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SEMI-MICRODETERMINATION OF NITROGEN IN ACTINIDE COMPOUNDS BY DUMAS METHOD

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**GOVERNMENT OF INDIA
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URANIUM NITRIDES

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BY DUMAS METHOD

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ABSTRACT

This report describes the application of the Dumas method for the semi-micro determination of nitrogen in actinide compounds and actinide complexes with organic ligands. The usual set up has been modified to make it adaptable for glove box operations. The carbon dioxide generator and nitrometer assemblies were located outside the glove box while the reaction tube and combustion furnaces were housed inside. The nitrogen gas collected in the nitrometer was read with the help of travelling microscope with a vernier attachment fitted in front of the nitrometer burette. The set up was standardised using acetanilide and employed for the determination of nitrogen in various substances such as uranium nitride, and a variety of substituted quinoline and pyrazolone derivatives of actinides as well as some ternary uranium-PMBP-sulphoxide complexes. Full details of the technique and the analytical data obtained are contained in this report.

INTRODUCTION

The determination of nitrogen is important in the characterisation of actinide compounds having ligands containing this element. When radioactive materials like plutonium complexes are analysed, they pose serious problems since it is essential to handle the entire operation inside the glove box for containment of radioactivity. There are two well established methods for the determination of nitrogen. Out of them, the Kjeldhal method involves long duration of sample digestion with concentrated sulphuric acid and problems associated with the quantitative release of nitrogen from complexes having complicated heterocyclic rings. This makes it less attractive for adaptation inside a glove box with radioactive materials. The other method, viz., Dumas, on the other hand, involving solid state reaction and short analysis times is much more attractive under these conditions. Recently, automatic nitrogen analyzers such as the Leco Analyser based on sample combustion at high temperatures and subsequent determination of the nitrogen using thermal conductivity detectors have been routinely employed for fast and accurate analysis. However, in this method, the decomposition products generated from complexes at high temperatures get deposited in the purification traps which get choked creating a lot of problems. Hence, the Dumas method was selected for analysis of nitrogen in actinide complexes. Several catalysts like nickel oxide, nickel acetate, copper oxide, copper acetate, potassium chlorate or potassium dichromate have been tried to facilitate decomposition of compounds having aromatic and heterocyclic rings. Of these, powdered potassium dichromate was found to be the most effective for decomposition of all types of compounds. The present report describes the adaptation of Dumas setup inside a glove box and the modifications incorporated therein. The three modifications are,

1) accurate measurements of volume of nitrogen by a travelling microscope with vernier attachment, 2) maintenance of increased flow rate (100 bubbles/min.) of carbon dioxide through the system so as to drive the evolved nitrogen towards the nitrometer which is positioned at a much longer distance outside the glove box and 3) use of 1:1 CuO + $K_2Cr_2O_7$ mixture for decomposing the nitrogenous compounds. The procedure incorporates some of the modifications suggested in the literature (1-9). The method has been standardised by estimating nitrogen in pure acetanilide to determine the precision and accuracy. Nitrogen content of several organic compounds and of their chelates with tetravalent uranium, plutonium and thorium and of several uranyl-PMBP-sulphoxide synergistic complexes have been successfully determined. This set up has also been used for the determination of total nitrogen contents of advanced fuels like uranium nitrides.

EXPERIMENTAL

Reagents:

Carbon dioxide: The crushed lumps of commercial dry ice of rice grain size were packed in a Dewar flask upto 3/4 of its volume and used as a carbon dioxide generator.

Copper metal turnings: M.A.R.(BDH) 2-4 mm. long.

Copper oxide:(powder form) 30-85 mesh M.A.R.(B.D.H.) quality was ignited to red heat in a carbon dioxide atmosphere for 15 min.cooled and kept in airtight bottle.

Mercury: Distilled pure.

Potassium hydroxide:(50 per cent w/w) A known amount was added to an equal weight of water, dissolved, cooled and filled in airtight PVC bottle.

Asbestos powder: Washed with distilled water and ignited.

Apparatus:

Fixed temperature furnace: This furnace which is 22 cm. long is always kept at 700 +/-20 deg. C. by means of controlling the current through a dimmerstat so that the permanent filling of CuO (wire form) + Cu metal turnings is always kept at 700 deg.C. throughout the experiment.

Mobile combustion furnace: This furnace which is 6" long is designed to generate 950 deg.C. in 20 min. and its temperature is controlled by varying the current through a dimmerstat. It can move across the entire length of 20 cm. of the reaction tube having the temporary filling.

Nitrometer: This consists of a glass bulb to which a standard 2ml. burette is fused at the top and has two openings on either side. One opening is connected to a 100ml. glass bulb reservoir containing 50 per cent. w/w KOH solution connected to the nitrometer through a tygon tube. The other side is connected to a three way stopcock with standard ball and socket joint through which the carrier gas containing nitrogen enters the alkali solution. This stopcock also serves as a vent for the carrier gas. A teflon stopcock is attached to the nitrometer on top of the burette for adjustment of the meniscus for initial reading of the nitrometer which also provides a vent for the carrier gas. Both the vents are connected to the glove box through a T joint. Pure mercury is filled in the bottom glass bulb so that it just blocks the entry of gas. A few mg. of mercurous chloride powder is also placed over the mercury surface so that the bubbles formed do not stick to the surface. A travelling microscope having a vernier attachment is fixed on the front door of the perspex box housing the nitrometer setup. The difference in levels of KOH before and after sample combustion gives the net volume of nitrogen. The whole length of the burette is calibrated to read volumes as a function of the distance traversed by the microscope.

Packing of quartz reaction tube:

Permanent filling: The reaction tube was packed at the exit end by an asbestos powder plug of length 0.2 cm. with the help of a thick glass rod. Copper oxide in wire form was filled upto 17 cm. followed by an asbestos plug of 0.2 cm.. This was followed by copper metal turnings upto 6 cm. and an asbestos plug of 0.2 cm. After the packings, the tube was rolled and tapped to make the filling dense and compact.

Temporary filling: In continuation of the permanent filling, temporary filling was packed containing 10 cm. of CuO in wire form followed by 7 cm. of CuO powder. In this case also, it was ensured that the packing was uniformly dense and compact. In use, the temporary filling was changed after about 10 determinations.

Procedure:

The carbon dioxide generator was isolated from the glove box line and the gas was vented through a water column for 30 min. to expel any air left in the Dewar flask. The carbon dioxide was now allowed to pass through the glove box line by opening the needle valve on the glove box side and the pressure controlled by controlled leakage through the water column. Rotaflo needle valves at the entry and exit points of the reaction tube were opened fully by turning the three way stopcock to allow carbon dioxide gas pass through the reaction tube. The fixed temperature furnace was switched on and the temperature raised to 700 deg.C. and the whole length of "permanent filling" allowed to get heated up in a stream of carbon dioxide for 30 min. to expel all residual gases locked in the system. The stopcock of the reaction tube was opened and a weighed sample containing about a mg. of nitrogen in a platinum boat having a thin layer of 1:1 mixture of CuO + potassium dichromate powders at the top and bottom was introduced and positioned over the CuO powder. The rotaflo needle valves at

the entry and exit points of the reaction tube were gradually adjusted to regulate the flow of carbon dioxide inside the nitrometer filled with the KOH solution so as to get a constant flow rate of 100 bubbles/min. The gas was allowed to flow for 5 mts. at this rate. It was ensured that bubbles originating at the mercury-KOH interface turn into microbubbles within 5 cm. height of the KOH solution by controlling the exit needle valve. The level of KOH solution in the nitrometer was raised to zero mark by raising the reservoir. The stopcock was closed and the initial height was read through the travelling microscope keeping the levels same. The mobile furnace was positioned in the middle of the sample and heating started gradually to attain a temperature of 950 deg.C. in about 20 min. The furnace was slowly moved in the forward direction throughout the length of temporary filling upto the fixed furnace. The first combustion was done in three successive steps of 5 min. time interval each. After the first combustion was over, the mobile furnace was again taken back to the original position and the second combustion was carried out in exactly the same manner. The combustion was continued for about 45 minutes till all the nitrogen was collected in the nitrometer as determined by its constant level. The final height of nitrometer level was read by the microscope after bringing the level of the reservoir solution to the level of solution inside the nitrometer. At the same time, the temperature just outside the nitrometer at the level of the liquid was noted by a digital thermometer within +/-0.1 deg.C. A blank determination was carried out in exactly the same manner without the sample in the boat. The nitrometer level was read again to arrive at the blank volume to be subtracted from the total volume of nitrogen collected. After the experiment, both the furnaces were switched off and the flow of carbon dioxide from the reaction tube was directed through the three way stopcock to the glove box atmosphere and the nitrometer burette stopcock. opened. The level of KOH solution in the

nitrometer was brought down by lowering the reservoir well below the graduated marks to prevent attack on glass and the burette stopcock finally closed. The furnaces were allowed to cool while maintaining the flow of carbon dioxide through the reaction tube. When both furnaces were sufficiently cooled, the flow of carbon dioxide was blocked by closing the rotaflo valves so that the fillings remain in carbon dioxide atmosphere and the gas allowed to escape through the water column outside the glove box.

CALCULATION OF RESULTS

Nitrometer reading after sample combustion = $0.02X/0.1620 = A$ ml.

Nitrometer reading after blank combustion = $0.02Y/0.1620 = B$ ml.

Volume of nitrogen released by sample = $(A - B)$ ml.

Percentage nitrogen in the sample = $(A - B) \times K \times 100/w$

where K is the weight of 1 ml. of nitrogen at the measured temperature and 757 mm. pressure determined from the standard nitrogen reduction table and w is the weight of sample in mg.

SUMMARY

Results of the analysis indicate that the nitrogen content of a variety of organic compounds and of complexes of actinides can be determined with a precision and accuracy of 2 per cent by this method. It was also observed that plutonium complexes gave quantitative release of nitrogen without the use of $K_2Cr_2O_7$ catalyst.

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TABLE - 1. ANALYSIS OF ACETANILIDE

S. No.	Weight of sample (mg)	Corrected volume of N ₂ (ml)	Measured Temp.deg.C.	Weight of 1ml. of N ₂ at measured Temp(mg)	Percentage nitrogen
1.	5.000	0.4422	27.0	1.13334	10.02
2.	5.800	0.5424	26.2	1.13713	10.64
3.	6.300	0.5852	26.4	1.13713	10.56
4.	6.100	0.5750	26.7	1.13334	10.68
5.	5.300	0.5014	25.4	1.13902	10.78
6.	5.600	0.5130	24.4	1.14477	10.49
7.	7.750	0.6874	25.8	1.13984	10.11
8.	6.200	0.5528	24.3	1.14477	10.21
9.	5.400	0.4970	24.5	1.14285	10.52
10.	5.900	0.5284	26.5	1.13522	10.17

Average % Nitrogen = 10.42 +/-0.25

Theoretical % Nitrogen = 10.37.

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TABLE - 2. ANALYSIS OF URANIUM NITRIDE

S.No.	Weight of sample (mg)	Corrected volume of N ₂ (ml)	Measured Temp.deg.C.	Wt.of 1ml. of N ₂ at measured Temp. (mg)	Percentage Nitrogen
1.	13.750	0.4737	24.5	1.14285	3.94
2.	15.750	0.5418	25.1	1.10493	3.93
3.	19.500	0.6894	24.7	1.14093	4.02
4.	17.300	0.6149	24.9	1.14093	4.05
5.	15.200	0.4927	24.6	1.14285	3.89
6.	14.050	0.4985	24.5	1.14285	4.06
7.	21.700	0.7495	24.8	1.14093	3.94
8.	17.630	0.6171	25.2	1.14093	3.99
9.	19.380	0.6761	24.8	1.14093	3.98
10.	17.620	0.6185	25.4	1.13750	3.99
Average % Nitrogen = 3.98 +/-0.06					
Percentage Nitrogen = 4.02 (Leco Analser)					

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TABLE - 3. ANALYSIS OF 1-PHENYL-3-METHYL-4-BENZOYL-PYRAZOLONE-5 (PMBP)

S.No.	Weight of sample (mg)	Corrected volume of N ₂ (ml)	Measured Temp.deg.C.	Wt.of 1ml. of N ₂ at measured Temp. (mg)	Percentage Nitrogen
1.	5.420	0.4694	24.7	1.14189	9.89
2.	5.750	0.4917	25.2	1.14093	9.76
3.	4.300	0.3858	24.9	1.14093	10.24
4.	7.500	0.6445	25.4	1.13996	9.80
5.	6.750	0.5988	24.8	1.14189	10.13
6.	6.300	0.5687	25.5	1.13902	10.28
7.	5.500	0.4906	24.6	1.14285	10.19
8.	6.100	0.5277	24.0	1.14477	9.90
9.	5.250	0.4661	24.8	1.14189	10.14
10.	10.790	0.9195	25.0	1.14093	9.72

Average % Nitrogen = 10.01 +/-0.21

Theoretical % Nitrogen = 10.14

TABLE - 4. ANALYSIS OF ORGANIC COMPOUNDS

Compound	Wt. of sample (mg)	Corrected volume of N ₂ (ml)	Measured Temp. deg.C.	Wt. of N ₂ of 1ml. at measured Temp (mg)	Percent Nitrogen
8-Hydroxy quinoline	8.000	0.6643	24.5	1.14285	9.38
	5.700	0.4627	25.1	1.14093	(9.64)
5-Chloro, 8-hydroxy quinoline	5.560	0.3911	24.7	1.14191	7.82
	4.800	0.3193	24.4	1.14288	(7.78)
8-Hydroxy, 7-iodo, quinoline-5, sulphonic acid	8.600	0.2897	24.5	1.14285	3.94
	10.900	0.3840	25.0	1.14093	(3.99)
Dinitro-PMBP	5.950	0.7821	24.6	1.14285	15.16
	5.380	0.7210	25.1	1.14093	(15.20)
N-Phenyl, benzoyl hydroxylamine	5.600	0.3348	23.9	1.14477	6.68
	4.750	0.3095	24.9	1.14093	(6.57)
PMAP	10.440	1.1945	27.2	1.13339	12.94
	9.200	1.0418	24.9	1.14093	(12.95)
PMTFP	10.050	0.9042	26.5	1.13034	10.33
	13.055	1.2125	26.7	1.13034	(10.30)
PMBP	4.300	0.3774	24.8	1.14093	10.05
	6.300	0.5566	25.6	1.13902	(10.14)

Figures in parentheses indicate calculated values.

TABLE - 5. ANALYSIS OF ACTINIDE COMPLEXES

Compound	Wt. of sample (mg)	Corrected volume of N ₂ (ml).	Measured Temp. deg.C.	Wt. of lml. of N ₂ at measured temp.(mg)	Percent Nitrogen
Th(PMBP) ₄	13.535	1.0615	27.3	1.13035	8.84
	13.125	1.0176	26.0	1.13713	(8.37)
Th(PMAP) ₄	8.720	0.7743	25.1	1.14093	10.18
	7.380	0.6591	24.1	1.14478	(10.25)
Th(PMTFP) ₄	9.370	0.7004	25.8	1.13713	8.46
	6.510	0.4804	25.3	1.14093	(8.48)
U(PMBP) ₄	8.715	0.6440	25.1	1.14093	8.43
U(PMAP) ₄	3.715	0.3330	24.8	1.14093	(8.30)
	6.550	0.5767	24.1	1.14478	10.15
U(PMTFP) ₄	9.760	0.7195	25.0	1.14093	(10.19)
	7.840	0.5752	26.3	1.13713	8.38
					(8.44)

(contd)

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TABLE - 5. ANALYSIS OF ACTINIDE COMPLEXES

Compound	Wt. of sample (mg)	Corrected volume of N ₂ (ml).	Measured Temp. deg. C.	Wt. of 1ml. of N ₂ at measured temp. (mg)	Percent Nitrogen
UO ₂ (PMBP) ₂ H ₂ O	22.700	1.3150	24.6	1.14285	6.65
	10.040	0.6050	25.3	1.14093	(6.64)
UO ₂ (PMBP) ₂ TBP	28.000	1.3820	24.9	1.14093	5.73
	14.000	0.7150	25.0	1.14093	(5.38)
UO ₂ (PMBP) ₂ DPSO	16.100	0.6900	24.0	1.14477	5.06
	14.250	0.6300	24.9	1.14093	(5.21)
UO ₂ (PMBP) ₂ DOSO	14.100	0.6320	25.5	1.13902	4.86
	9.850	0.3970	24.8	1.14093	(5.10)
UO ₂ (PMBP) ₂ DHSO	18.200	0.8470	24.1	1.14477	5.33
					(5.45)

Figures in parentheses indicate calculated values

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TABLE - 6. ANALYSIS OF PLUTONIUM COMPLEXES

Compound	Wt .of sample (mg)	Corrected volume of N ₂ (ml).	Measured Temp. deg.C.	Wt. of lml. of N ₂ at measured temp(mg)	Percent Nitrogen
Pu(8-Hy.Q.) ₄	8.945	0.5232	26.3	1.13722	6.83 +/-0.13 (6.87)
	8.920	0.5342	26.1	1.13722	
	10.360	0.6348	26.9	1.13339	
	4.970	0.2872	27.5	1.13334	
Pu(PMBP) ₄	7.710	0.5416	25.0	1.14093	8.26 +/-0.17 (8.29)
	8.000	0.5093	25.6	1.13902	
	9.010	0.6603	25.5	1.13902	
	10.785	0.7800	25.6	1.13902	
Pu(PMTFP) ₄	7.940	0.5905	24.2	1.14477	8.48 +/-0.03 (8.43)
	6.340	0.4695	25.3	1.14093	
Pu(PMAP) ₄	8.920	0.7920	25.2	1.14093	9.91 +/-0.21 (10.18)
	6.000	0.5087	25.0	1.14093	

Figures in parentheses indicate calculated values

TABLE -7. STANDARD NITROGEN REDUCTION TABLE (log K)

Temp. deg.C.	755mm.	756mm.	757mm.	758mm.	759mm.	760mm
20	06347	06404	06462	06519	06576	06633
21	06199	06256	06314	06371	06428	06485
22	06051	06108	06166	06223	06280	06337
23	05904	05961	06019	06076	06133	06190
24	05757	05814	05872	05929	05986	06043
25	05611	05668	05726	05783	05840	05897
26	05466	05523	05581	05638	05695	05752
27	05321	05378	05436	05493	05550	05607
28	05177	05234	05292	05349	05406	05463
29	05033	05090	05148	05205	05262	05319
30	04890	04947	05005	05062	05119	05176

At 0 deg.C. and 760 mm., 1 ml. of Nitrogen = 1.2505 mg.
 This table gives the logarithm of the weight of 1ml. of N₂(Ref.9)

ABBREVIATIONS

- 8-Hy.Q** = **8-Hydroxyquinoline**
PMBP = **1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5**
PMAP = **1-Phenyl-3-methyl-4-acetyl-pyrazolone-5**
PMTFP = **1-Phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5**
TBP = **Tributyl phoshate**
DPSO = **Diphenyl sulphoxide**
DOSO = **Diocetyl sulphoxide**
DHSO = **Dihexyl sulphoxide**

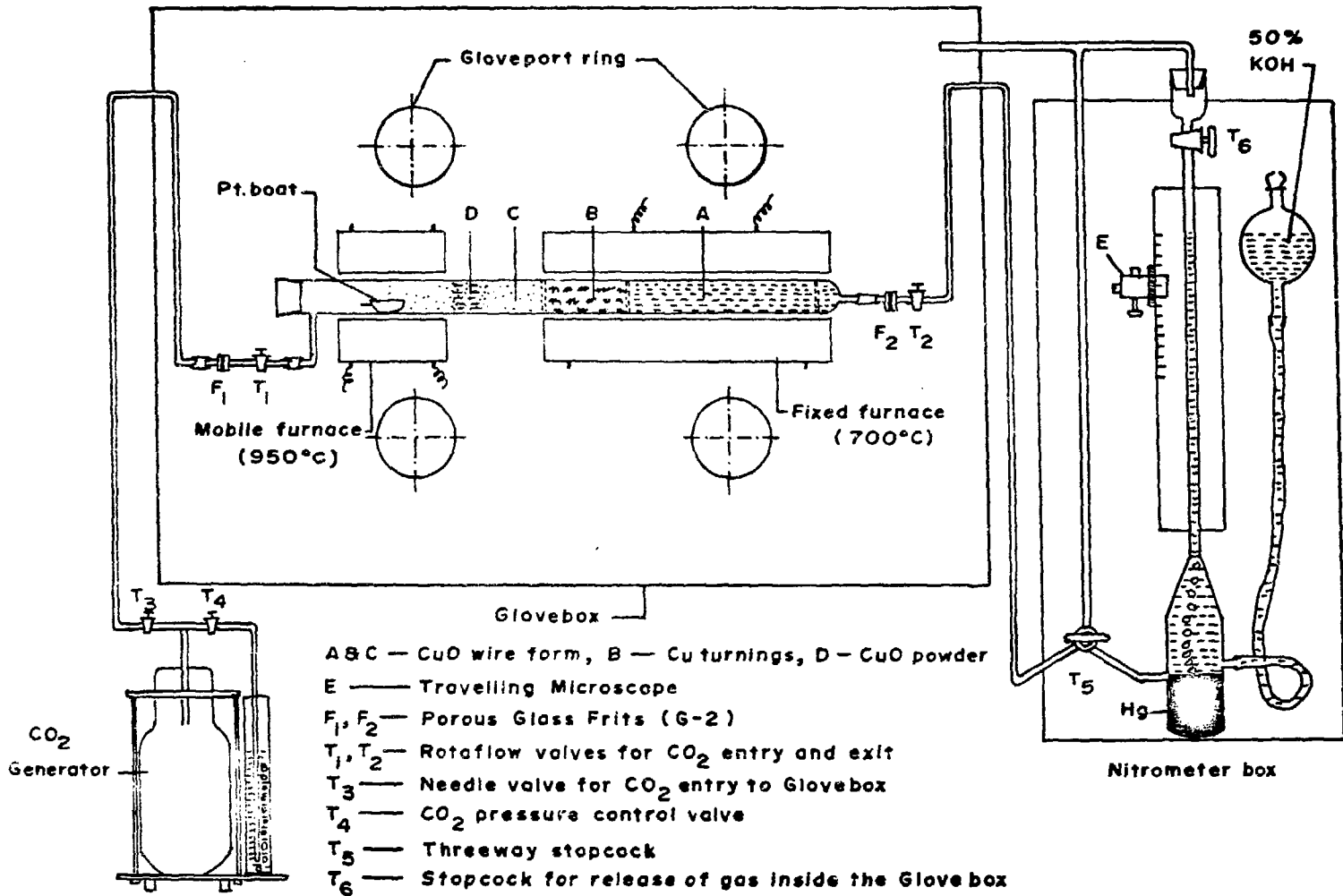


FIG.-1. SCHEMATIC DIAGRAM OF THE DUMA'S APPARATUS

