. SAMPLING REQUIREMENTS

- 1. Determination of the direction of air current by means of a flow tester (smoke tube, air current meter)
- 2. Assessment of the ventilation efficiency (in the area of the work place) for instance by means of a carbon dioxide determination (with adequate ventilation, it can generally be expected that the volume concentration of the  $CO_2$  will not exceed 0.1%)
- 3. Humidity
- 4. Oxygen measurement: This measurement is required only if oxygen depletion, displacement or enrichment is to be expected (measurement should always be made however before confined spaces are entered, see also Section IV.8. Oxygen measurement will not indicate the absence of toxic substances. (As an example shows, the oxygen content changes by only about 0.02% in the presence of a dangerous CO concentration of 0.1%. This is a decrease which can be detected by measuring techniques only if very sophisticated equipment is used. On the other hand, the direct measurement of CO can be carried out easily)
- 5. Measurement of contaminants at the work place (see also Section VII)
- 6. Measurement of contaminants in the breathing zone (see also Section VII)
- 7. Leak test on reaction vessels, pipeline etc.
- 8. Test for absence of gas in confined spaces. Possibility of liberation of gas from sludge or surfaces has to be considered).

#### V. SAMPLING PROCEDURES

1. General

- In all cases the sample should be analysed without delay to avoid loss of substance by adsorption, permeation, chemical reaction etc.

- Where necessary the influence of temperature and pressure on sampling volume must be taken into consideration.
- Whether a substance can be sampled and stored in the sampling device should be determined in the laboratory prior to field use.
- Different basic methods for collecting gaseous samples may be used. An actual sample of air can be taken in a flask, bottle, bag or other suitable container or the vapours can be sampled by passage through an absorbing, or adsorbing medium. In addition, direct instrumental measurement is possible.
- The collection of grab or instantaneous samples is usually complete within a few minutes. This type of sampling is used when tests are conducted at a predetermined point of time (e.g. when peak concentrations are sought).
- When the contaminant concentration varies with time and the determination of the time weighted average is desired, a single grab sample is of questionable value, and continuous or integrated sampling should normally be employed. The gas or vapour in these cases is sampled by reaction with an absorbing solution, or collection on a solid adsorbent (absorbent), or by direct evaluation of its physical or chemical properties.
- Continuous sampling requires a constant flow rate of an air moving device. Pumps have to be calibrated and checked on a regular basis (e.g. before and after each test series); for pump calibration only calibrated gas meters or flow meters should be used.

#### 2. Evacuated flasks (Fig. 1)

By means of a vacuum pump, the flask is evacuated. The sample is taken by opening the flask.

#### 3. Gas or liquid containers (Figs. 2 and 3)

Any sealable container (of suitable material) can be used as displacement sampler. Original air is replaced by test air by drawing the sample through the container with a pump. The volume of air swept out should be 10 times the container volume. An alternative method for sampling with these containers is to fill them with water and allow

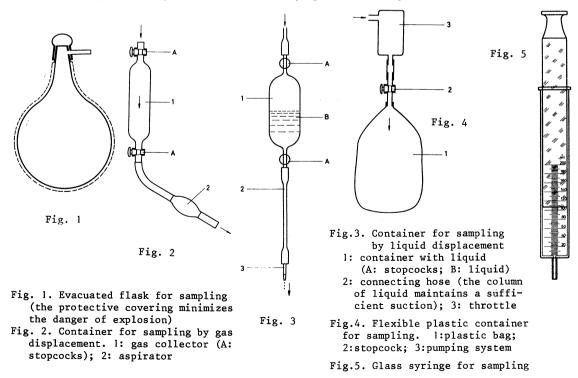
An alternative method for sampling with these containers is to fill them with water and allow the water to drain out in the test area. The liquid becomes replaced by test air (this procedure is not suitable for collecting water soluble gases).

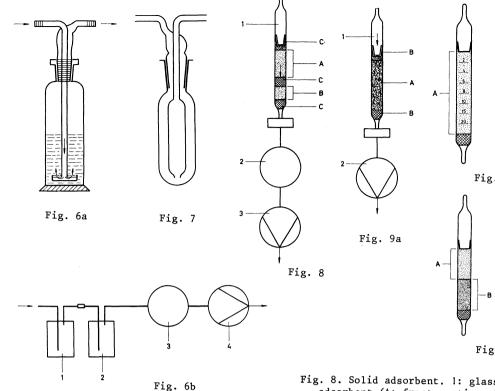
## 4. Flexible plastic container (Fig. 4)

Plastic containers (bags) are normally filled by a pump; they should be used with caution since storage stabilities for gases - due to adsorption or permeability - vary considerably. As the sample - before entering the container - flows through the pump, adsorption and chemical changes of the gas in the pumping system must be avoided.

# 5. Glass syringe (Fig. 5)

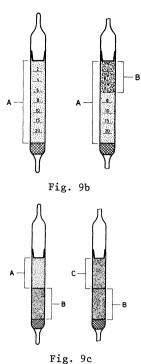
These are samplers of a predetermined volume by operation of a piston.





- Fig. 6a. Gas washing bottle (fritted bubbler). The bottle contains absorption liquid (by means of a pumping system the sample is drawn-through)
- Fig. 6b. Diagram of sampling equipment. 1: gas washing bottle (front-bottle); 2: gas washing bottle (back up-bottle); 3: gas meter (or other volume or flow measuring device); 4: pumping system
- Fig. 7. Cold trap. (By means of a pumping system the sample is drawn-through. The trap is immersed in a cooling system)

#### 6. Absorbers (Figs. 6a and 6b)



- Fig. 8. Solid adsorbent. 1: glass tube with adsorbent (A: front section of adsorbent, B: back section of adsorbent, C: fixing elements); 2: gas meter (or other volume or flow measuring device); 3: pumping system
- Fig. 9a. Detector tube. 1: glass tube with filling material (A: indicating layer, B: fixing elements); 2: pumping system
- Fig. 9b. Scale-type detector tube (unused/ used). A: indicating layer; B: coloured stain-length
- Fig. 9c. Colour-matching type detector tube (unused/used). A: indicating layer; B: colour comparison layer; C: coloured layer matches colour of comparison layer

Absorbers used - in connection with an air moving device - for the collection of gases and vapours can be gas washing bottles (various types are available, e.g. fritted bubblers, impingers); the sampling volume has to be determined by means of a gas meter or other measuring device.

It is often necessary to use a second (or third) absorber in series to check the absorption efficiency.

# 7. Cold traps (Fig. 7)

Cold traps are used for sampling substances - usually gases or vapours - primarily for identification purposes. The substance is separated from air at a suitable low sampling rate by condensation, passing it through a chamber immersed in a cooling system (e.g. dry ice). This sampling technique causes formation of condensation mists when the sample air is cooled. In order to prevent that such mists pass through the cold traps, one has to provide a filter (e.g. glass wool plug) within the trap. The sampling volume has to be determined by means of a gas meter or other measuring device.

It is often necessary to use a second (or third) trap in series to check efficiency.

#### 8. Solid adsorbents (Fig. 8)

Activated charcoal, silica gel and other solid materials - in connection with an air moving device - can be used for collecting gases and vapours; the sampling volume has to be determined by means of a gas meter or other measuring device.

#### VI. DETECTOR TUBES

Sampling and analysis are combined in one procedure.

For grab tests but also for continuous tests suitable detector tubes (Figs. 9a, b and c) are available (with short-term tubes the measuring result is obtained within minutes; long-term tubes can be used up to several hours). When the air sample is passed through the tube, the gas or vapour to be measured yields a direct colour reaction in the filling preparation; at a given sampling volume the length or intensity of the stain are the measure of the concentration.

Detector tubes are easy to handle, but all information stated in the operating instructions must be considered. It is - for example - not permitted to interchange tubes and pump from different manufacturers. The tube manufacturer should be contacted if questions should occur (e.g. influence of interfering substances on tube reading).

# VII. MEASUREMENT OF GASES AND VAPOURS BY MEANS OF SHORT-TERM AND LONG-TERM METHODS

#### 1. General

It can be assumed that the concentration of the contaminants in the working area of the employee vary as a function of space and time. It is therefore only possible to lay down a satisfactory measurement programme when a pre-knowledge about the situation exists. For testing one has to distinguish between

- short-term methods (sampling period of minutes)

and

- long-term methods (sampling period of hours)

As a consequence the following requirements should be considered.

2. Short-term measurements for the determination of instantaneous concentrations at specific locations

Rule-of-thumb instructions cannot be given for these measurements. Fig. 10 refers to measurements at the work place and Fig. 11 to measurements in the breathing zone. It will be necessary to observe the overall trend of the operations; if, for example, peak concentrations are suspected, the measurement must be carried out immediately. Since concentration peaks usually occur for brief moments only, the measuring system used must react instantly.

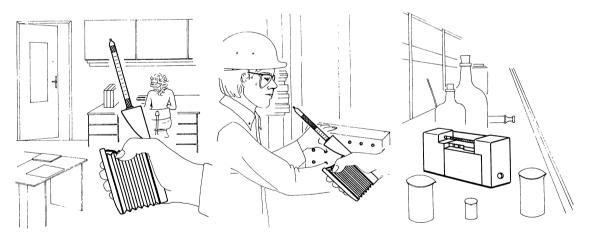


Fig. 10

Fig. 11

Fig. 12

Fig. 10. Short-term measurements at workplaces by means of detector tubes Fig. 11. Short-term measurements in the breathing zone by means of detector tubes Fig. 12. Long-term measurements at workplaces by means of detector tubes (area monitoring)

3. Long-term measurements for the determination of the average concentration over an extended period of time

Area monitoring (Fig. 12) gives an indication of the concentration at a certain place; the sampling system is located at a fixed measuring point.

Personal monitoring (Fig. 13) is used for evaluating the exposure of the worker; for this type of measurement the sampling system is worn by the worker on his body, the sampling point is usually as near the breathing zone as possible.

> 4. Estimation of the fluctuation-range of the concentration over an extended period of time by short-term measurements

The sampling programme should be planned according to established statistical rules (see annex). All possible situations cannot be covered, but it should be used at least as a basis for planning further sampling which could then meet practical requirements in a more appropriate way.

> 5. Combination of tests as set out in Sections VII.3, VII.4 Fig. 13. Long-term meaand in addition VII.2 surements at work-

This measuring programme covers

- determination of the average concentration
- estimation of fluctuation-range of the concentration (by random short-term tests)

- determination of instantaneous concentrations (specific short-term tests) By means of this overall programme it is possible to evaluate both, the average concentration (long-term test) and the fluctuation-range of the concentration (short-term tests). If the additional results of the determination of instantaneous concentrations (specific short-term tests) are outside of the estimated fluctuation-range (random short-term tests) one can assume abrupt changes in the production-sequence.

#### VIII. ANNEX

Statistical rules for the estimation of the fluctuation-range of the concentration over an extended period of time.

#### 1. General

If the measurements have to be conducted by short-term methods then a total of ten individual measurements should be the basis for the programme. The samples are taken as "snapshots" during the period of monitoring (e.g. eight hours). The measuring moments must be selected at random. The results are then evaluated graphically by plotting them in a probability network; the fluctuation range of the concentration is estimated.

It may appear rather arbitrary to set up such a sampling plan, on a total of ten individual measurements. Studies conducted have shown that this number can be considered adequate to meet the conditions generally to be expected in practice, provided the frequency of the occurrence of different concentrations follows the so-called logarithmic normal distribution.

### 2. Frequency distribution of gas concentrations at the work place

The frequency distribution - in this framework - shows how often different concentrations occur. On the basis of experience obtained so far about the frequency distribution of gas concentrations at work places, a logarithmic normal connection can be assumed. For the determination of dust in the air of work places particularly a relationship between the dust concentration and the frequency of occurrence of the concentrations was observed a long time ago. This relation can be described by the logarithmic normal distribution; Juda and Budzinski (1) reported on this distribution.

The curve of the logarithmic normal distribution is shown in Fig. 14. For comparison's sake, the mathematical Gaussian bell-shaped curve is given in Fig. 15; the normal distribution can be described by this curve. While the normal distribution has a symmetrical shape, the curve for the logarithmic normal distribution has a steeper slope on the left side and is flatter on the right side. The logarithmic normal distribution will be encountered whenever the parameters, e.g., the gas concentration, cannot drop below a certain value, such as zero, but when high values can occur, even if there are rare events. According to Sachs (2), the logarithmic normal distribution is observed whenever biological or economic aspects predominate. This includes, among other things, the income of wage earners.

The National Institute for Occupational Safety and Health (NIOSH) in the USA proposed adjusting sample-taking and evaluation of the measurement results at work places to the logarithmic normal distribution (3).

# 3. Random selection of ten short-term measuring intervals

The sequence of short-term measurements and the statistical evaluation are best explained by way of an example as follows.



ig. 13. Long-term measurements at workplaces by means of detector tubes (personal monitoring) First step (duration of a single measurement). Estimate the duration of a single measurement of the short-term method: it is assumed for this example to be 4 minutes in practice. The duration will depend on the type of method and may differ from 4 min, but the general principle will still apply.

Second step (subdividing the monitoring period). Subdivision of the entire monitoring period into time intervals corresponding to the duration of a single measurement (4 min). The monitoring period is to begin at 6.00 a.m. Duration of the monitoring period: eight hours (corresponding to one work shift).

The corresponding time intervals (4 min each) are listed in Table 1 (tables for other time intervals can be compiled without difficulty by the user himself); a total of nine hours is taken into account because - as will be shown later - the intermissions are not included in the monitoring period.

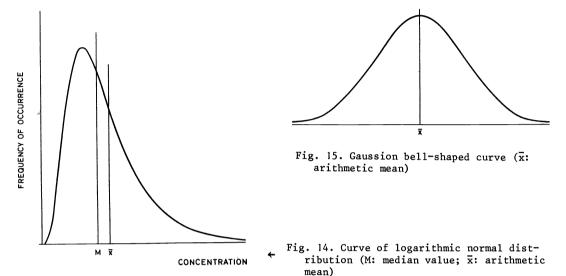


Table 1: Measurement time intervals from 1	to 135	(basis for one	measurement: 4	$4 \min$
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Hours	1	2	3	4	5	6	7	8	9
Minutes +									
0.00-0.04	1	16	31	46	61	76	91	106	121
0.04-0.08	2	17	32	47	62	77	92	107	122
0.08-0.12	3	18	33	48	63	78	93	108	123
0.12-0.16	4	19	34	49	64	79	94	109	124
0.16-0.20	5	20	35	50	65	80	95	110	125
0.20-0.24	6	21	36	51	66	81	96	111	126
0.24-0.28	7	22	37	52	67	82	97	112	127
0.28-0.32	8	23	38	53	68	83	98	113	128
0.32-0.36	9	24	39	54	69	84	99	114	129
0.36-0.40	10	<b>2</b> 5	40	55	70	85	100	115	130
0.40-0.44	11	<b>2</b> 6	41	56	71	86	101	116	131
0.44-0.48	12	27	42	57	72	87	102	117	132
0.48-0.52	13	28	43	58	73	88	103	118	133
0.52-0.56	14	29	44	59	74	89	104	119	134
0.56-0.60	15	30	45	60	75	90	105	120	135

The work hour "1" of Table 1 would last from 6.00 a.m. to 7.00 a.m. in our example. Hour "2" would last from 7.00 a.m. to 8.00 a.m.

In our example, the period from 6.00 a.m. to 6.04 a.m. can be found in Table 1 as time interval No. 1. This is followed by time interval No. 2, lasting from 6.04 a.m. to 6.08 a.m. Each hour must be subdivided into 15 time intervals. Nine hours will result in a total of 135 intervals.

Third step (random selection of the measuring time intervals). Ten intervals must be selected at random from the 135 possibilities. According to Lindner (4) the procedure normally used in games of chance can be employed; in these games, the random situation is reached by shuffling cards, drawing balls, or turning a lottery wheel. Kayser (5) recommends special random dies on which the following numbers are printed:

First die:	0,	1,	2,	3,	4,	5,
Second die:	0,	6,	12,	18,	24,	30,
Third die:	0,	36,	72,	108,	144,	180.

When the dice are thrown, the sum of numbers is formed; three dice cover the range from 0 to 215. (Instead of dice also a specially programmed pocket calculator can be used). Random numbers obtained by throwing die have been compiled in Table 2. All numbers above 135 have been omitted because they are not required for selecting the time intervals of our example. The decision as to which column of Table 2 is to be used can be taken arbitrarily. It is also possible to write the figures 1, 2, 3 and 4 on one card each and to draw a card. If the card carrying ig. 2 is drawn, the random numbers of the second column of Table 2 are to be used.

Intermissions are left out in the measurement programme. If time intervals occur during intermissions, more than ten numbers must therefore be obtained from the series of random numbers. The random numbers in our example are 79, 31, 50, etc. Since there is an intermission between 8.00 a.m. and 8.15 a.m., the time intervals identified by the numbers 31 to 34 must be omitted. The same holds for the period from 11.30 a.m. till noon; in this case, the numbers 83 to 90 are omitted.

This leaves us with the following intervals for the measurement: 29, 44, 50, 68, 76, 79, 80, 101, 111, 121.

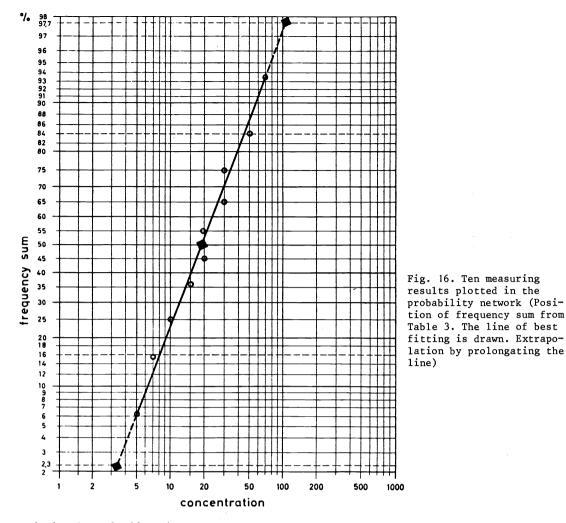
Fourth step (condition of the measurements). Ten measurements (by way of a short-term method) are carried out at the intervals mentioned. The following results are obtained:

<u>Time interval</u>	Time	CO concn. (ppm)	Time interval	Time	CO concn. (ppm)
29	7.52 - 7.56	15	79	11.12 - 11.16	70
44	8.52 - 8.56	5	80	11.16 - 11.20	50
50	9.16 - 9.20	30	101	12.40 - 12.44	30
68	10.28 - 10.32	7	111	13.20 - 13.24	20
76	11.00 - 11.04	20	121	14.00 - 14.04	10

Fifth step (arrangement of the measured data). The ten individual measured data are arranged in the order of increasing concentration, starting with the lowest value: 5 ppm, 7 ppm, 10 ppm, 15 ppm, 20 ppm, 20 ppm, 30 ppm, 50 ppm, 70 ppm.

Sixth step (graphic rement results). Th	evaluation of the measu-	Table 2: R	andom numbers		
plotted in a probabi	e results are then lity network, with the e concentration as coor-	<u>Column 1</u>	Column 2	Column 3	Column 4
dinates. The positi	ons for entering the data	64	79	81	129
are obtained from Ta	ble 3, and the following	55	31	20	7
data are used:		106	50	134	36
Concentration	Frequency sum	103	44	102	104
		123	101	64	31
( <u>ppm</u> )	( <u>%</u> )	78	29	29	89
5	6.2	117	121	98	48
7	15.9	68	76	78	82
10	25.5	83	84	6	113
15	35.2	27	80	88	25
20	45.2	72	111	100	21
20	54.8	120	68	111	129
30	64.8	110	129	67	8
30	74.5	21	27	58	48
50	84.1	75	47	12	110
70	93.8	L			

Ten points are obtained through which a straight line matching the data as well as possible must be drawn (Figure 16).



# Deviation from the linearity

It will not always be possible to represent the relationship between the frequency sum and the concentration by a straight line. Leidel (6) made proposals as to how the data are to be treated in the absence of logarithmic normality (i.e., no linear correlation between the frequency sum and the concentration, as shown in Fig. 17 for instance); the desired linearity can often be obtained by a process termed transformation in mathematics. The possible advantages of this technique in arriving at practical conclusions is yet to be examined on the basis of an extended series of measurements.

The following conclusions can be drawn from the non-modified graphic presentation. Any deviation from the linearity indicates that the concentrations do not follow a logarithmic normal distribution; this, in turn, suggests that there were changes in the concentration during the monitoring period which were not subject to random distribution. This may include, for instance, basic changes in the ventilation conditions (e.g., failure of fans), appearance of new leaks, other unforseen changes in the work place environment or completion of a specific operation.

In such instance, the monitoring periods should be subdivided differently in case of repeat measurements. A graphic evaluation of the new results may then usually yield the desired linearity.

# Estimate of the concentration range

If there is a correlation, represented by a straight line, an estimate can be obtained from the system of coordinates as to the range within which about 68% or about 95% of the concentrations are to be expected.

In order to estimate the 68% range (i.e. the single standard deviation) the points of intersection of the 16% and 84% horizontal lines with the curve must be associated on the abscissa with the corresponding concentrations (in our example, 68% of the concentrations are to be expected between about 8 ppm and 45 ppm).

The 95% range is obtained from the 2.3% and 97.7% horizontal lines (transferred to our example, 95% of the concentrations are within the range from about 3 ppm to about 110 ppm).

(The plotting position in the probability network according to illustr.16 is obtained from the frequency sum and the measured value.) Table 3: Frequency sum 7 for a number of random samples from n = 5 to n = 12

10 11 <u>93,8</u> 85,5 94,4 78,5 86,9	Number of	Designatio	n of the	the individual measured value	ial mea	sured v	alue						
12, 3 $30, 8$ $50, 0$ $69, 2$ $87, 7$ $87, 7$ $10, 2$ $26, 1$ $42, 1$ $57, 9$ $73, 9$ $89, 8$ $8, 9$ $22, 4$ $36, 3$ $50, 0$ $63, 7$ $77, 6$ $91, 2$ $7, 8$ $19, 8$ $31, 9$ $44, 0$ $56, 0$ $68, 1$ $80, 2$ $92, 2$ $7, 8$ $19, 8$ $31, 9$ $44, 0$ $56, 0$ $68, 1$ $80, 2$ $92, 2$ $6, 8$ $17, 6$ $28, 4$ $39, 4$ $50, 0$ $68, 1$ $80, 2$ $92, 2$ $6, 8$ $17, 6$ $28, 4$ $39, 4$ $50, 0$ $68, 1$ $80, 2$ $92, 2$ $6, 8$ $17, 6$ $28, 4$ $39, 4$ $50, 0$ $68, 1$ $74, 5$ $84, 1$ $93, 2$ $5, 6$ $14, 5$ $23, 3$ $41, 3$ $50, 0$ $58, 7$ $67, 7$ $76, 7$ $85, 5$ $94, 4$ $5, 6$ $14, 5$ $23, 3$ $41, 3$ $50, 0$ $54, 0$ $62, 2$ $70, 5$ $78, 6$ $94, 4$	random samples	1	5		4	ъ	ю	~	ω	თ	10	11	12
10,2 $26,1$ $42,1$ $57,9$ $73,9$ $89,8$ $89,8$ $8,9$ $22,4$ $36,3$ $50,0$ $63,7$ $77,6$ $91,2$ $7,8$ $19,8$ $31,9$ $44,0$ $56,0$ $68,1$ $80,2$ $92,2$ $7,8$ $19,8$ $31,9$ $44,0$ $56,0$ $68,1$ $80,2$ $92,2$ $6,8$ $17,6$ $28,4$ $39,4$ $50,0$ $60,6$ $71,6$ $82,4$ $93,2$ $6,2$ $15,9$ $25,5$ $35,2$ $45,2$ $54,8$ $64,8$ $74,5$ $84,1$ $93,2$ $5,6$ $14,5$ $23,3$ $32,3$ $41,3$ $50,0$ $58,7$ $67,7$ $76,7$ $85,5$ $94,4$ $5,2$ $13,1$ $21,5$ $23,7$ $46,0$ $54,0$ $62,2$ $70,5$ $78,6$ $94,6$	מי	12, 3	30, 8	50,0	69, 2	87,7							
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7,8       19.8       31,9       44,0       56,0       68,1       80,2       92,2       92,2         6,8       17,6       28,4       39,4       50,0       60,6       71,6       82,4       93,2 $6,2$ 15,9       25,5       35,2       45,2       54,8 $64,8$ 74,5 $84,1$ 93,2         5,6       14,5       23,3       32,3       41,3       50,0       58,7 $67,7$ 76,7       85,5       94,4         5,2       13,1       21,5       29,5       37,8       46,0       54,0       62,2       70,5       78,5       86,9	<i>L</i> -	8,9	22, 4	36, 3	50,0	63, 7	77, 6	91,2					
6,8         17,6         28,4         39,4         50,0         60,6         71,6         82,4         93,2         93,2 $6,2$ $15,9$ $25,5$ $35,2$ $45,2$ $54,8$ $64,8$ $74,5$ $84,1$ $93,8$ $5,6$ $14,5$ $23,3$ $32,3$ $41,3$ $50,0$ $58,7$ $67,7$ $76,7$ $85,5$ $94,4$ $5,2$ $13,1$ $21,5$ $23,5$ $46,0$ $54,0$ $62,2$ $70,5$ $78,7$	œ	7, 8	19,8	31,9	44,0	56,0	68, 1	80, 2	92,2				
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5,6     14,5     23,3     32,3     41,3     50,0     58,7     67,7     76,7     85,5     94,4       5,2     13,1     21,5     29,5     37,8     46,0     54,0     62,2     70,5     78,5     86,9	키	6, 2	15,9	25, 5	35, 2	45,2	54,8	64, 8	74, 5	84,1	93, 8		
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	12	5,2	13,1	21,5	29,5	37,8	46,0	54,0	62,2	70, 5	78,5	86,9	94,9

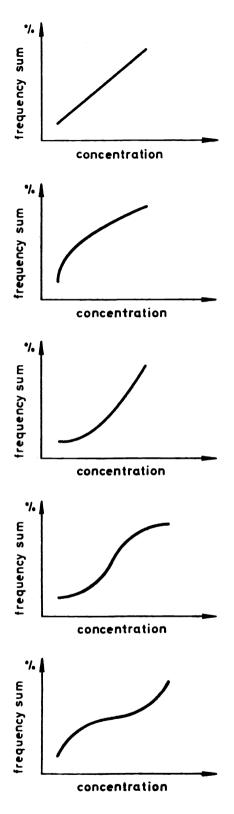


Fig. 17. Examples of relationship between frequency sum and concentration (Non-linearity occurs when frequency distribution of concentration differs from logarithmic normal distribution)

## Estimate of the median value (graphic)

The intersection of the 50% horizontal line with the curve yields the median value of the concentrations (in this framework also the geometric mean) on the abscissa (in our example, this value is about 19 ppm).

# Calculation of the median value

The median value cannot only be determined graphically, but also mathematically. To this end, the logarithmus of the various measured values must be picked out (table of logarithms), and the arithmetic mean of the logarithms is calculated.

Measured value	Logarithm		
( <u>ppm</u> )			
15	1.1761		
5	0.6990		
30	1.4771		
7	0.8451		
20	1.3010		
70	1.8451		
50	1.6990		
30	1.4771		
20	1.3010		
10	1.0000		
	12.8205	Sum	
	1.282	Arithmetic	mean

By looking up the numerical value of 1.282 (table of logarithms), the result 19 ppm is obtained; this is the CO concentration corresponding to the median value which had already been obtained graphically.

#### Explanation of the median value

In specialized literature the "median" is defined as the value which halves the frequency distribution, so that each portion contains 50% of the individual values. In the example selected by us, 50% of the data would be above 19 ppm, and 50% below this value. Due to the mathematical connection, the median value of measurement results is lower than the arithmetic mean. If we were to calculate the arithmetic mean of the ten individual values of our example, we would obtain about 26 ppm. The median value provides more information for the evaluation of frequencies which correspond to the logarithmic normal distribution.

#### 4. Summary

In Section VIII a method has been set out for processing the results of a series of single short-term tests in order to evaluate the fluctuation-range of the concentration over an extended period of time. In situations where the correlation outlined in the subsection Deviation from the linearity cannot be obtained or where practical situations make the proposed procedure difficult to adapt, other methods should be used (e.g. continuous monitoring by instruments).

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