MEASURING STREAM DISCHARGE USING THE DYE-DILUTION METHOD (CHEMICAL GAUGING)

by

HANS M. KELLER

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This study was carried out by Mr Keller while he was a visiting scientist on the staff of the Protection Forestry Branch, Forest Research Institute, New Zealand Forest Service.

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1. SUMMARY

Field and laboratory procedures are given for chemical gauging by the dye-dilution method, using sodium dichromate and a 2-gallon injection container.

Injecting at a constant rate i, the stream discharge q is equal to the dilution ratio K multiplied by the injection rate, i.e., $q = K \cdot i$, where K is the ratio of the initial concentration N_1 to the down-stream concentration N_2. Comparing the down-stream dilutions with a series of standard dilutions of the initial concentrated solution, the dilution ratio K can be directly determined in the laboratory and the discharge q calculated.

Practical hints are given for the calibration of the injection rates, the preparation of the initial solution, the precautions to be taken in the field, and the acquisition of quick but accurate results in the laboratory. Forms for use in the field as well as for the analysis in the laboratory are proposed.

With clean and careful handling of equipment and chemicals standard errors of about $\pm 2\frac{1}{2}$ percent should be obtained.

In turbulent mountain streams and small rivers this method has been found suitable, inexpensive, and relatively quick. However, at the time of writing no way had yet been found to record stream flow automatically on this basis.

2. INTRODUCTION

Measuring the discharge of streams and rivers under turbulent flow conditions has been a problem for some time, and in steep turbulent mountain streams the traditional current-meter methods cannot be used unless the measuring site is first prepared and a controlled even flow established. However, chemical gauging by the dye-dilution method, first developed in France for testing hydro-electric turbines and subsequently adapted for use in open channels and natural streams (Dumas 1952), has now provided a quick, accurate, and inexpensive answer to the problem.

A series of tests of the dye-dilution method was carried out in 1965—66 in the high country of Canterbury, New Zealand, with most of the work being done in the Camp Stream catchment of the Craigieburn Range, an experimental basin selected for the purposes of the International Hydrological Decade. The principle of the method and the requirements, equipment, and procedures suited to small mountain streams are described in this paper.

3. PRINCIPLE

A solution of a chemical substance of known concentration is injected at a constant rate at one cross section of the stream. The subsequent dilution is measured at another cross section sufficiently down stream for complete mixing to have taken place.

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Given the rate of injection i (litres/second), the initial concentration N_1 (grams/litre), and the final concentration N_2 (g/l), the discharge q (l/s) is calculated as follows (Dumas 1952):

$$i.N_1 = (q + i)N_2 \qquad \dots (1)$$

$$\frac{i}{q + i} = \frac{N_2}{N_1} \qquad \dots (2)$$

$$q = \left(\frac{N_1}{N_2}\right)i - i \qquad \dots (3)$$

Since the rate of injection i is very small in relation to the discharge q, equation (3) can be written:

$$q = \left(\frac{N_1}{N_2}\right)i \quad \text{or} \quad q = K.i \qquad \dots (4)$$

where N_1/N_2 is the dilution ratio K. If the rate of injection i is given by the injection equipment, and the dilution ratio K is determined by comparison of the initial concentration N_1 with the diluted sample concentration N_2, the discharge q can be determined by means of equation (4).

4. REQUIREMENTS

For good results the chemical used should meet the following requirements (Dumas 1953a). It should:

— be highly soluble in water at temperatures from $0-15^\circ$C;
— have a good colouring effect or be easily traceable at low concentrations;
— be stable with respect to light, organic material, and suspended sediments;
— be non-toxic to fish and other animal life in the concentrations used;
— be naturally absent from the stream, or be found only in very low concentrations.

Sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$) was found to meet these requirements most closely, although it is unstable if exposed to light for long periods and can be affected by organic matter and reducing agents in the water (Dumas 1953a, 1953b; B.S.I. 1964). It has a high solubility; it is possible to use concentrations of up to approximately 600 g/l in practice. Concentrations as low as 0.2 mg/l can still be determined accurately by utilising the colour reaction with diphenylcarbazide, this usually being done with an instrument such as a colorimeter. Sodium dichromate is physically stable and is absorbed to only a small extent by materials likely to be found in a stream. It is also non-toxic in concentrations less than 2 mg/l. The dye fluorescein has a very strong colouring effect but is otherwise unsuitable — however, it is often used as a preliminary check of the suitability of the measuring reach.

It is essential that the measuring reach suit requirements: it should be as short as possible; dead water zones should be absent or small; the stream should be unbranched and turbulent; inflow to and outflow from the reach should not occur. These properties are best tested by observing the stream after a small amount of fluorescein has been added to it.

5. EQUIPMENT

The two main pieces of equipment used in chemical gaugings are the constant-rate-injection apparatus and the colorimeter for dilution analysis.

For gaugings in streams and small rivers an injection apparatus incorporating the principle of the Mariott flask is used (see fig. 1). For larger rivers, however, other systems are recommended (B.S.I. 1964). The equipment used in this study consisted of a 2-gallon (8.55-litre) copper container with an air-inlet pipe and an outlet pipe. The outflow was regulated by precalibrated interchangeable brass nozzles such as are used on sprinkling systems. The container was also equipped with a handle that could be hooked on to a supporting tripod for placing in the stream. This apparatus could be improved by attaching a clear-view pipe to the outside of the container to make the level of the solution visible.

The dilution ratio K was calculated directly by preparing standard dilutions of the initial solution and comparing these, by means of a colorimeter, with the samples taken at the down-stream cross section. This comparison was made by measuring the percentage absorbance of light at a wavelength of

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Labels on figure:
- handle
- clip
- rubber tubing
- 12 in. × 6 in. copper vessel
- copper tubing
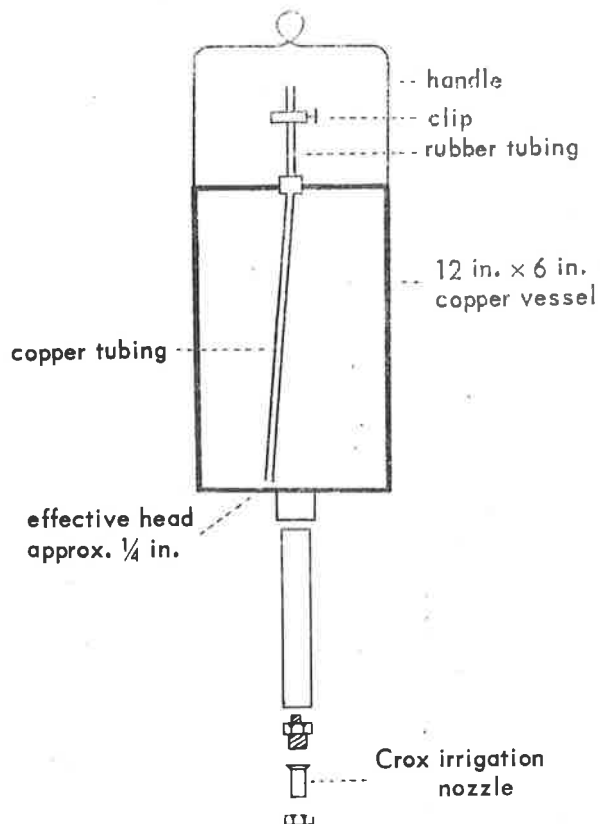- effective head approx. ¼ in.
- Crox irrigation nozzle

FIG. 1: Injection apparatus as used by N.Z. Forest Service
for chemical gaugings at Camp Stream.

540 nanometres (Dodero 1953; B.S.I. 1964) after adding a colour reagent to the standard as well as the down-stream dilutions. With this method it was not necessary to determine actual concentrations. The Bausch and Lomb Spectronic 20 colorimeter was found satisfactory for this dilution analysis. With this equipment, which uses test tubes of 11.7 mm inside diameter, final concentrations of 0.5 to 1.0 mg/1 sodium dichromate could easily be measured. By using test tubes of larger diameters, even lower concentrations could be determined.

Besides the injection container with nozzles and tripod, the following items were also used in the field: 50-ml sample bottles for the initial solution; 100-ml plastic bottles for sampling at the down-stream cross section; a funnel and tin to fill the container; fluorescein to test the measuring reach; colour reagent to test the outcome of the down-stream dilution in the field; a portable stage marker (a calibrated iron rod) to check discharge fluctuations during the measurement. If several measurements are to be made at the same site it is better to install a permanent stage marker, as this would enable discharge estimates to be improved when future gaugings are made. In the laboratory, only glassware (beakers, volumetric flasks, and pipettes) was used in addition to the colorimeter.

6. PROCEDURES

6.1 Preliminary Preparations

All nozzles are calibrated to ensure an accurate injection rate i and should be checked by means of a stopwatch and volumetric flask. Standard errors of the mean for the injection rate ranged from 0.08 to 0.13 percent; however, it was found that water temperature altered the rate of outflow through the the nozzles, and injection rates changed by about 0.15 to 0.20 percent per degree Celsius. If water-temperature differences between calibration and measuring conditions in the field of 10°C were observed, the gauging result would then be altered by 1.5 to 2.0 percent. By taking the temperature of the water in the stream during the measurement, and by using this water to make up the initial solution, the appropriate rate of outflow could always be applied.

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The calibration for the size of nozzle most often used for gaugings in Camp Stream is shown in table 1.

TABLE 1: Calibration of a nozzle for outflow and temperature.

Temperature (°C)	Rate of outflow (ml/s)	Standard error of the mean	
		Standard deviation (ml/s)	Percentage of mean
6	10.67		
8	10.70	0.0086	0.081
10	10.73		
12	10.76		
14	10.80	0.0434	0.402
16	10.84		
18	10.89		
20	10.95		
23.5	11.18	0.0150	0.134

The next step was to construct a table for estimating the amount of sodium dichromate to be used for a measurement. The required amount G depends on the discharge q, the rate of outflow i, the volume of the container V, and the final concentration N_2 aimed for at the down-stream cross section. In effect, what must be estimated is the initial concentration N_1. From equation (4):

$$N_1 = \frac{N_2 \cdot q}{i} \qquad \dots \text{(5)}$$

$$= \frac{G}{V} \qquad \dots \text{(6)}$$

Combining equations (5) and (6) gives

$$G = \frac{V \cdot N_2 \cdot q}{i} \qquad \dots \text{(7)}$$

where V is given by the container, i is given by the nozzle used, N_2 is to be chosen, and q is to be estimated. For all measurements it was decided to aim for a final concentration N_2 of 1 mg/l, which gives an absorbance reading of 0.245 percent and still allows a fair over- or underestimate of the discharge q. When full, the container had a volume of 8.55 litres for which an initial solution had to be prepared. While gauging, however, only 8 litres flowed out through the nozzle at a constant rate. The 550-ml 'dead' portion is discharged at a decreasing rate because of the decreasing pressure resulting after the water level in the container reaches the end of the air inlet. With all these given factors:

$$G = \frac{8.55 \times 0.001 \times q}{i} = 8.55\left(\frac{q}{i}\right)$$

where q is estimated in litres per second, i is given in ml/s, and G is given in grams.

The discharge q must be estimated and the right nozzle chosen before the required amount of chemical can be calculated. To make these calculations in the field easier the table was prepared (for a container of 8.55 litres and a final concentration of 1 mg/l) so that it would give the required amounts of sodium dichromate for various nozzles and for a range of stream discharges. The table was prepared for average rates of injection and, since injection rates of a single nozzle vary little, the table could be used satisfactorily for the full range of outflow. A portion of this table is given in table 2.

A further step in the preparations required that the chemical be prepared so that it is ready in the field in the desired quantities with a minimum of handling. This becomes very important during periods of rain. A quick and clean field procedure was necessary, so sodium dichromate was filled into small plastic bags in portions of 2, 5, 10, 25, 50, and 100 grams; this ensured that the required amount to the nearest 2 g would be readily available. This arrangement was found satisfactory.

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TABLE 2: Amounts of sodium dichromate required for various discharges as calculated for an 8.55-litre container and a final concentration N_2 of 1 mg/l.

Estimated discharge		Required amount of chemical for full container (grams)	
l/s	cusecs	NOZZLE I $i = 7.84$ ml/s Period of constant injection: 17 min	NOZZLE II $i = 10.76$ ml/s Period of constant injection: 12 min
10	0.35	10.9	7.9
20	0.71	21.8	15.9
40	1.41	43.6	31.8
60	2.12	65.4	47.7
80	2.82	87.2	63.6
100	3.53	109.0	79.5

Finally, the sample bottles had to be organised. Fifty-millilitre glass bottles for sampling the initial solution were numbered and kept apart from the 100-ml plastic bottles, which were also numbered, and put in plastic bags in groups of seven to be used for down-stream sampling.

6.2 Field Procedure

The step-by-step procedure is as follows:

6.2.1 A measuring reach in the stream is selected, if possible avoiding dead-water zones, inflow and outflow, and branched channels and favouring turbulent, narrow, and swift portions of the stream. The point of injection and the down-stream cross section are marked.

6.2.2 A calibrated stage marker (iron rod) is put into the stream within the measuring reach.

6.2.3 At the point of injection a little fluorescein is added to the stream. The elapsed time is noted when the last of the coloured water has passed through the down-stream cross section. It is possible to judge turbulence and mixing at the same time, and the measuring reach can be altered if it appears that the site is not suitable. By adding 5 to 8 minutes (for initial and down-stream sampling) to the time of travel the minimum outflow time is obtained. A nozzle is chosen which will ensure a period of constant injection at least equal to the minimum outflow time.

6.2.4 The discharge of the stream is estimated in litres per second or cusecs.

6.2.5 The required amount of sodium dichromate is found by reading the appropriate nozzle and discharge from table 2.

6.2.6 The initial solution is prepared by half-filling the container and adding the calculated amount of sodium dichromate. The container is shaken well to ensure that the chemical has been completely and evenly dissolved, and then filled completely.

6.2.7 The container is hooked on to the tripod and the air inlet opened. As the solution starts to flow out the time is recorded, and after at least 10 to 15 seconds it is sampled, first rinsing the sample bottle with the solution. The number of the bottle should then be recorded.

6.2.8 The stage-height reading is recorded.

6.2.9 The air and water temperatures are recorded.

6.2.10 When the time of travel determined in section 6.2.3 has elapsed, a field test is made with the colour reagent in a test tube (see section 6.3). If the water becomes noticeably red the discharge has been estimated satisfactorily and the measurement can be taken to the laboratory for analysis.

6.2.11 Three to 4 minutes before the period of constant injection is over, the seven samples at the down-stream cross section are taken at half-minute intervals. These water samples should be taken from various points on the cross section. When the cross section is large it is advisable to increase the number of samples.

6.2.12 Before the samples are taken for analysis, take a second stage-height reading and compare it with the stage height at the beginning of the measurement. To ensure good results only small fluctuations can be accepted.

6.2.13 If further gaugings are to follow, the container need not be cleaned, but it should be rinsed after each day of gauging.

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6.2.14 If water-quality samples are required they should be taken immediately above the injection point.

6.2.15 The sample of initial solution as well as the down-stream samples should be kept cool and dark until they are analysed in the laboratory.

The type of field form which was used for more than 100 measurements in 1965–6 in Camp Stream is illustrated in appendix 1.

6.3 *Laboratory Procedure*

Analysis of the samples should be carried out as soon as possible after they have been taken. Before starting the laboratory analysis it is advisable to switch on the colorimeter to allow it at least 10 minutes to warm up, and to prepare the colour reagent before anything else is begun.

The colour reagent is prepared as follows (Dodero 1953):

Solution A: Dilute one part concentrated sulphuric acid (H_2SO_4) with four parts distilled water, e.g., take 80 ml distilled water and slowly add sulphuric acid to make 100 ml.

Solution B: Dissolve 0.25 g diphenylcarbazide, $(C_6H_5NH.NH)_2CO$, crystals in 100 ml 96 percent ethanol.

When solutions A and B have been mixed in equal parts the colour reagent is ready for use. Separately, solutions A and B can be kept for a long period; once they are mixed the compound reagent should not be used after 24 hours.

The step-by-step procedure is as follows:

6.3.1 Estimate the dilution ratio $K = \dfrac{N_1}{N_2} = \dfrac{q}{i}$, where q and i are both in the same units.

6.3.2 Using tap water, prepare at least three standard dilutions from the initial injection solution for dilution ratios $0.5K$, $1.0K$, and $1.5K$. If discharge estimates are believed to be good, dilutions can be prepared instead for $0.8K$, $1.0K$, and $1.2K$. It is recommended that the amount of initial solution used in the preparation of each dilution should never be less than 5 ml. With a 10-ml graduated pipette and 100-, 250-, 500-, and 1,000-ml volumetric flasks, standard dilutions can be prepared in two steps up to a dilution ratio of 1:20,000. A table for the preparation of standard dilutions is given in appendix 2.

6.3.3 Put 20 ml of each standard dilution and each down-stream sample in small beakers. Add 2 ml of colour reagent to each of the beakers, stir, and wait 5 minutes.

6.3.4 Check visually to see if the down-stream samples fit into the range of the prepared standard dilutions. If not, an additional dilution must be made in order to extend the range.

6.3.5 Set the colorimeter on a wavelength of 540 nm and adjust the zero reading with distilled water.

6.3.6 Using the same test tube all the time, measure the percentage absorbance of each sample, standard dilutions as well as down-stream samples. Check the zero reading with distilled water after each measurement.

6.3.7 Plot the rating curve with absorbance of the standard dilutions on the abscissa and values of $10^6/K$ on the ordinate. These latter values represent the concentration, in parts per million, of the initial solution present in the diluted sample. The reason for expressing the dilution ratio K as a concentration is because absorbance increases linearly with increasing concentration.

6.3.8 Check the rating curve. All three (or more) standard dilutions should give a straight line if absorbance values are plotted against $10^6/K$; if this is not the case then the standard dilutions must be repeated. For every gauging a new rating curve is necessary.

6.3.9 Compute the average absorbance of all the down-stream samples. Read from the rating curve graphically the concentration in parts per million of initial solution (i.e. $10^6/K$). A numerical check is simple because of the linear relationship.

6.3.10 Calculate the discharge q in l/s by means of equation (4):

$$q = i.K. = \frac{i.10^6}{10^6/K}$$

where i is given (in l/s) by the size of the nozzle used, and $10^6/K$ is determined graphically or numerically from the rating curve.

The laboratory form used is shown in appendix 3.

Absorption readings of the down-stream samples should vary little (standard error of the mean: ±2.0 percent). Larger variations may be due to stream-flow fluctuations, improper mixing because of a lack

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of turbulence or because of inflow just above the down-stream cross section, non-homogeneity of the initial solution, down-stream samples being taken too early or too late, and erroneous readings from the colorimeter.

7. ACCURACY OF THE METHOD

Measurements taken very carefully and with a large number of samples approach an accuracy of ±1.0 percent (B.S.I. 1964). In order to speed up measurements and to simplify the analysis, the number of samples collected at the down-stream cross section was reduced to seven and tap water was used for the standard dilution instead of water taken from the stream. The following estimate of standard errors, however, will show that even with this simplified procedure a reasonable degree of accuracy was obtained.

		%
Injection	— Rate of outflow i:	±0.20
Dilution ratio K —	Absorbance values from down-stream samples:	±2.0
	Preparation of standard dilutions:	±0.50
	Rating curve:	±1.0
	Variation of initial solution:	±0.2
	Overall standard error for estimate of K:	±2.30
Overall standard error for estimate of discharge q:		±2.31

If error can be kept within these limits, the measurements will yield very useful information on stream discharge. If measurements and analyses are carried out in an orderly and clean manner good results should be obtained, even when little time is available in the field or in the laboratory. In the case of Camp Stream measurements, it has been found that 20 minutes in the field and 45 minutes in the laboratory is sufficient for a trained person to complete one discharge measurement.

8. REFERENCES

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Field Form for Stream Discharge Measurement No. . . . .

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Date: . . ./. . ./. . . Time (at start of injection): . . . .

Air temperature (°C): . . . . Water temperature (°C): . . . .

Weather: . . . .

Location — Dye input: . . . .

Down-stream sampling: . . . .

Initial solution — Discharge estimate: . . . . l/s, ... cusecs

Minimum outflow time (period of constant injection): . . . . min

Total $Na_2Cr_2O_7$: . . . . g Concentration: . . . . g/l

Sample bottle no. . . . .

Nozzle — Size: . . . . Rate of outflow: . . . . ml/s

Water-quality sample no. . . . .

Stage height — Beginning: . . . . End: . . . .

Down-stream sampling — First sample after: . . . . min

Last sample after: . . . . min

Sample bottles no. . . . .

Gauging made by: . . . .

Remarks: . . . .

APPENDIX 2: Guide to Preparing Standard Dilutions

For each value of K the standard dilution is prepared in two steps. At each step the corresponding volume in millilitres is transferred (using a 10-ml graduated pipette) to the volumetric flask of the size shown at the top of the column, and this is then filled to the mark with tap water.

Dilution ratio K	$10^6/K$ (ppm initial solution)	FIRST — Dilute to			SECOND — Dilute to			
		100ml	500ml	1,000ml	100ml	250ml	500ml	1,000ml
30	33,333	10			33.3			
50	20,000	10			10			
75	13,333	10			13.3			
100	10,000			10				
100	10,000	10			10			
125	8,000	10			8			
150	6,667	10			6.67			
200	5,000	10			5			
300	3,333	10			3.33	8.34		
400	2,500	10			2.5	6.25		
500	2,000	10			2	5	10	
600	1,667	10					8.33	
667	1,500	10					7.5	
700	1,428	10					7.14	
750	1,333	10					6.67	
800	1,250	10					6.25	
833	1,200	10					6.0	
900	1,111	10					5.55	
1,000	1,000	10					5	
1,000	1,000			10	10			10
1,100	909		10		4.55			
1,200	833		10		4.17			
1,250	800		10		4.0	10		
1,300	769		10		3.85	9.62		
1,400	714		10			8.93		
1,500	667		10			8.33		
1,600	625		10			7.81		
1,700	585		10			7.35		
1,800	556		10			6.95		
1,900	527		10			6.58		
2,000	500		10			6.25		
2,000	500			10	5			
2,500	400			10	4	10		
3,000	333			10	3.33	8.32		
3,333	300			10	3.0	7.5		
4,000	250			10	2.5	6.25		
5,000	200			10	2.0	5.0	10	
6,000	167			10		4.16	8.32	
6,667	150			10		3.75	7.5	
7,000	142.8			10		3.58	7.15	
8,000	125			10		3.125	6.25	
9,000	111			10		2.78	5.55	
10,000	100			10		2.5	5.0	10
11,000	90.9			10			4.54	9.08
12,000	83.3			10			4.16	8.33
12,500	80			10			4.0	8.00
13,000	76.9			10			3.85	7.69
14,000	71.4			10			3.57	7.14
15,000	66.7			10			3.33	6.67
16,000	62.5			10			3.125	6.25
17,000	58.8			10			2.94	5.88
18,000	55.6			10			2.78	5.56
19,000	52.7			10			2.63	5.27
20,000	50			10			2.50	5.00
40,000	25			10			1.25	
80,000	12.5			10			0.63	

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Laboratory Analysis of Stream Discharge Measurement No. ....

Date of Analysis: .../.../...   Date of measurement: .../.../...

Location: ....

Estimated discharge q: ....l/s   Rate of outflow i: ....ml/s ......l/s

Estimated dilution ratio K (=q/i): ....   Initial solution bottle no. ....

Standard dilutions —

Dilution ratio K	$10^6/K$ (ppm initial solution)	Percentage absorbance at 540 nm

Down-stream samples —

No.	Percentage absorbance at 540 nm

Average absorbance:

...........%

Corresponding value of $10^6/K$: .....ppm

Discharge $q = \dfrac{i.10^6}{10^6/K}$:

.........l/s

Analysed by: ....

Remarks: ....

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