

PROCESS FOR PURIFICATION OF DIMETHYL SULPHOXIDE
(DMSO)

The present invention relates to a process
for the purification of dimethyl sulphoxide (DMSO) and
5 to the DMSO thus purified.

The DMSO currently available on the market is
a product which is already of good purity. Its
commercial specifications are generally:

10	purity	:	≥ 99.7 % by
			chromatography
	acidity	:	≤ 0.04 mg KOH/g by
			potentiometry
	crystallization		
	point	:	≤ 18.1°C
15	visual appearance	:	≤ clear
	water content	:	≤ 0.15 %
	colour (APHA)	:	≤ 10

French Patent specification FR 2 014 385
describes a process for the preparation of purified
20 DMSO using an ion exchange resin. In both examples of
this specification a strongly basic resin of the
Amberlite IR-A 400 or Merck III type is employed to
treat dimethyl sulphide/DMSO/10 % sulphuric acid
ternary mixtures. In fact, in this known process the
25 purification seems to be essentially brought about by a
fractional distillation of an aqueous solution of DMSO
treated beforehand with an anion exchanger.

Analyses of trace metals have now been performed on a number of samples of commercial DMSO from various sources. These analyses are reported in Table 1.

5 The sodium, iron, potassium, calcium, chromium, copper, nickel and zinc concentrations were measured using ICP (plasma torch - atomic emission spectrometry, Perkin Elmer instrument, Optima 3000 model) and are expressed in ppb (1 ppb = 1 part by
10 weight per thousand million = 1 μ g per kg).

The list of the metallic elements which appears in Table 1 is not exhaustive in respect of the metallic elements present in these samples.

TABLE 1

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Sample	Metal cations							
	Na	Fe	K	Ca	Cr	Cu	Ni	Zn
1	40	13	60	20	2	10	8	10
2	39	60	3	13	13	<2	18	3
3	30	40	3	20	12	<2	15	3
4	30	40	3	14	13	<2	15	3
5	30	<1	20	25	<2	<2	<3	<3
6	70	90	65	55	15	2	25	60
Detection limit	2	1	3	2	2	2	3	3

For some applications, as for example in electronics or in pharmacy, the DMSOs analysed above contain too many metallic impurities. A DMSO containing less than 10 ppb of each alkali and alkaline-earth metal and metal contaminant would generally be
5 necessary for most of the uses in the above mentioned two technical fields.

The objective of the present invention is to find a process for purification of commercial DMSO
10 which is already of good purity, the latter being nevertheless insufficient for some applications.

Ion exchange by making use of resins is a technique which is widely employed in the case of aqueous media and particularly allows deionized water
15 to be obtained. The exchange of anions in a liquid DMSO medium of low water content has already been carried out by Alan M. Phipps, Anal. Chem. 40(12) pp. 1769-1773, 1968, with the aim of measuring the quantities of anions bound to the resin in experimental conditions
20 approaching thermodynamic equilibrium.

According to one aspect, the present invention provides a process for purification of dimethyl sulphoxide to decrease its content of alkali metal, alkaline-earth metal and/or other metal cations,
25 which process comprises placing the DMSO to be purified in contact with at least two cation exchange resins at least one of which is a resin of sulphonic type, it

being possible for the other (or the others) to be of chelating type.

A DMSO of low water content is advantageously treated, this content being preferably lower than or
5 equal to 0.15 % by weight relative to the total weight.

In accordance with the present invention any cation M^{n+} (n having a value from 1 to 4) is retained and exchanged with H^+ protons or NH_4^+ cations originating from the resins employed in acidic form or
10 in ammonium form.

A highly efficient purification of virtually anhydrous DMSO can be obtained by the combined use of a resin of chelating type which possesses, for example, aminophosphonic or iminodiacetic groups, which is
15 effective for exchanging iron and metals with a multiple charge (M^{n+} , n = 2, 3 and 4) and a resin of sulphonic type, which is effective for exchanging sodium and single-charge ions.

The cationic resins employed are preferably
20 based on a polystyrene-divinylbenzene copolymer. These resins, in fact, have a backbone which withstands chemical attacks and in particular, they do not dissolve in DMSO.

The contact of the DMSO to be purified with
25 the resins suitably takes place at a temperature ranging from 18.45°C (melting point of DMSO) to 120°C (heat stability limit temperature of the resins). This

temperature is advantageously between 19 and 80°C,
preferably between 20 and 50°C.

The DMSO to be purified may be placed in
contact with a mixture of the various resins or
5 successively with each of the various resins.

The operation may be carried out
noncontinuously (batchwise) or continuously in the
conditions and equipment which are well known to a
person skilled in the art. The separation of the
10 purified DMSO from the resins can take place using any
suitable known means, especially by filtration,
percolation or centrifuging.

Iron and sodium have been adopted as tracer
elements and indicators of the general content of
15 alkali and alkaline-earth metal and metal cations, to
define the quality of the purified DMSO capable of
being obtained by the process according to the
invention.

According to another aspect, the present
20 invention also provides purified DMSO characterized in
that it has an Fe cation content lower than or equal to
1 ppb and an Na cation content lower than or equal to
2 ppb, the respective limits of detection of the
analysis method using plasma torch - atomic emission
25 spectrometry.

The invention is further illustrated with
reference to the following experimental part describing
an example of embodiment of the present invention.

Experimental part

I. Method of analysis:

ICP (plasma torch - atomic emission spectrometry) was employed for the traces of metals in the DMSO: the sample is introduced into a plasma torch, the various elements present are excited and emit photons whose energy is characteristic of the element, since it is defined by the electron structure of the element in question. A Perkin Elmer instrument (Optima 3000 DV model) was employed routinely.

II. Methodology:

Principle: the trace metals are in M^{n+} form. On passing the DMSO over two cation exchange resins, themselves in H^+ form, the M^{n+} ions in solution are replaced with $n H^+$.

III. Test:

Principle: to simplify the analyses, sodium and iron were chosen as tracers representing all the metallic impurities present in the DMSO.

Sodium is characteristic of atmospheric and accidental contamination (dust, environment), and iron is characteristic of contamination that can originate from the process (unit made of stainless steel).

DMSO doped with 1000 ppb of iron and 1000 ppb of sodium was successively placed in contact with two cation exchange resins, in H^+ form (2 g of each resin per 100 g of DMSO) at 25°C. After a first cationic exchange with a resin of chelating type the DMSO was

separated from the solid by filtration on a polyethylene sinter of 70 μm porosity and was then placed in contact with a resin of sulphonic type. Samples of DMSO were taken in the course of time during
5 each of the stages, to follow the changes in the iron and sodium concentrations.

Amberlyst®35 resin marketed by Rohm & Haas was employed as resin of sulphonic type and the aminophosphonic resin S940 from Purolite as chelating
10 resin. These resins were pretreated to obtain the H^+ form in the following manner: 540 ml of 5% HCl are passed through 90 ml of resin at a flow rate which is constant and such that the operation takes 30 to 45 minutes. After having been rinsed with deionized water
15 until the water coming out is neutral, the resin was dried by being suspended in methanol and vacuum evaporation in the rotary evaporator (90°C , 2000 Pa) until a constant weight was observed.

The iron and sodium contents as a function of
20 the time for the first and second exchange are collated in Table 2.

TABLE 2

	Time (min)	Fe (ppb)	Na (ppb)
Purolite®S940 resin	0	1390	1330
	30	64	1120
	60	<1	960
	90	<1	880
	120	<1	800
Amberlyst®A35 resin	5	<1	<2
	30	<1	<2
	60	<1	<2
	120	<1	<2



CLAIMS

1. Process for purification of dimethyl sulphoxide (DMSO) to decrease its content of alkali metal, alkaline-earth metal and/or other metal cations,
5 which comprises, placing the DMSO to be purified in contact with at least two cation exchange resins at least one of which is a resin of sulphonic type, it being possible for the other (or the others) to be of chelating type, these resins being employed in the
10 acidic or ammonium form.
2. Process according to Claim 1, in which a DMSO of low water content is treated.
3. Process according to claim 2, in which the water content is lower than or equal to 0.15 % by
15 weight relative to the total weight.
4. Process according to any one of Claims 1 to 3, in which each resin is based on a polystyrene-divinylbenzene copolymer.
5. Process according to any one of Claims 1
20 to 4, in which the DMSO to be purified is contacted with the exchange resins at a temperature of 19 to 80°C.
6. Process according to Claim 5, in which the temperature is between 20 and 50°C.
- 25 7. Purified dimethyl sulphoxide obtained by the process claimed in any one of claims 1 to 6.
8. DMSO capable of being obtained by the process claimed in any one of Claims 1 to 6, which has



an Fe cation content lower than or equal to 1 ppb and
an Na cation content lower than or equal to 2 ppb, the
respective limits of detection of the analysis method
using plasma torch-atomic emission spectrometry.